STUDIES OF BINUCLEAR COMPLEXES OF TRANSITION METALS

by

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Submitted to the Department of Chemistry on June , 1974,
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ABSTRACT

CHAPTER I

The crystal structure of the form of rhenium(IV) chloride which is obtained by reaction of Re_3Cl_9 with $ReCl_5$ or $SbCl_3$ with $ReCl_5$ has been investigated. This substance proves to be identical with that first reported in 1967. The structure is here described in detail. The crystals belong to the monoclinic system, with unit cell parameters $a = 6.362(2)$Å, $b = 6.273(2)$Å, $c = 12.165(4)$Å, $\beta = 93.15(5)^\circ$, $d_{calcd} = 4.49$ g cm^{-3} for $Z = 4$, and $d_{measd} = 4.50$ g cm^{-3}. Successful refinement was carried out in the space group $P2/c$ using 1227 measured intensities, corrected for absorption. In the final cycle of full-matrix, anisotropic refinement the unit-weighted and weighted residuals were both 0.049. The structure consists of confacial bioctahedra, Re_2Cl_9, which are linked by shared terminal chlorine atoms. The Re–Re distance is 2.728(2)Å which is indicative of metal-to-metal bonding. X-Ray powder diffraction patterns show that the form of $ReCl_4$ obtained by dechlorinating $ReCl_5$ with $CCl_2{=}CCl_2$ has a different structure.

CHAPTER II

When tetraacetatodimolybdenum is dissolved in aqueous hydrobromic acid and a solution of CsBr is added, a precipitate of microcrystalline $Cs_3Mo_2Br_8$ is formed. By a special technique, crystallographically useful single crystals were obtained and the substance has been structurally characterized. The structure consists of Cs^+ cations and $Mo_2Br_8^{3-}$ anions, the latter having the shape of an M_2X_9 confacial bioctahedron but with crystallographically disordered vacancies in the bridging positions. The dimensions of the $Mo_2Br_8^{3-}$ ion indicate that there is bonding interaction of medium strength between the molybdenum atoms. The crystals belong to the hexagonal system, with space groups $P\bar{6}2c$, $P6_3/mmc$ and $P6_3mc$ admissible on the basis of systematic absences. $P6_3mc$ was eliminated convincingly on the basis of unsatisfactory refinement, but no clear choice between the other two space groups was possible using diffraction data. The unit-cell parameters are $a = 7.757(3)$, $c = 17.804(7)$Å, $Z = 2$; $d_{calc} = 4.40$; $d_{obs} = 4.33$ g cm^{-3}. The Mo-Mo distance is 2.439(7); Mo-Br(terminal) = 2.554(3); Mo-Br(bridge) = 2.672(5)Å.

CHAPTER III

The structure of dimolybdenum tetraacetate, previously reported in part by Lawton and Mason (J. Amer. Chem. Soc., (1965) **87**, 921) has been redetermined using more extensive, counter-diffractometer data. Crystals are triclinic, $P\bar{1}$, $a = 8.418(2)$Å, $b = 5.500(1)$Å, $c = 7.529(1)$Å, $\alpha = 84.13(2)°$, $\beta = 105.24(2)°$, $\gamma = 106.00(2)°$, 22° C; $M = 428.05$; $Z = 1$; $d_c = 2.20$ g cm^{-3}. The Mo-Mo distance now obtained is 2.0934(8)Å and the intermolecular O...Mo contacts are 2.645(4)Å.

CHAPTER IV

The potentially bidentate ligand, tetramethyldiphosphinedisulfide $(CH_3)_4P_2S_2$, has been found to react with copper(II) chloride dihydrate, $CuCl_2.2H_2O$, in ethanol at room temperature to yield, as the major product, a white compound. This is apparently the same substance reported in 1965 by Meek and Nicpon as the sole product and formulated as $(Cu(S_2P_2Me_4)_2)(CuCl_2)$. An X-ray crystallographic investigation has shown that the white substance is a molecular, dinuclear compound (which may, of course, dissociate or otherwise rearrange in solution) in which each Cu(I) is surrounded by a tetrahedral array of three sulfur atoms and one chlorine atom. The $Me_4P_2S_2$ ligands have a gauche rotational configuration and each one chelates to one Cu(I) atom to form a five-membered ring. The $Me_4P_2S_4CuCl$ halves of the molecule are joined by two bridging sulfur atoms, one from each half, thus forming a planar Cu_2S_2 rhombic ring. The entire molecule has as its only symmetry element an inversion center. The principal crystallographic data are: space group, $P2_1/n$; $a = 7.998(1)$Å; $b = 9.688(2)$Å; $c = 14.473(3)$Å; $\beta = 104.90(1)°$, $V = 1083.7(3)$Å^3; $Z = 2$.

CHAPTER V

It has been found that the reaction of $CuCl_2 \cdot 2H_2O$ with $Me_4P_2S_2$ in ethanol at room temperature affords a small amount of a brown, crystalline product as well as the major, white Cu(I) product; $((Me_4P_2S_2)CuCl)_2$. The brown compound decomposes to form the white one if left in contact with the reaction mixture for a few hours. X-ray crystallographic investigation has shown that the brown compound has the stoichiometry $(Me_4P_2S_2)CuCl_2$ and that it crystallizes as an infinite polymer in which $CuCl_2$ groups ($\angle Cl-Cu-Cl = 142.4°$) are connected by $Me_4P_2S_2$ molecules. The latter retain their anti rotational configuration and are thus incapable of chelating. The angle is 137.3°, thus the coordination geometry at copper(II) is a flattened tetrahedron. The mean metal-ligand distances are: Cu-Cl, 2.22Å and Cu-S = 2.33Å. The principal crystallographic data are: space group, $P2_1/c$; $a = 6.138(1)$Å; $b = 15.452(5)$Å; $c = 12.465(7)$Å; $\beta = 93.30(4)°$; $V = 1180.1(8)$Å^3; $Z = 4$.

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CHAPTER I

THE CHEMISTRY OF RHENIUM(IV) CHLORIDE. STRUCTURE OF ONE OF THE POLYMORPHS (β) AND EVIDENCE FOR A NEW POLYMORPH (γ)

INTRODUCTION

The earliest report of the preparation of rhenium(IV) chloride has not been confirmed.[1,2,3] In 1966, an authentic sample of $ReCl_4$ was produced by accident in a commercial laboratory. Its identity has been confirmed[4] and some of its chemistry has been investigated.[5,6] Only recently have reproducible methods for the preparation of pure material of composition $ReCl_4$ been published.[7,8,9,10] Some fundamental questions still remain concerning rhenium(IV) chloride. This paper will attempt to answer some of them.

In our earlier report on the chemical properties of the "new" form of $ReCl_4$, we proposed that this form be designated β-$ReCl_4$, to distinguish it from the previously reported form, for which the designation α-$ReCl_4$ was proposed. In view of the now doubtful existence of α material, the need for the distinguishing prefixes, α and β, might rightly be questioned. For several reasons, we consider it wise to continue using the prefix β. First, it has already acquired currency in secondary literature and it clearly identified the one substance of stoichiometry $ReCl_4$ whose existence, structure, and properties have previously been well documented and accepted. Its use will thus avoid ambiguity. Second, as will be shown later, there appears to be still another polymorph of $ReCl_4$, even though it is not produced by the previously described synthesis of "α-$ReCl_4$."

The previous structural characterization[4] of β-$ReCl_4$ was undertaken using the material obtained commercially. However, the investigation was not entirely satisfactory by contemporary standards of X-ray crystallography. The crystal fragments available were far from ideal for purposes of a single-crystal structural study and there were indications that disorder and/or twinning may have interfered. The structure failed to refine to an R value below 17%, although there seemed little doubt that its main features were correct. We considered it desirable to obtain a data set which would lead to a structure more secure in its details and accurate in its numerical parameters. It was also of interest to determine if all of the newly reported methods of preparation actually give the same polymorph of $ReCl_4$ and whether one or more of these are identical with the β form. Thus, a fresh single-crystal structural study was carried out using material prepared by the reaction of $ReCl_5$ with Re_3Cl_9 and powder diffraction patterns for various preparations of $ReCl_4$, including the original commercial one, were recorded and compared. These studies are reported here.

EXPERIMENTAL SECTION

Preparation. - The method of Canterford and Colton[7] was used to obtain single crystals of β-$ReCl_4$. $ReCl_5$ and Re_3Cl_9 were heated in a sealed Vycor tube at 300° for 24 hours. $ReCl_5$ was used in slight stoichiometric excess. After 24 hours, half of the sealed tube was pulled out of the furnace and the excess $ReCl_5$ was condensed in this cooler part. Most of the $ReCl_4$ remained in the hot end of the tube as a black mass, but some crystalline material adhered to the middle section of the tube. The tube was cooled and opened in an inert atmosphere box. The crystalline $ReCl_4$ from the middle of the tube was collected separately. Some crystals were placed in capillaries which were promptly sealed. Other portions were analyzed, giving chlorine contents of 43.0 and 42.9%. The theoretical value for $ReCl_4$ is 43.3%.

Samples of $ReCl_4$ were also prepared by reduction of $ReCl_5$ with $SbCl_3$ following the procedure of Frais, Guest, and Lock[8] and by dechlorination of $ReCl_5$ with $Cl_2C{=}CCl_2$ either in refluxing CCl_4, following the procedure of Brignole and Cotton,[9] or in neat $Cl_2C{=}CCl_2$ according to Muller and Waschinski.[10]

X-Ray Powder Patterns. - These were recorded on samples of $ReCl_4$ prepared by each of the methods just mentioned and on a sample of the material originally supplied by Shattuck Chemical Co.[4,5,6,11] All samples were prepared in a dry nitrogen atmosphere and sealed in glass capillaries 0.5 mm in diameter. The patterns were recorded on film using conventional equipment supplied by the General Electric Co., with nickel-filtered Cu Kα radiation. Intensities were estimated visually on a scale of 1-10.

Single-Crystal Diffraction Data. - A crystal of $ReCl_4$ approximately 0.2 x 0.1 x 0.1 mm was used throughout. Oscillation, Weissenberg, and precession photographs showed that the crystal belonged to the monoclinic system. The only systematic absence found was for $h0l, l = 2n + 1$. This suggests that the space group is either Pc or $P2/c$.

The crystal was then mounted on a General Electric manual diffractometer and aligned with the a* axis parallel to the ϕ axis of the eucentric goniometer. Using Mo Kα radiation filtered with Nb foil (0.04 mm), preliminary measurements revealed strong reflections out to 2θ values as high as 100°. Unit cell parameters were therefore evaluated not only by measuring the settings for the Mo Kα maxima of about 30 reflections but also by measurements of the $K\alpha_1$-$K\alpha_2$ separations for about 20 high-angle (35-100°) reflections. A takeoff angle of 1° was used. These data give the following unit cell dimensions: $a = 6.362(2)$Å, $b = 6.273(2)$Å, $c = 12.165(4)$Å, $\beta = 93.15(5)°$. With these unit cell dimensions, the density calculated for $Z = 4$ is 4.49 g cm^{-3}. The density measured pycnometrically is 4.50 g cm^{-3}.

The intensities of 1227 independent reflections, including 109 which should be systematically absent in $P2/c$ with $2\theta \leq 55°$ were measured on the diffractometer. A moving crystal-moving counter technique was used, with a constant scan range of 2.67°. Peak intensity was measured for 40 sec and background was measured for 20 sec each at 1.33° above and below the peak. A takeoff angle of 3° was used, and the pulse-height discriminator was set to accept 95% of the Mo Kα peak. During the data collection process the intensities of the 200, 020, and 006 peaks were checked regularly. They showed only random fluctuations which were within ± 3%.

The intensities, I, were taken as $I = P - B_1 - B_2$ where P, B_1, and B_2 are the peak counts and the two background counts, respectively. The observed structure factors were calculated from the equation $|F_o| = (I/Lp)^{\frac{1}{2}}$ where Lp is the Lorentz and polarization correction. The estimated standard deviation of $|F_o|$, $\sigma(F_o)$, was set equal to $[\sigma_I{}^2 + (0.02I)^2]^{\frac{1}{2}}(Lp)^{-\frac{1}{2}}$.

Solution and Refinement. - The atomic positional parameters previously obtained[4] were used as input for a cycle of isotropic full-matrix least-squares refinement in the space group P2/c. The result strongly implied that the input parameters were correct. Four more cycles were run, leading to the following discrepancy indices: $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o| = 0.086$, $R_2 = (\Sigma w||F_o| - |F_c||^2)/\Sigma w|F_o|^2 = 0.107$. The weighting factors, w, were set equal to $(\sigma(F_o))^{-2}$.

The data were now corrected for absorption using the linear absorption coefficient $\mu = 286.3 \text{ cm}^{-1}$. The shape of the crystal was measured as carefully as possible under a microscope. It was approximated by a solid of eight faces. As a partial check on the adequacy of this approximation, the transmission coefficient as a function of ϕ at $\chi = 90°$ was calculated and found to be in acceptable agreement with the observed variations in intensities.

Refinement was continued using absorption-corrected data and anisotropic temperature factors, leading to $R_1 = 0.051$ and $R_2 = 0.056$. Nine reflections for which $||F_o| - |F_c||/\sigma \geq 10$ were then omitted and refinement converged with $R_1 = R_2 = 0.049$. A difference electron density map showed no significant peaks. There was considerable random noise in the vicinity of the rhenium atom.

The following computer programs were used: PDATA (B. G. DeBoer) for calculating diffractometer settings, REDUCE (B. G. DeBoer and J. G. Norman, Jr.) for data reduction, SFIX (a local version of C. T. Prewitt's SFLS-5) for least-squares refinement, based on minimization of the function $w||F_o| - |F_c||^2$, FORDAP (A. Zalkin) for Fourier synthesis, STAN1 (B. G. DeBoer) for molecular geometry, ABSCOR (N. W. Alcock, B. Lee, and V. W. Day) for absorption corrections, ORTEP (C. K. Johnson) for preparing illistrations, SPADEX (Z. Cs. Mester) for calculating indices for powder patterns. The list of the observed and calculated structure factors is shown in Table I.

RESULTS

Structure of β-Rhenium(IV) Chloride. - The final atomic positional and temperature parameters are recorded in Table II. Figure 1 shows the structure in projection on the ac plane. It defines the atom numbering scheme followed in the tables and emphasizes the arrangement of chains of linked Re_2Cl_9 bioctahedra parallel to the 'a' direction. The crystallographic twofold axes pass through Cl(4) and Cl(5). Figure 2 shows the contents of one unit cell projected in the c* direction and indicates clearly the angle at the bridging atom, Cl(5). Tables III and IV present various interatomic distances and angles.

Comparison of Different Preparations. - Table V lists the d spacings obtained by powder diffractometry for four different samples. The column headed "commercial sample" is for the material, originally purchased from Shattuck Chemical Co., on which all of the work reported in ref. 4, 5, 6, 11 was conducted. The columns headed preparation 1, 2, and 3 refer to the following. Preparation 1, the same batch of material from which the specimen for the single-crystal study was obtained, was prepared by the reaction of Re_3Cl_9 with $ReCl_5$. Preparation 2, material was prepared by the method of Brignole and Cotton.[9] Preparation 3, material was prepared using neat tetrachloroethylene, as described by Muller and Waschinski.[10]

The films for the commercial sample and preparation 1 are essentially indistinguishable to the eye. As shown in Table V, the former contains a few more lines than the latter, but all are very weak. A set of indices is given for these two powder patterns. These indices were computed from the single-crystal data for preparation 1. It is clear that all of the observed powder lines in the commercial sample, with the exception of a few weak ones, match lines of similar relative intensity in preparation 1 and can be indexed satisfactorily for β-$ReCl_4$. Frais, Guest, and Lock[8] previously made a similar comparison of powder data for their preparations with d spacings calculated from the preliminary single-crystal data.[12] The present work is conclusive as to the identity of the original commercial sample and the β-$ReCl_4$ prepared by the reaction of Re_3Cl_9 with $ReCl_5$, since it involves not only successful indexing of the powder pattern for the latter, but direct comparison of the two powder patterns.

Finally, in Table V are listed the powder lines for preparations in which $ReCl_5$ was dechlorinated by $Cl_2C{=}CCl_2$ under different experimental conditions. It is evident that the two products are identical with each other but different from β-$ReCl_4$.

DISCUSSION

Structure of β-$ReCl_4$. - The present study confirms the previously reported[4] structure of β-$ReCl_4$. With the present data set, refinement proceeded satisfactorily in the space group P2/c to unit-weighted and weighted residuals of 0.049, thus removing all uncertainty about the correctness of the structure.

The structure can be described as zig-zag chains of Re_2Cl_9 confacial bioctahedra, in which one terminal chlorine atom at each end is shared between two bioctahedra. The chains run parallel to the crystallographic a axis. The angle at the bridging chlorine atom (Cl(5)) that is shared by two bioctahedra is 127°. Single chlorine bridges (as opposed to sets of two or three) of this type are not very common, although a few have been observed previously, as, for example, connecting the clusters in Nb_6Cl_{14} and $(Mo_6Cl_8)Cl_4$.

A check of Wyckoff's compilation[13] indicates that the β-$ReCl_4$ structure is unique among metal tetrahalides. Presumably one reason why this unique structure is adopted here is that it allows for direct Re–Re interaction, across the shared octahedral face. The Re–Re distance of 2.728Å is indicative of a metal–metal bond. It may be compared with the Re–Re distances of 2.74 and 2.76Å in the hexagonally close packed metal,[14] and with Re–Re distances in various other bi- and tri-nuclear compounds in which Re–Re bonds of various strengths exist.[15] Thus, in compounds based on the Re_3 trinuclear cluster, where double bonds occur, the distances are about 2.48Å, and in the various binuclear species containing quadruple bonds, the Re-Re distances are about 2.24Å. In the molecules Re_2Cl_3-$O(PPh_3)_2(C_2H_5COO)_2$ and $Re_2Cl_5O(PPh_3)_2(C_2H_5COO)$, where octahedrally coordinated rhenium atoms share an edge, the Re-Re distances are 2.51 and 2.52Å, respectively. Thus the distance of 2.728Å found here is relatively long but still short enough to be consistent with the occurrence of an attractive Re-Re interaction. It will be shown below that the overall dimensions of the Re_2Cl_9 bioctahedron imply that there is such an attractive interaction, though not an especially strong one, as compared with that in the isoelectronic $W_2Cl_9^{3-}$ ion.

Comparison with Other M_2X_9 Structures. - In a recent paper the structural criteria for determining the nature (i.e., attractive or repulsive) and strength of the M-M interaction in confacial bioctahedra have been discussed and applied to a number of known structures.[16] The important parameter for β-$ReCl_4$ in this connection are summarized in Table VI and contrasted with those for the $M_2Cl_9^{3-}$ systems, containing Cr, Mo and W, in which the M-M interaction ranges from repulsive to moderately attractive to strongly attractive. These $M_2Cl_9^{3-}$ ions are isoelectronic (i.e., contain d^3 M ions) with β-$ReCl_4$. It should be noted though that in β-$ReCl_4$ the bioctahedron is significantly distorted from D_{3h} symmetry, particularly by the participation of one terminal chlorine atom in bridging between two bioctahedra. Thus some of the individual distances and angles of a given type deviate appreciably from the mean values for that type.

The bioctahedron in β-$ReCl_4$ is most similar to $Mo_2Cl_9^{3-}$. Clearly, the M-M interaction is not repulsive, as it is in $Cr_2Cl_9^{3-}$, but it is not nearly so strongly attractive as that in $W_2Cl_9^{3-}$. A "diagonal relationship" in which the Mo^{3+} and Re^{4+} species have similar structures is not particularly surprising. The two are isoelectronic, but each, for different reasons, will tend to form less strong M-M bonds than that in $W_2Cl_9^{3-}$. For molybdenum the interaction is weaker in accord with the general trend toward weaker bonding as a group is ascended. For β-$ReCl_4$ the increased positive charge of the 4+ ion presumably has the effect of contracting the 5d orbitals, as compared with those in W^{3+}, and thus reducing the effectiveness of metal-metal overlap.

Even though the M-M bonding is weaker in $Mo_2Cl_9^{3-}$ than it is in $W_2Cl_9^{3-}$, it is still sufficient to give a spinsinglet ground state[17] in $Mo_2Cl_9^{3-}$. The Re-Re bond in β-$ReCl_4$ is slightly longer than that in $Mo_2Cl_9^{3-}$, and Table VIsuggests that the Re-Re interaction may be correspondingly a little weaker than that in $Mo_2Cl_9^{3-}$.

Polymorphs of $ReCl_4$. - As noted in the introductory section, the actual existence of α-$ReCl_4$ is doubtful at best. The existence of the β form is now fully established. Its structure is accurately known, and its powder diffraction pattern (Table V) can serve as a convenient means of identification. Several methods for its preparation are also available and have been reproduced in two or more laboratories. Recently, the region of stability of β-$ReCl_4$ in the phase diagram of the Re-Cl system has been defined.[18]

In their report of the preparation of $ReCl_4$ by dechlorination of $ReCl_5$ with $Cl_2C{=}CCl_2$ in refluxing CCl_4, Brignole and Cotton[9] (B and C) noted that while their product gave several reactions which were qualitatively the same as those reported for β-$ReCl_4$, it had several solubility differences. The possibility that the substance obtained by B and C's method was a different polymorph of $ReCl_4$ was, of course, considered and work was undertaken to check on this. It was soon found by the present authors that B and C's material has a different powder pattern from that of β-$ReCl_4$. We delayed publishing this result in order to omplete an accurate redetermination of the structure of β-$ReCl_4$. In the meantime, Muller and Waschinski[10] (M and W) reported their results using unsaturated chlorocarbons to dechlorinate $ReCl_5$. They concluded that both $Cl_2C{=}CClCCl_3$ and neat $Cl_2C{=}CCl_2$ afforded a product which was not β-$ReCl_4$. They proposed calling this γ-$ReCl_4$ and, most appropriately, put the question of whether the B and C material would not also be γ-$ReCl_4$.

Our results and conclusions are in good agreement with those of M and W. As Table V shows, the substances obtained by B and C's method ($CCl_2{=}CCl_2$ in CCl_4) and M and W's method (neat $CCl_2{=}CCl_2$) are identical with each other but different from β-$ReCl_4$.

Our experience with γ-$ReCl_4$ indicates that it will be extremely difficult, if not impossible, to obtain single crystals of this substance large enough to use for structure determination. M and W report a set of unit cell dimensions which they derived from a powder pattern for γ-$ReCl_4$. We have found that this unit cell is capable of providing indices for all of the powder lines we observe for γ-$ReCl_4$. This does not, of course prove it to be correct.

<u>Magnetic Measurements</u>. - Magnetic susceptibility measurements have been carried out employing the Faraday method on both of the β and γ polymorphs. The suscep-

tibilities for β-$ReCl_4$ were recorded between 60K° and 295K° at which temperatures the values were 620×10^{-6} and 460×10^{-6} cgs units per formula unit, respectively. These values have been corrected for diamagnetic contribution of -132×10^{-6} in the same units. The variation of susceptibilities with the temperature had no resemblance to the Curie law. The crystal structure showed that the rhenium atoms form dinuclear clusters with relatively large inter cluster distances. The magnetic behaviour of such a system can be expected to follow the predictions of the Heisenberg theory of antiferromagnetic interaction between two d^3 configurations with $S = 3/2$. This approximation turned out to be inadequate and we were unable to make any correlation between the structure and magnetic susceptibilities.

Magnetic susceptibilities for γ-$ReCl_4$ were measured between 61K° and 294K°, where the values were 565×10^{-6} and 354×10^{-6} cgs units per formula unit, respectively. Again diamagnetic corrections have been made on all susceptibility data.

The susceptibilities followed a similar pattern as in the previous case and we failed to abstract any structural information from them.

Comparison with Technetium(IV) Chloride. - The structures of β-$ReCl_4$ and the only known polymorph[19] of $TcCl_4$ are quite different. While in each case the metal atom is surrounded by a distorted octahedron of chlorine atoms, the linking of these octahedra by means of shared chlorine atoms follows quite different patterns. In $TcCl_4$ the octahedra share edges in such a way as to leave the unshared chlorine atoms of each octahedron in cis positions. The Tc-Tc distances are 3.62Å and the angles in the rhombus formed by the two metal atoms and the bridging chlorine atoms imply that the metal atoms are repelling each other.

Comparison of the $TcCl_4$ and β-$ReCl_4$ structures affords a good example of the normal trend[15a] toward increased metal-metal bonding as a group is descended, provided other factors remain constant.

TABLE I

THE OBSERVED AND FINAL CALCULATED STRUCTURE FACTORS LISTED AS $10|F_o|$ AND $10|F_c|$, IN ELECTRONS

H= 0

K	L	FOBS	FCALC
0	2	1311	1270
0	4	107	155
0	6	2640	2546
0	8	1523	1429
0	10	1347	1285
0	12	187	301
0	14	1399	1265
1	0	594	564
1	1	3749	4265
1	2	344	297
1	3	1361	1322
1	4	2366	2429
1	5	1399	1052
1	6	714	681
1	7	2329	2965
1	8	153	77
1	9	2147	2143
1	10	204	187
1	11	1249	1172
1	12	669	623
1	13	944	965
1	14	160	266
1	15	1453	1367
2	0	2494	2415
2	1	643	603
2	2	2174	2232
2	3	72	321
2	4	201	204
2	5	730	733
2	6	2176	2302
2	7	186	115
2	8	1091	1134
2	9	912	911
2	10	1964	1964
2	11	42	73
2	12	44	132
2	13	78	151
2	14	1153	1124
2	15	528	579
3	0	303	859
3	1	2852	2944
3	2	1126	1173
3	3	1322	1397
3	4	111	94
3	5	1413	1469
3	6	414	336
3	7	2136	2215
3	8	949	980
3	9	2234	2312
3	10	429	421
3	11	377	362
3	12	46	42
3	13	391	414
3	14	149	415
4	0	1339	1409
4	1	1273	1261
4	2	2256	2191
4	3	275	271
4	4	194	81
4	5	521	531
4	6	1342	1438
4	7	1959	1961
4	8	2385	2554
4	9	525	679
4	10	1249	1242
4	11	348	351
4	12	155	133
4	13	177	224
5	0	1307	1232
5	1	1584	1648
5	2	760	771
5	3	925	945
5	4	902	933
5	5	762	775
5	6	685	726
5	7	1743	1793
5	8	1162	1165
5	9	1710	1787
5	10	660	682
5	11	457	442
5	12	263	285
6	0	2599	2566
6	1	1279	1273
6	2	1358	1342
6	3	780	789
6	4	213	196
6	5	124	81
6	6	1062	1065
6	7	1394	1136
6	8	851	855
6	9	753	737
6	10	667	573
7	0	1489	1497
7	1	1603	1582
7	2	614	692
7	3	504	483
7	4	500	439
7	5	223	255
7	6	1041	1063
7	7	915	945
7	8	787	403
8	0	305	772
8	1	358	493
8	2	461	425
8	3	243	225

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0	0	2104	1791
0	2	2076	1844
0	4	3340	3261
0	6	3415	3442
0	8	594	527
0	10	567	521
0	12	2153	2006
0	14	1431	1335
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1	-14	169	140
1	-13	1299	1239
1	-12	79	45
1	-11	2599	2559
1	-10	659	634
1	-9	1858	1874
1	-8	186	135
1	-6	146	137
1	-5	2560	2608
1	-4	900	710
1	-3	2553	2352
1	-2	219	215
1	-1	3616	3134
1	0	62	131
1	2	106	104
1	3	2394	2414
1	4	844	745
1	5	4388	4538
1	6	67	33
1	7	2305	2310
1	8	313	332
1	9	61	45
1	10	305	272
1	11	1546	1553
1	12	232	233
1	13	1614	1563
1	14	349	306
1	15	921	903
2	-15	318	295
2	-14	693	667
2	-13	219	213
2	-12	1835	1833
2	-11	715	728
2	-10	2327	2253
2	-9	152	132
2	-8	1030	945
2	-7	1400	1350
2	-6	1054	1310
2	-5	407	406
2	-4	3737	2743
2	-3	862	771
2	-2	1000	1094
2	-1	453	387
2	0	1551	1458
2	1	2501	2558
2	2	1255	1276
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2	4	3038	3321
2	5	717	747
2	6	2757	2773
2	7	621	542
2	8	1173	1239
2	9	933	915
2	10	891	880
2	11	684	668
2	12	1673	1655
2	13	163	157
2	14	1447	1368
2	15	296	251
3	-14	171	157
3	-13	706	763
3	-12	357	400
3	-11	1255	1235
3	-10	823	816
3	-9	1633	1572
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3	-7	275	262
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3	-5	2347	2221
3	-4	1156	1136
3	-3	4653	5073
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3	0	856	855
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3	3	2081	2253
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3	5	1216	1235
3	6	642	571
3	7	1361	1301
3	8	224	234
3	9	229	247
3	10	593	512
3	11	1240	1241
3	12	340	349
3	13	1987	1964
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4	-11	555	544
4	-10	1487	1421
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4	-6	649	533
4	-5	655	505
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4	1	1293	1312
4	2	815	771
4	3	1222	1252
4	4	1953	2003
4	5	860	873
4	6	1514	1531
4	7	705	734
4	8	1025	1073
4	9	670	533
4	10	983	699
4	11	149	126
4	12	1335	1362
4	13	770	765
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5	-11	1684	1655
5	-10	594	507
5	-9	1269	1235
5	-8	810	763
5	-7	46	175
5	-6	351	335
5	-5	1023	965
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5	-2	1220	1165
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5	0	273	235
5	1	326	323
5	2	774	745
5	3	1745	1712
5	4	965	1007
5	5	2279	2361
5	6	1318	1345
5	7	1514	1670
5	8	450	453
5	9	181	109
5	10	89	53
5	11	916	919
5	12	909	919
6	-10	1171	1152
6	-9	502	510
6	-8	773	738
6	-7	91	92
6	-6	537	580
6	-5	1653	1639
6	-4	1371	1343
6	-3	1397	1064
6	-2	1572	1517
6	-1	1263	1275
6	0	623	563
6	1	185	30
6	2	775	802
6	3	525	525
6	4	1486	1512
6	5	1273	1311
6	6	1459	1476
6	7	571	612
6	8	404	410
6	9	45	20
6	10	234	275
7	-7	172	3
7	-6	379	350
7	-5	974	956
7	-4	1211	1153
7	-3	1002	971
7	-2	1294	1236
7	-1	1137	1102
7	0	414	400
7	1	49	45
7	2	591	585
7	3	638	663
7	4	977	1009
7	5	1337	1387
7	6	878	896
7	7	597	699
8	-2	702	667
8	-1	755	751
8	0	357	400
8	1	342	331
8	2	268	298

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0	0	3121	2967
0	2	1130	961
0	4	2224	2129
0	6	173	186
0	8	1771	1656
0	10	3383	3215
0	12	2055	1893
0	14	183	166
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1	-14	81	99
1	-13	1564	1773
1	-12	497	526
1	-11	677	687
1	-10	929	929
1	-9	663	613
1	-8	176	89
1	-7	3319	3044
1	-6	559	558
1	-5	3088	3099
1	-4	169	123
1	-3	1940	1752
1	-2	2615	2468
1	-1	1520	1404
1	0	675	634
1	1	3361	3335
1	2	365	365
1	3	2914	3100
1	4	123	84
1	5	1614	1640
1	6	1678	1495
1	7	1263	1743
1	8	317	291
1	9	2232	2148
1	10	414	407
1	11	2305	2182
1	12	137	190
1	13	461	463
1	14	327	323
2	-15	422	460
2	-14	1768	1850
2	-13	84	59
2	-12	1440	1447
2	-11	569	538
2	-10	241	93
2	-9	322	309
2	-8	1517	1469
2	-7	155	143
2	-6	2154	2134
2	-5	1024	986
2	-4	2268	2116
2	-3	220	106
2	-2	448	312
2	-1	416	348
2	0	2544	2611
2	1	583	608
2	3	933	969
2	4	2555	2579
2	5	242	228
2	6	79	78
2	7	247	192
2	8	1561	1667
2	9	945	942
2	10	1729	1705
2	11	171	137
2	12	1045	1007
2	13	276	217
2	14	224	128
3	-14	420	454
3	-13	1459	1439
3	-12	325	322
3	-11	1072	1047
3	-10	244	7
3	-9	1121	1080
3	-8	659	651
3	-7	2050	1967
3	-6	805	763
3	-4	1101	1055
3	-3	1045	984
3	-2	116	60
3	-1	1125	1084
3	0	319	322
3	1	2648	2827
3	2	1175	1206
3	3	2613	2827
3	4	399	395
3	5	738	756
3	6	125	72
3	7	523	514
3	8	744	734
3	9	1920	1963
3	10	598	625
3	11	1428	1436
3	12	455	423
3	13	944	935
4	-13	712	693
4	-12	1183	1136
4	-11	250	322
4	-10	89	51
4	-9	101	125
4	-8	1533	1435
4	-7	1065	1040
4	-6	1723	1637
4	-5	993	965
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4	-2	240	25
4	-1	649	636
4	0	1378	1374
4	1	1112	1121
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4	3	907	900
4	4	1499	1572
4	5	502	534
4	6	83	114
4	7	207	242
4	8	1468	1483
4	9	530	544
4	10	1378	1396
4	11	731	756
4	12	956	952
4	13	251	243
5	-12	459	388
5	-11	662	626
5	-10	449	421
5	-9	636	636
5	-8	683	683
5	-7	1326	1293
5	-6	1012	978
5	-5	1568	1549
5	-4	832	809
5	-3	865	786
5	-2	1039	1027
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5	0	852	864
5	1	2061	2131
5	2	1263	1248
5	3	2226	2257
5	4	1028	1075
5	5	785	790
5	6	632	636
5	7	570	573
5	8	828	825
5	9	1274	1302
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6	-8	1133	1111
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6	-6	2128	2086
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6	-3	1004	931
6	-2	175	129
6	-1	202	74
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6	3	984	1041
6	4	863	860
6	5	272	283
6	6	222	200
6	7	807	817
6	8	795	792
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7	-5	1277	1307
7	-4	573	611
7	-3	694	689
7	-2	449	416
7	-1	434	388
7	0	1037	1069
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7	2	874	936
7	3	727	723
7	4	878	871
7	5	491	505
7	6	405	365

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0	-2	1293	1454
0	0	3310	3321
0	2	1216	1188
0	4	834	781
0	6	2820	2714
0	8	2202	2064
0	10	1591	1448
0	12	876	800
0	14	1306	1258
1	-14	44	68
1	-13	77	81
1	-12	89	38
1	-11	1231	1289
1	-10	455	489
1	-9	1839	1876
1	-8	78	55
1	-7	2056	2032
1	-6	336	377
1	-5	268	198
1	-4	362	358
1	-3	2149	2082
1	-2	290	248
1	-1	4487	4713
1	0	355	330
1	1	2386	2611
1	2	200	188
1	3	260	245
1	4	175	179
1	5	2127	2214
1	6	154	171
1	7	1977	1964
1	8	518	488
1	9	1609	1498
1	10	84	28
1	11	187	176
1	12	47	97
1	13	1119	1040
1	14	485	441
2	-14	619	648
2	-13	478	450
2	-12	584	556
2	-11	396	417
2	-10	1900	1890
2	-9	303	278
2	-8	2198	2152
2	-7	565	511
2	-6	1265	1224
2	-5	1551	1519
2	-4	1076	1032
2	-3	389	351
2	-2	3209	2974
2	-1	658	664
2	0	3093	3288
2	1	832	871
2	2	1395	1476
2	3	1478	1568
2	4	1003	1031
2	5	644	681
2	6	2163	2234
2	7	514	504
2	8	2028	2034
2	9	160	173
2	10	695	677
2	11	571	520
2	12	526	529
2	13	146	113
3	-13	379	368
3	-12	217	245
3	-11	1543	1590
3	-10	791	761
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3	-8	542	542
3	-7	1926	1903
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3	-1	1221	1130
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3	1	1722	1746
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3	4	680	710
3	5	1378	1418
3	6	668	653
3	7	3046	3169
3	8	783	775
3	9	1845	1849
3	10	279	275
3	11	101	57
3	12	156	107
3	13	943	967
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4	-10	1946	1904
4	-9	1070	1076
4	-8	1922	1884
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4	-4	925	898
4	-3	1058	1040
4	-2	1764	1710
4	-1	945	910
4	0	1860	1886
4	1	865	878
4	2	1016	1010
4	3	1063	1045
4	4	918	922
4	5	192	188
4	6	1849	1901
4	7	963	1002
4	8	2068	2121
4	9	567	619
4	10	411	434
4	11	383	334
4	12	309	281
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5	-10	509	515
5	-9	1168	1175
5	-8	1071	1070
5	-7	1079	1063
5	-6	90	100
5	-5	326	313
5	-4	504	494
5	-3	1796	1582
5	-2	132	1241
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5	4	81	62

K	L	FOBS	FCALC
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6	-9	880	874
6	-8	1203	1179
6	-7	977	970
6	-6	425	427
6	-5	213	41
6	-4	551	546
6	-3	576	536
6	-2	1556	1536
6	-1	1345	1353
6	0	1504	1494
6	1	568	586
6	2	644	648
6	3	76	93
6	4	311	294
6	5	979	975
6	6	1088	1110
6	7	844	882
6	8	985	1029
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7	-5	98	47
7	-4	442	453
7	-3	734	604
7	-2	1002	970
7	-1	1494	1444
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7	1	764	747
7	2	469	482
7	3	123	110
7	4	169	205
7	5	860	880

H= 4

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0	10	1522	1417
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1	-13	1566	1683
1	-12	435	466
1	-11	1753	1849
1	-10	67	74
1	-9	1197	1240
1	-8	1005	1022
1	-7	1043	1020
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1	-5	2345	2241
1	-4	301	206
1	-3	2876	2824
1	-2	241	171
1	-1	1391	1321
1	0	1641	1665
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1	2	298	216
1	3	2472	2638
1	4	276	288
1	5	2611	2725
1	6	422	407
1	7	787	794
1	8	812	787
1	9	521	501
1	10	574	556
1	11	1716	1613
1	12	50	80
1	13	1315	1211
2	-13	85	105
2	-12	1330	1391
2	-11	669	681
2	-10	1402	1394
2	-9	191	151
2	-8	298	318
2	-7	139	91
2	-6	1930	1846
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2	-4	3501	3449
2	-3	455	441
2	-2	2515	2464
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2	1	85	46
2	2	1659	1764
2	3	709	760
2	4	1840	1930
2	5	302	299
2	6	1370	1399
2	7	242	257
2	8	198	198
2	9	477	449
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2	11	89	75
2	12	1855	1721
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3	-9	613	608
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3	3	1978	2082
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3	5	1883	1949
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3	8	126	37
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3	10	163	225
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3	12	469	445
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4	-2	1585	1542
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4	3	656	696
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4	5	925	958
4	6	1380	1402
4	7	332	334
4	8	164	111
4	9	290	265
4	10	803	810
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5	-9	540	548
5	-8	611	605
5	-7	425	383
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5	-5	1758	1710
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5	-1	906	896
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5	1	609	625
5	2	762	794
5	3	1360	1408
5	4	1033	990
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5	6	439	487
5	7	566	579
5	8	443	441
5	9	418	430
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6	-6	770	754
6	-5	723	731
6	-4	797	768
6	-3	1795	1105
6	-2	976	876
6	-1	269	201
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6	2	736	832
6	3	994	970
6	4	1858	1827
6	5	769	991
6	6	1199	1189
6	7	430	475
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7	2	400	385

H= 5

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0	4	1533	1498
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1	-7	2949	2883
1	-6	418	425
1	-5	2172	2040
1	-4	78	85
1	-3	266	253
1	-2	155	28
1	-1	2029	1925
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1	1	1719	1877
1	2	283	337
1	3	1729	1799
1	4	130	116
1	5	113	151
1	6	80	37
1	7	1164	1171
1	8	563	553
1	9	2205	2143
1	10	87	71
1	11	1456	1359
2	-12	713	754
2	-11	569	613
2	-10	573	576
2	-9	87	74
2	-8	1906	1835
2	-7	616	614
2	-6	2358	2319
2	-5	519	482
2	-4	1197	1150
2	-3	1266	1160
2	-2	815	762
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2	1	597	623
2	2	2029	2151
2	3	130	96
2	4	857	888
2	5	558	549
2	6	582	587
2	7	43	47
2	8	1654	1674
2	9	364	397
2	10	1602	1584
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3	-9	984	984
3	-8	371	393
3	-7	1081	1036
3	-6	812	763
3	-5	1420	1339
3	-4	91	131
3	-3	284	273
3	-2	487	478
3	-1	1309	1303
3	0	758	763
3	1	3227	3381
3	2	683	720
3	3	1910	2005
3	4	399	425
3	5	213	183
3	6	187	132
3	7	1265	1326
3	8	512	533
3	9	1046	1048
3	10	391	368
4	-10	653	626
4	-9	658	644
4	-8	1135	1134
4	-7	587	595
4	-6	1587	1550
4	-5	809	793
4	-4	714	644
4	-3	921	898
4	-2	549	532
4	-1	287	210
4	0	1993	1999
4	1	960	983
4	2	2084	2140
4	3	681	693
4	4	732	758
4	5	532	539
4	6	316	352
4	7	878	855
4	8	1204	1252
4	9	594	562
5	-8	961	958
5	-7	1773	1733
5	-6	800	772
5	-5	1453	1399
5	-4	776	762
5	-3	53	38
5	-2	158	133
5	-1	861	857
5	0	811	803
5	1	1249	1269
5	2	751	793
5	3	815	814
5	4	221	264
5	5	237	222
5	6	509	524
5	7	861	808
6	-5	520	532
6	-4	736	564
6	-3	101	108
6	-2	280	335
6	-1	896	841
6	0	1037	995
6	1	837	852
6	2	1179	1145
6	3	950	915
6	4	651	629

H= 6

K	L	FOBS	FCALC
0	-10	994	1043
0	-8	1191	1244
0	-6	333	345
0	-4	1322	1331
0	-2	3447	3665
0	0	2318	2247
0	2	133	130
0	4	1665	1621
0	6	1150	1126
0	8	1007	967
0	10	235	171
1	-11	1198	1281
1	-10	82	32
1	-9	1700	1783
1	-8	273	264
1	-7	861	822
1	-6	969	944
1	-5	565	511
1	-4	189	187
1	-3	2297	2219
1	-2	298	262
1	-1	2408	2315
1	0	382	355
1	1	1011	1057
1	2	578	959
1	3	567	575
1	4	473	533
1	5	1681	1748
1	6	259	248
1	7	1564	1565
1	8	88	23
1	9	976	952
1	10	430	434
2	-10	1973	1998
2	-9	128	181
2	-8	1626	1607
2	-7	530	521
2	-6	149	111
2	-5	100	121
2	-4	1317	1251
2	-3	334	296
2	-2	1735	1635
2	-1	527	533
2	0	1397	1395
2	1	156	59
2	2	191	250
2	3	275	317
2	4	1193	1235
2	5	83	132
2	6	2091	2161
2	7	449	479
2	8	1512	1523
2	9	108	131
3	-9	1489	1508
3	-8	347	315
3	-7	1029	1009
3	-6	175	81
3	-5	644	621
3	-4	592	525
3	-3	1589	1485
3	-2	643	572
3	-1	1925	1891
3	0	717	719
3	1	1046	1031
3	2	154	31
3	3	579	608
3	4	229	208
3	5	1507	1563
3	6	574	599
3	7	1611	1648
3	8	285	295
4	-8	1233	1224
4	-7	189	261
4	-6	116	160
4	-5	55	106
4	-4	1319	1240
4	-3	660	671
4	-2	109	1272
4	-1	822	818
4	0	113	1344
4	1	468	429
4	2	52	92
4	3	311	293
4	4	713	750
4	5	754	794
4	6	1654	1704
5	-5	517	487
5	-4	562	676
5	-3	1189	1157
5	-2	865	855
5	-1	1188	1156
5	0	545	490
5	1	524	562
5	2	629	605
5	3	368	358
5	4	321	357

H= 7

K	L	FOBS	FCALC
0	-8	627	632
0	-6	1327	1379
0	-4	1903	1957
0	-2	976	998
0	0	568	509
0	2	1798	1823
0	4	1687	1911
0	6	564	545
1	-8	81	9
1	-7	1115	1140
1	-6	178	275
1	-5	1467	1442
1	-4	189	126
1	-3	1471	1425
1	-2	269	276
1	-1	338	199
1	0	132	61
1	1	1039	1048
1	2	351	342
1	3	2192	2299
1	4	231	160
1	5	1458	1508
1	6	141	91
1	7	260	230
2	-8	425	433
2	-7	470	485
2	-6	1588	1564
2	-5	333	361
2	-4	1749	1678
2	-3	221	180
2	-2	903	862
2	-1	879	867
2	0	459	494
2	1	95	43
2	2	1492	1583
2	3	319	304
2	4	1639	1733
2	5	515	504
2	6	878	917
3	-6	630	616
3	-5	2498	2390
3	-4	478	479
3	-3	1740	1668
3	-2	472	427
3	-1	277	220
3	0	123	65
3	1	1208	1203
3	2	339	409
3	3	900	930
3	4	468	482
3	5	838	864
4	-4	1627	1596
4	-3	571	514
4	-2	933	878
4	-1	518	481
4	0	387	406
4	1	787	758
4	2	1044	1107

H= 8

K	L	FOBS	FCALC
0	-4	280	235
0	-2	1189	1187
0	0	1005	945
0	2	1009	996
1	-4	691	642
1	-3	539	482
1	-2	476	437
1	-1	1516	1358
1	0	145	232
1	1	1674	1531
1	2	147	25
2	-1	409	325
2	0	1938	1938

TABLE II

ATOMIC POSITIONAL PARAMETERS AND ANISOTROPIC TEMPERATURE PARAMETERS[a,b]

a) Numbers in parentheses are estimated standard deviations, occurring in the least significant figure listed.

b) The form of the temperature parameter expression is: $\exp(-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*))$.

Atom	x	y	z
Re	0.18466(6)	0.26727(6)	0.31251(3)
Cl(1)	0.2520(5)	0.1129(5)	0.4787(3)
Cl(2)	0.1337(4)	0.4071(6)	0.1272(2)
Cl(3)	0.3569(5)	0.5683(5)	0.3653(3)
Cl(4)	0.0	-0.0503(6)	0.25
Cl(5)	0.50	0.0930(7)	0.25

Equiv isotropic B	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
1.00	0.77(2)	1.13(2)	1.12(2)	0.00(1)	0.17(1)	0.00(1)
2.12	2.2(1)	2.5(1)	1.7(1)	0.0(1)	0.0(1)	0.5(1)
1.79	1.1(1)	2.7(1)	1.6(1)	-0.5(1)	0.4(1)	0.6(1)
1.90	1.8(1)	1.6(1)	2.3(1)	-0.3(1)	0.2(1)	-0.5(1)
1.80	1.4(2)	1.3(2)	2.7(2)	0.0(0)	-0.2(1)	0.0(0)
1.79	0.9(1)	1.5(2)	3.1(2)	0.0(0)	0.9(1)	0.0(0)

TABLE III

BOND DISTANCES, ANGSTROMS[a]

a) Numbers in parentheses are estimated standard deviations, occurring in the least significant figure listed.

Re-Re	2.728(2)	Cl(1)-Cl(4)	3.297(4)
Re-Cl(1)	2.261(3)	Cl(1)-Cl(5)	3.275(4)
Re-Cl(2)	2.424(3)	Cl(2)-Cl(3)	3.314(5)
Re-Cl(2')	2.361(3)	Cl(2)-Cl(2')	3.519(6)
Re-Cl(3)	2.259(3)	Cl(2)-Cl(4)	3.366(5)
Re-Cl(4)	2.414(3)	Cl(2)-Cl(5)	3.341(4)
Re-Cl(5)	2.442(2)	Cl(3)-Cl(2')	3.287(4)
Cl(1)-Cl(3)	3.257(5)	Cl(3)-Cl(5)	3.439(5)
Cl(1)-Cl(2')	3.277(5)	Cl(4)-Cl(5)	3.306(2)

TABLE IV

BOND ANGLES, DEGREES[a]

a) Numbers in parentheses are estimated standard deviations, occurring in the least significant figure listed.

Cl(1)-Re-Cl(2)	174.6(1)	Cl(3)-Re-Cl(2')	90.7(1)
Cl(1)-Re-Cl(2')	90.3(1)	Cl(3)-Re-Cl(5)	93.9(1)
Cl(1)-Re-Cl(3)	92.2(1)	Cl(3)-Re-Cl(4)	178.1(1)
Cl(1)-Re-Cl(4)	89.6(1)	Cl(5)-Re-Cl(4)	85.8(1)
Cl(1)-Re-Cl(5)	88.2(1)	Cl(4)-Re-Cl(2')	89.7(1)
Cl(2)-Re-Cl(2')	94.7(1)	Cl(5)-Re-Cl(2')	175.2(1)
Cl(2)-Re-Cl(3)	90.0(1)	Re-Cl(2)-Re'	69.5(1)
Cl(2)-Re-Cl(4)	88.2(1)	Re-Cl(4)-Re'	68.8(1)
Cl(2)-Re-Cl(5)	86.7(1)	Re-Cl(5)-Re(2)	126.8(2)

TABLE V

POWDER PATTERNS FOR FOUR SAMPLES OF RHENIUM(IV) CHLORIDE WITH DIFFERENT ORIGINS[a]

hkl indices	Commercial sample	Preparation 1	Preparation 2	Preparation 3
	6.535 (2)			
010	6.215 (3)		8.867 (4)	8.934 (5)
002	5.926 (6)	6.046 (7)	7.167 (4)	7.182 (3)
	5.698 (2)			6.537 (1)
011	5.588 (10)	5.574 (10)	6.057 (1)	6.088 (1)
$10\bar{2}$	4.450 (5)	4.506 (7)	5.513 (10)	5.455 (10)
$11\bar{1}$	4.201 (5)	4.220 (7)	5.082 (2)	5.040 (1)
013 (?)	3.357 (1)		4.695 (2)	4.733 (1)
200, 020	3.126 (2)	3.159 (3)	4.379 (7)	4.369 (8)
$11\bar{3}$, 021, 004	3.022 (2)	3.068 (3)	4.018 (1)	3.978 (1)
113	2.921 (2)	2.965 (2)	3.579 (1)	
022, $21\bar{1}$	2.776 (8)	2.793 (5)	3.408 (1)	
211	2.714 (8)	2.718 (7)	3.215 (2)	3.198 (2)
104	2.663 (1)	2.661 (1)	3.132 (2)	3.115 (1)
$21\bar{2}$	2.603 (2)	2.611 (2)	2.945 (2)	2.931 (2)
$11\bar{4}$	2.557 (2)	2.553 (2)	2.867 (2)	2.858 (1)
$21\bar{3}$, $12\bar{3}$	2.414 (1)		2.734 (7)	2.718 (7)
	2.359 (2)		2.622 (3)	2.600 (2)
$20\bar{4}$	2.257 (3)	2.257 (2)	2.558 (2)	
$22\bar{1}$, 220	2.217 (1)	2.225 (2)	2.472 (3)	2.485 (1)
204	2.156 (3)	2.154 (2)	2.369 (6)	2.359 (7)
115, $12\bar{4}$	208.5 (7)	2.087 (5)	2.261 (4)	2.248 (3)
031, 222	2.053 (7)	2.060 (5)	2.181 (1)	
006, 310, 214	2.019 (6)	2.029 (4)	2.138 (1)	
$31\bar{1}$	1.985 (8)	1.987 (6)	2.082 (4)	2.075 (5)
302, $13\bar{1}$, 311	1.953 (3)	1.945 (3)	2.026 (4)	2.023 (5)
025, 223, 016	1.922 (1)		1.976 (2)	
$21\bar{5}$	1.884 (4)	1.893 (2)	1.950 (1)	1.942 (1)
033, $12\bar{5}$	1.852 (1)		1.905 (1)	1.900 (2)
$22\bar{4}$	1.824 (1)	1.826 (2)	1.853 (1)	1.841 (2)
$13\bar{3}$	1.788 (6)	1.786 (5)	1.826 (4)	1.816 (3)
$20\bar{6}$	1.749 (2)	1.751 (4)	1.764 (4)	1.751 (3)
$31\bar{4}$	1.719 (1)	1.720 (1)	1.693 (2)	1.699 (1)
026	1.698 (2)	1.697 (1)		1.671 (1)
017	1.670 (4)	1.665 (2)	1.613 (2)	1.608 (1)
126	1.618 (1)	1.617 (2)		1.553 (2)
323	1.588 (1)	1.581 (1)	1.529 (2)	1.523 (2)
$13\bar{5}$	1.546 (1)	1.541 (1)	1.487 (2)	1.476 (1)
402	1.513 (4)	1.509 (2)	1.438 (2)	1.433 (1)
$14\bar{2}$	1.481 (1)	1.481 (1)	1.390 (3)	1.384 (3)
$31\bar{6}$, 043	1.462 (1)	1.460 (1)	1.371 (3)	1.368 (3)
$40\bar{4}$	1.449 (1)			
$14\bar{3}$, 332	1.433 (1)	1.432 (1)		
$33\bar{3}$	1.412 (1)	1.411 (1)		
325	1.391 (2)	1.392 (1)		
422	1.364 (4)	1.365 (3)		
$24\bar{3}$	1.339 (1)	1.333 (1)		
243	1.319 (2)	1.317 (1)		
$42\bar{4}$	1.305 (4)	1.305 (1)		

---

[a] *d* spacings are in ångströms; numbers in parentheses are relative intensities, visually estimated. The origin of the specimens is explained in the text.

TABLE VI

COMPARISON OF THE BIOCTAHEDRON IN β-$ReCl_4$ WITH SOME OTHERS

a) Cf. ref. 16 for definitions of the parameters.

b) d = 1.30Å; d' = 1.36Å.

Structure parameter[a]	β-ReCl$_4$	$Cr_2Cl_9{}^{3-}$	$Mo_2Cl_9{}^{3-}$	$W_2Cl_9{}^{3-}$
M-M, Å	2.73	3.12	2.66	2.41
d'/d	1.05[b]	1.23	0.98	0.90
90° $-\alpha'$, deg	-0.9	4.2	-4.2	-8.0
β -70.53°, deg	-1.2	5.9	-6.0	-12.5

FIGURE I

A projection of the structure in the y direction. The y axis is directed away from the reader. The crystallographic twofold axes pass through Cl(4) and Cl(5).

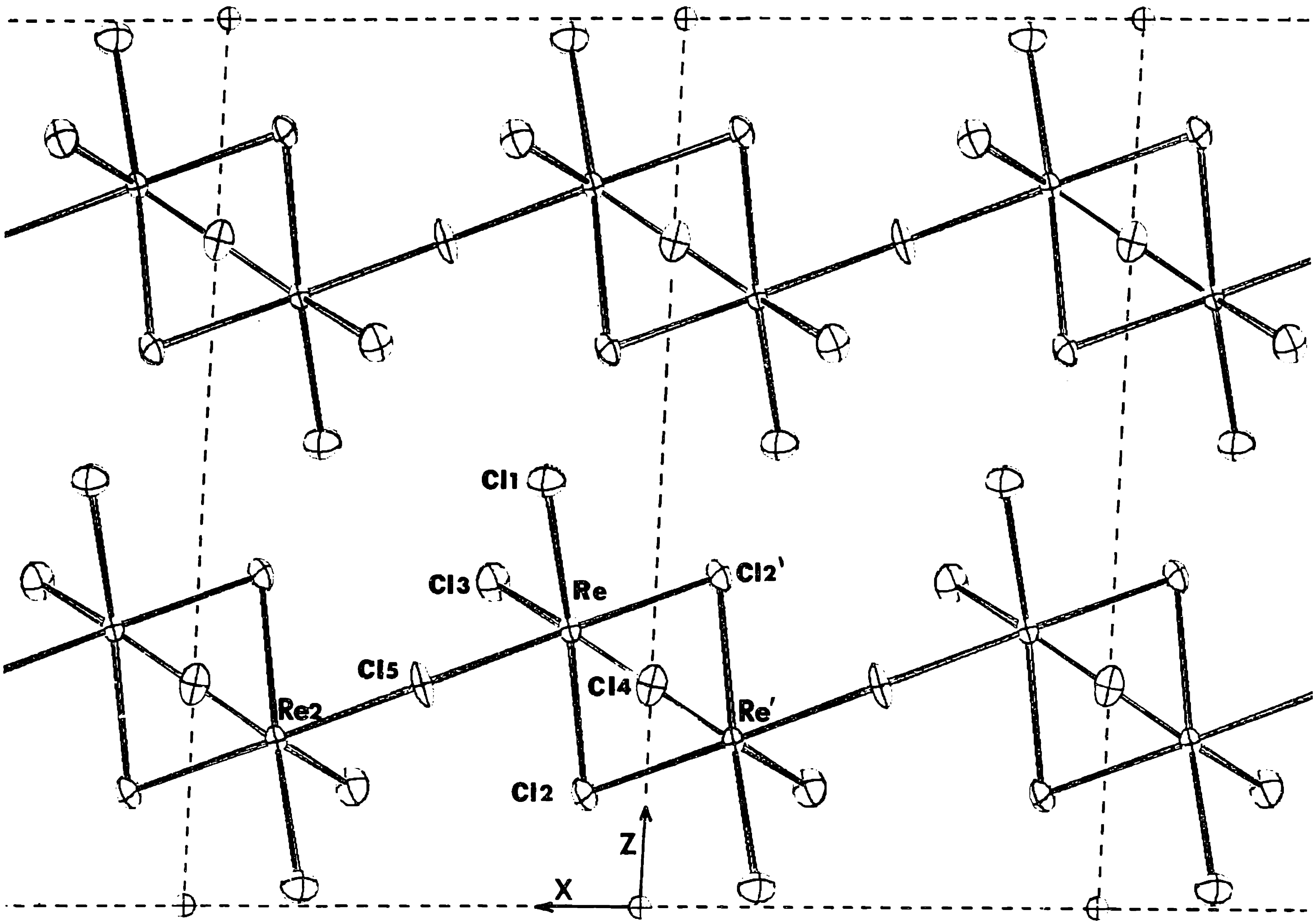
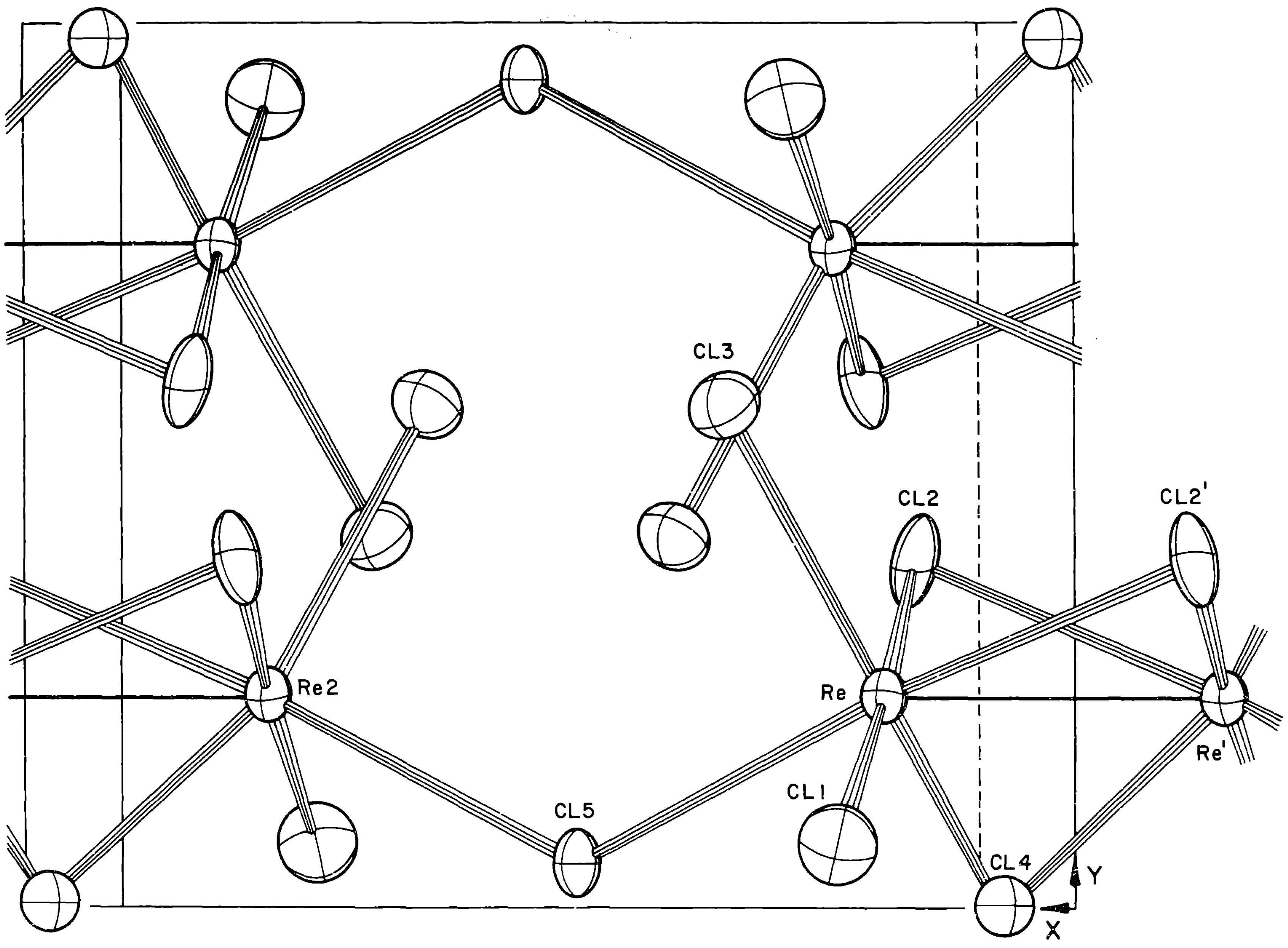

Cl1
Cl3
Re
Cl2'
Cl5
Cl4
Re2
Re'
Cl2
Z
X

FIGURE 2

A projection of the structure in the c* direction.


CL3
CL2
CL2'
Re2
Re
Re'
CL1
CL5
CL4
Y
X

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CHAPTER II

THE STRUCTURE OF TRICESIUM OCTABROMODIMOLYBDATE; AN EXAMPLE OF A SPACE-GROUP AMBIGUITY

INTRODUCTION

In a previous study it has been shown that the reaction of $Mo_2(CH_3CO_2)_4$ with 12N HCl at 60° in presence of large alkali cations, M^I (M^I = Rb,Cs) leads to the isolation of the compounds $M^I_3Mo_2Cl_8$. A crystallographic study[1] of the rubidium compound produced the surprising result that the compound is structurally very similar to a number of $M^I_3M^{III}_2X_9$ compounds. The differences are: 1) $Rb_3Mo_2Cl_8$ contains $Cl_3Mo(\mu\text{-}Cl)_2MoCl_3$ anions which are derived from a true D_{3h} bioctahedron by removal of one bridging chlorine (μ-Cl). This deletion occurs randomly, so that the structure can be refined with an occupancy factor of 0.67 for the μ-Cl atoms. 2) The space group for $Rb_3Mo_2Cl_8$ was $P\bar{6}2c$, which is noncentric, rather than the centric $P6_3/mmc$ which is found for many $M^I_3M^{III}_2X_9$ compounds (see below).

In the course of further chemical studies of reactions of $Mo_2(CH_3CO_2)_4$ with mineral acids, the stoichiometrically analogous bromo compound, $Cs_3Mo_2Br_8$, has been obtained and studied crystallographically. The crystallographic and structural work is reported here as it presents some features which are perhaps of more than routine interest. Again, from systematic absences and Laue symmetry, the three space groups $P\bar{6}2c$, $P6_3/mmc$ and $P6_3mc$ had to be considered. In this case again $P6_3mc$ could be eliminated convincingly. However, for $Cs_3Mo_2Br_8$, with a larger data set than for $Rb_3Mo_2Cl_8$, a convincing choice between $P\bar{6}2c$ and $P6_3/mmc$ could not be made on the basis of their performance in the refinement.

EXPERIMENTAL

Preparation of $Cs_3Mo_2Br_8$. - Tricesium octabromodimolybdenum was prepared by mixing stoichiometric quantities of dimolybdenum tetracetate with cesium bromide, each dissolved in concentrated hydrobromic acid. The chemistry of this reaction is sensitive to conditions of temperature, concentration and purity of reagents. Further investigations are in progress and a detailed report will be published in due course. Ordinarily, the reaction does not yield crystals suitable for X-ray diffraction studies. Recrystallization did not prove feasible because of the lack of a suitable solvent. Therefore the method of crystal growth by diffusion was applied. A U-shaped glass tube having a replaceable center part equipped with a fritted disc was constructed, see Figure 1. Solutions of CsBr and of $Mo_2(O_2CCH_3)_4$ in concentrated hydrobromic acid were put into separate ends of the U tube; the whole apparatus was then placed in a refrigerator. After three days several reddish-yellow plate-like crystals appeared on both surfaces of the fritted disk. The bulk microcrystalline material ordinarily obtained has been shown to be the same substance as that obtained in the form of larger crystals. The X-ray powder diffraction pattern of the bulk material can be satisfactorily indexed using the unit-cell and space-group data obtained from the larger crystals.

Collection of X-ray Data. - A Syntex $P\bar{1}$, computer-controlled, four-circle diffractometer equipped with a graphite-crystal incidentbeam monochromator was used to examine a crystal of dimensions 0.083x0.033x0.001 cm, with faces later identified as (100), $(\bar{1}00)$, $(0\bar{1}0)$, $(1\bar{1}0)$, $(1\bar{2}0)$, and $(\bar{1}20)$. A hexagonal unit cell similar to that reported[1] for $Rb_3Mo_2Cl_8$ was obtained. Least-squares refinement of fifteen centered reflections produced the orientation matrix for data collection and gave cell constants a = b = 7.757(3) and c = 17.804(7)Å. For V = 927.6(6)$Å^3$ and Z = 2 the calculated density is 4.40gcm^{-3}; this is in good agreement with the observed density of 4.33 g cm^{-3} measured by displacement in carbon tetrachloride.

Data were collected in the range $0° < 2\theta \leq 45°$ using Mo Kα radiation. It later appeared that a larger data set would have been helpful. While the structure is adequately overdetermined (ca. 10:1), reflections beyond $2\theta = 45°$ might have improved the chances of distinguishing centric and noncentric space groups. These reflections would result primarily from scattering by inner core electrons, although this is probably also the case for many reflections with $2\theta < 45°$, because the structure consists only of heavy atoms (Cs, Mo, and Br). At the time, data collection was terminated because of the sufficient overdeterminancy and because the last data shell ($40° < 2\theta \leq 45°$) showed a large drop-off in the fraction of reflections which are significantly above backgroud. The $\theta-2\theta$ scan technique with a variable scan rate from 2.0 to 24.0°/min was used. The scan range was from $2\theta_{MoK\alpha_1}-0.8°$ to $2\theta_{MoK\alpha_2}+0.8°$. Additional details about data collection have been described previously[2]. In order to check the stability of the X-ray measurements three reflections were selected as standards and their intensities were recorded periodically throughout data collection. No significant change in these intensities was observed.

A total of 313 reflections were collected and the usual data reduction procedures were applied. The following crystallographic computer programs were used on the IBM 360: DATARED by Frenz for data reduction; AGNOST by Cahen, which is based on Coppens's DATAPP and the Tompa analytical subroutines of Cullen's program, for absorption corrections; JIMDAP by Ibers, a version of Zalkin's FORDAP, for Fourier summations; NUCLS by Ibers and Doedens, based on Busing and Levy's ORFLS, for least-squares refinement; SADIAN by Baur for calculating atomic distances and angles; RSCAN by Doedens for structure-factor analysis; ORTEP by Johnson for plotting; ORFFE by Busing and Martin Levy and modified by Brown, Johnson, and Thiessen, for calculating errors or derived parameters; and LIST by Snyder for listing the data. The parameter p used in the calculation of standard deviations on the intensities ($\sigma(F_o^2)$) was assigned the value 0.05. The high linear absorption coefficient (μ = 253.5 cm^{-1} for Mo Kα radiation) and the platelet shape of the crystal necessitated an absorption correction. A numerical correction gave transmission factors varying from 9 to 70% with an average of 61%. A comparison of observed and calculated structure factors showed that an extinction correction was unnecessary.

Refinement of X-ray Data. - Systematic extinctions of $l \neq 2n$ for $hh2\bar{h}l$ (except 221, see below) and no conditions for $hkil$ or $h\bar{h}0l$ are consistent with three space groups: noncentric $P6_3mc$ (No. 186), noncentric $P\bar{6}2c$ (No. 190), and centric $P6_3/mmc$ (No. 194). Because of the similarity in cell constants and the identical systematic absences for the present work and that of $Rb_3Mo_2Cl_8$, it was assumed that the analogy extended to the crystal and molecular structure. Hence space group $P\bar{6}2c$ was selected and refinement was begun with Cs, Mo, and Br atoms in positions derived from the structure of $Rb_3Mo_2Cl_8$. Only the 202 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the full-matrix least-squares refinement on F_c in which the quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and w is $4F_o^2/\sigma^2(F_o^2)$. Scattering factors were from Cromer's tabulation.[3] Included in calculations for F_c were[4] anomalous dispersion effects for all atoms.[5]

Individual isotropic refinement resulted in conventional and weighted agreement factors of $R_1 = 0.083$ and $R_2 = 0.098$. As discussed later, reflections 221 and 2,2,15, which were omitted from refinement because the space-group symmetry requires them to be absent, had observed intensities significantly above background. No satisfactory explanation for their high intensities could be decuded. Three cycles of anisotropic refinement gave R values of 0.053 and 0.068. With the rejection of two additional reflections (F_o vs. F_c for 002 and 061 were 133 vs. 93 and 37 vs. 9) the agreement factors were reduced to 0.043 and 0.052. In view of the large data set (relative to the number of variables) and the fact that the calculated structure factors for the two rejected reflections are largely independent of the various space group refinements (see below), the intensities of these reflections were considered to be spurious.

In the final stage of refinement in the noncentric space group $P\bar{6}2c$ there existed a high correlation between anisotropic temperature factors β_{11} and β_{12} for both Br(1) and Br(2); the correlation coefficients were 0.69 and 0.96 respectively. In addition, the errors in the x coordinates for each of the Br atoms were an order of magnitude greater than those in other parameters. Since these observations suggested the possibility of a space group of higher symmetry, refinements were carried out in the centric space group $P6_3/mmc$.

In all previous studies of $M_2X_9^{3-}$ structures the centric space group has been assumed. These include $Cs_3Cr_2Cl_9$,[6] $Cs_3Cr_2Br_9$, $Cs_3Mo_2Cl_9$, $Cs_3Mo_2Br_9$,[7] $K_3W_2Cl_9$,[8] $Cs_3Tl_2Cl_9$,[9,10] $Cs_3Bi_2I_9$,[11] and $((CH_3)_4N)_3Sb_3Br_9.Br_2$[12]. In none of the reports of these structures is there an indication that the noncentric space group was tested.

As shown in Table I, statistics on the distribution of intensities favor the centric space group. However, it is known that a centric distribution can be obtained even for a noncentrosymmetric crystal when certain symmetry or near-symmetry elements are present in the cell.[13] This test is, therefore, by itself inconclusive.

Using the centric space group, three cycles of anisotropic least-squares refinement resulted in R values of 0.046 and 0.056. All correlation coefficients were less than 0.56 and the errors in the x coordinates were normal. Variables included a scale factor, an occupancy factor for Br(1), and positional and anisotropic temperature parameters not fixed by space-group symmetry. Thus refinement in $P\bar{6}2c$ included 25 variables, while $P6_3/mmc$ required 20 variables. On the basis of Hamilton's R-factor ratio test [14] for a ratio of 1.068, the hypothesis that the centric space group is correct can be rejected on the 0.995 confidence level, i.e., if this were the only criterion for judgement we would be quite sure that the space group is noncentric. Structure factors based on the parameters derived from the noncentric refinement were calculated for 500 Freidel pairs of reflections within the bounds of the experiment. Of these, only twelve pairs having $k|F_c|>10$ differed by more than 10%. Examination of these twelve pairs on the diffractometer showed that most of the intensities were barely above background and that the difference between pairs was random and not generally significant. No attempt has been made to test for a piezoelectric effect; the often unreliable nature of this experiment did not encourage us to seek or construct facilities for the test. Thus one is left with the choice between the statistical test on the R values suggesting the noncentric space group on the one hand and the least-squares correlation coefficients as well as the intensity distribution suggesting the centric space group on the other. A summary of results obtained from refinement in both space groups is given in Table II.

For the sake of completeness, refinement was also attempted in the third possible space group $P6_3mc$. Isotropic refinement gave $R_1=0.185$ and $R_2=0.239$ and produced many high correlations among parameters. Anisotropic refinement diverged and caused non-positive-definite temperature factors for two atoms. Thus space group $P6_3mc$ is definitely unacceptable.

A comparison of $\Sigma\, w(|F_o| - |F_c|)^2$ as a function of indices, $\lambda^{-1} \sin \theta$, $|F_o|$, etc. showed no significant trends in the data after refinement in $P\bar{6}2c$ or $P6_3/mmc$. In the last cycles of refinement in both $P6_3/mmc$ and $P\bar{6}2c$ no parameter shifted by more than 0.01 times its standard deviation. A list of $|F_o|$ and $|F_c|$ values for refinement in $P6_3/mmc$ is given in Table III.

A disturbing feature of this work is the presence of the 221 reflection, a reflection expected to be extinguished by the c glide plane. Of the 38 unique reflections examined in the class $hh\overline{2h}l$ with $l = 2n + 1$, 36 reflections are definitely unobserved. The 2,2,15 reflection with $I = 134$ and $\sigma(I) = 36$ (where I is the observed intensity corrected only for background and $\sigma(I)$ is the standard deviation based on counting statistics alone) is of marginal significance. However, the 221 reflection has $I = 512$ and $\sigma(I) = 58$. Another crystal mounted in a different orientation showed a diffuse spot on precession films for this reflection, thus ruling out most causes of spurious reflections, e.g. Renninger effects. If we accept this reflection as genuine, the crystal must not contain a c glide plane, although the successful refinement in space group $P6_3/mmc$ suggests that the actual crystal symmetry must be very close to satisfying the c glide condition. In space groups not including the c glide plane the hkl and khl reflections are no longer equivalent and since both forms had not been collected, refinement in these space groups was precluded. However, had this been possible it is doubtful that it would have clarified the situation. A poor refinement would substantiate the results obtained from the present refinement but not explain the presence of the 221 reflection; on the other hand, a good refinement could explain the presence of the 221 reflection but would still leave ambigous the question of space group since the structure successfully refined in space group $P6_3/mmc$. Because the crystal which was used to collect data later decomposed and since no other suitable crystals were available or readily obtainable, it was decided that the achievement of what seemed likely to be only another ambiguous result was not worth the large amount of effort and cost involved. In any event it is doubtful that the molecular structure could change significantly from that reported here. Nor is it likely that the confirmation of the presence or absence of the glide plane would clarify the ambiguity between centric and noncentric space groups.

RESULTS

The final positional and thermal parameters obtained from refinement in $P6_3/mmc$ are presented in Table IV, and V. Root-mean-square vibrational amplitudes are given in

Table VI. Interatomic distances and angles are presented in Tables II and VII, respectively. Figure 2 is a stereo pair showing the contents of the unit cell.

DISCUSSION

Leaving aside the space-group abmiguity, which has been fully discussed in the Experimental section, and causes no significant uncertainty in the structural parameters, the structure of $Cs_3Mo_2Br_8$ is very similar to that of $Rb_3Mo_2Cl_8$. According to all the criteria previously proposed[15] for evaluating the nature and magnitude of the direct metal-to-metal interaction in confacial bioctahedra, the Mo-Mo interaction is unquestionably of a bonding nature, but slightly less strong than that in $Mo_2Cl_8^{3-}$. Thus in $Mo_2Cl_8^{3-}$ the Mo-Mo distance is 2.38(1)Å, while in $Mo_2Br_8^{3-}$ it is 2.439(7)Å.

An interesting comparison can be made between the pair $Mo_2X_8^{3-}$ (X=Cl,Br) on the one hand and the pair $Mo_2X_9^{3-}$ (X=Cl,Br) on the other.[7] Both of the nonahalo anions have much longer Mo-Mo distances (2.66, 2.82Å) than their octahalo analogs (2.38, 2.44Å), and according to all criteria[15] have markedly weaker Mo-Mo bonding interactions.

The metal-to-halogen bonds in the two sets of compounds are presumably very similar since corresponding bond distances differ very little, except for the Mo-Br(bridge) bond distances. In $Mo_2Br_9^{3-}$ the distance is 2.624 Å, while in $Mo_2Br_8^{3-}$ it is 2.672 Å.

The rather strong Mo-Mo interaction in $Mo_2Br_8^{3-}$ reduces the Mo-Br-Mo angle to the remarkably low value of 54.3(2)°. This is smaller than any previously observed bridge angle in a confacial bioctahedron. So far as we know it is the smallest angle ever reported at a bridging halogen atom in any compound.

Related to this uniquely low bridge angle is the parameter d'/d'' (the ratio of the distance (d') of the metal atom to the plane of the set of bridging halogen atoms to the distance (d'') of the metal atom from the plane of the terminal set of halogen atoms). The smaller this ratio, the stronger the M-M attraction must be. The value in this structure is 1.22Å/1.45Å=0.84. This is the smallest value yet observed. Previously the smallest was that in $Mo_2Cl_8^{3-}$, namely 0.89. This is further evidence for a strong Mo-Mo bond in $Mo_2Br_8^{3-}$ although it should not be taken to imply that it is stronger than that $Mo_2Cl_8^{3-}$.

The very short Mo-Mo distance in $Mo_2Br_8^{3-}$ would lead one to predict that the ion would have only one unpaired electron. Even in $Mo_2Cl_9^{3-}$, were Mo-Mo = 2.66Å, there is only a small temperature-independent paramagnetism, although $Mo_2Br_9^{3-}$ (Mo-Mo = 2.82Å) appears to possess unpaired electrons.[16]

Undoubtedly the greater deformation of the (incomplete) bioctahedra in the $Mo_2X_8^{3-}$ structures, compared to the $Mo_2X_9^{3-}$ ones occurs because, in effect, there is only 2/3 as much resistance to compression along the threefold axis. A comparison may also be made with the recently reported structure of molybdenum(III) bromide.[17] This consists of infinite stacks of $MoBr_6$ octahedra, sharing opposite faces. The Mo-Mo distances are alternately 2.92 and 3.14Å. The Mo-Br distances range from 2.53 to 2.57Å. The planes of the triangular sets of Br atoms are separated by 3.68Å as compared to only 2.67Å between the planes of the terminal and bridging sets in $Mo_2Br_8^{3-}$. This shows very dramatically the great structural influence of the Mo-Mo bonding coupled with the incompleteness of the bridging set of bromine atoms.

Note added in proof: Powder samples of $Cs_3Mo_2Br_8$ and $Cs_3Mo_2Cl_8$ were examined for second harmonic generation (SHG) since lack of an inversion center is a necessary condition for SHG.[18] Negative results were obtained for each compound. In each case both 1.06μ to green (0.54μ) conversion and 1.32μ to red (0.66μ) conversion were examined. Increasing the power of the laser resulted only in burning the sample. These results tend to indicate that the crystals are centric; if they are, in fact acentric, the harmonic is either very weak or it is being absorbed. While the indication of the centric space group is quite acceptable in the present case, its significance is uncertain for the chloro compound where refinement definitely favored the acentric space group. Since the SHG criterion thus appears to be inconclusive, the space group ambiguity is considered to be still unresolved.

TABLE I

DISTRIBUTION OF $|E|$ VALUES

	Observed	Theoretical (centric)	Theoretical (noncentric)
Av. $\vert E\vert$	0.720	0.798	0.886
Av. $\vert E\vert^2$	0.948	1.000	1.000
Av. $\vert E^2 - 1\vert$	1.077	0.968	0.736
$\vert E\vert > 1$(%)	27.5	27.5	37.0
$\vert E\vert > 2$(%)	6.1	5.0	1.8
$\vert E\vert > 3$(%)	0.32	0.30	0.01

TABLE II

COMPARISON OF REFINEMENTS IN TWO SPACE GROUPS

		Noncentric $P\bar{6}2c$	Centric $P6_3/mmc$
R values R_1		0.0428	0.0455
R_2		0.0519	0.0555
Correlation coefficients between β_{11} and β_{12}	Br(1)	0.69	< 0.5
	Br(2)	0.95	< 0.5
Error in x coordinate	Br(1)	0.0028	0.0004
	Br(2)	0.0014	0.0002
Occupancy factor for Br(1)		0.70	0.70
Bond distances (Å)			
Mo-Mo		2.438(7)	2.439(7)
Mo-Br(1)		2.679(6)	2.672(5)
Mo-Br(2)		2.554(3)	2.554(3)
Br(1)-Br(2)		3.560(15)	3.494(3)
Br(1)-Br(2')		3.435(15)	3.494(3)
Br(1)-Br(1')		3.634(10)	3.640(9)
Br(2)-Br(2')		3.639(4)	3.638(5)

TABLE III

VALUES OF $10|F_o|$ AND $10|F_c|$ (IN ELECTRONS) FOR $Cs_3Mo_2Br_8$ AFTER REFINEMENT IN SPACE GROUP $P6_3/mmc$

H= 0

K	L	FOBS	FCALC
0	4	1409	1297
0	6	4809	4927
0	10	581	625
0	12	2750	2839
0	14	1792	1742
0	16	1149	1153
0	18	760	798
1	0	890	833
1	1	1079	1039
1	2	577	575
1	3	737	700
1	3	737	700
1	5	1906	1851
1	6	411	421
1	7	271	281
1	8	1583	1597
1	9	255	209
1	10	285	213
1	11	1630	1348
1	12	336	231
1	13	1209	1179
1	14	418	424
1	15	833	834
1	16	373	361
1	17	563	632
2	0	1166	1142
2	1	1298	1271
2	2	2483	2494
2	3	4165	4151
2	4	3164	3206
2	5	1506	1517
2	6	455	416
2	7	2715	2772
2	8	2086	2130
2	9	1215	1229
2	10	2095	2167
2	12	394	398
2	14	600	616
2	15	906	824
2	16	702	656
2	17	364	211
2	18	666	609
3	0	1984	2001
3	1	631	615
3	2	545	541
3	3	396	393
3	4	576	580
3	5	217	216
3	7	680	659
3	8	1488	1524
3	10	636	657
3	12	867	926
3	13	402	390
3	14	281	222
3	16	1165	1086
4	0	755	771
4	1	779	754
4	2	1422	1428
4	3	2373	2414
4	4	1916	1920
4	5	1064	1008
4	6	230	209
4	7	1823	1828
4	8	1268	1342
4	9	737	728
4	10	1354	1407
4	14	335	363
4	15	587	552
4	16	430	417
5	0	372	422
5	1	395	400
5	3	840	878
5	5	521	535
5	6	748	739
5	7	248	256
5	8	876	915
5	11	296	314
5	13	562	576
6	0	2322	2365
6	4	433	368
6	6	1191	1173
6	10	283	270
7	0	411	444
7	2	326	256
7	4	458	444

H= 1

K	L	FOBS	FCALC
1	0	2416	2445
1	2	606	601
1	4	679	686
1	8	1958	2035
1	10	749	739
1	12	1135	1081
1	14	509	363
1	16	1284	1219
1	18	335	398
2	1	847	812
2	2	288	280
2	3	1119	1126
2	5	1185	1193
2	6	779	783
2	7	310	277
2	8	1392	1405
2	9	214	171
2	10	228	202
2	11	798	831
2	13	910	996
2	14	549	518
2	15	867	836
2	16	450	430
3	0	575	535
3	1	629	628
3	2	295	314
3	3	402	399
3	4	324	363
3	5	1110	1151
3	6	295	299
3	7	219	212
3	8	999	1015
3	9	258	232
3	11	935	917
3	13	779	802
3	14	311	256
3	15	625	636
4	0	1303	1286
4	1	393	436
4	2	383	390
4	3	294	304
4	4	357	363
4	7	514	480
4	8	987	1064
4	10	431	420
4	12	597	638
5	1	412	387
5	3	492	506
5	5	527	559
5	6	370	362
5	7	291	148
5	8	654	637
5	11	329	423
6	0	425	405
6	2	257	207
6	4	353	348
6	5	533	522
6	8	408	390
6	8	408	390

H= 2

K	L	FOBS	FCALC
2	0	5126	5599
2	2	444	484
2	4	768	795
2	6	2789	2855
2	6	2789	2855
2	10	474	481
2	12	1786	1854
2	14	1099	1181
2	16	764	756
3	0	736	744
3	1	458	487
3	2	434	470
3	4	687	684
3	5	1029	1042
3	8	835	822
3	9	387	371
3	10	471	439
3	11	879	903
3	12	249	189
3	12	249	189
3	13	723	705
3	15	419	417
4	0	514	485
4	1	432	400
4	2	917	883
4	3	1726	1672
4	4	1197	1207
4	5	659	614
4	6	307	163
4	7	1203	1186
4	8	957	892
4	9	616	542
4	10	936	921
5	0	822	824
5	1	458	441
5	2	271	280
5	3	326	347
5	7	456	513
5	8	489	547
6	0	309	299
6	1	264	196

H= 3

K	L	FOBS	FCALC
3	0	958	954
3	2	271	266
3	4	254	261
3	8	978	991
3	10	316	290
3	12	591	536
4	0	287	299
4	1	315	313
4	3	616	636
4	5	393	395
4	6	555	525
4	8	664	643
5	0	264	202
5	1	276	230

H= 4

K	L	FOBS	FCALC
4	0	1676	1618

TABLE IV

POSITIONAL PARAMETERS FOR $Cs_3Mo_2Br_8$[a]

a) Numbers in parentheses in this and all other tables are estimated standard deviations in the last significant digit.

Atom	No. of Positions, Wyckoff notation	Symmetry	x	y	z
Cs(1)	2b	$\bar{6}m2$	0	0	1/4
Cs(2)	4f	3m	1/3	2/3	0.5720(1)
Mo	4f	3m	1/3	2/3	0.1816(2)
Br(1)[b]	6h	mm	0.5103(4)	2x	1/4
Br(2)	12k	m	0.1770(2)	2x	0.0999(2)

b) The final occupancy factor was 0.70(1).

TABLE V

ANISOTROPIC THERMAL PARAMETERS FOR $Cs_3Mo_2Br_8$[a]

a) The form of the thermal ellipsoid is

$$\exp(-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl))$$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cs(1)	0.0226(8)	β_{11}	0.0023(2)	$\beta_{11}/2$	0	0
Cs(2)	0.0248(6)	β_{11}	0.0016(1)	$\beta_{11}/2$	0	0
Mo	0.0181(7)	β_{11}	0.0014(1)	$\beta_{11}/2$	0	0
Br(1)	0.0369(2)	0.0156(2)	0.0014(2)	$\beta_{22}/2$	0	0
Br(2)	0.0240(7)	0.0154(7)	0.0038(1)	$\beta_{22}/2$	-0.0010(5)	$\beta_{13}/2$

TABLE VI

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)

	Minimum	Intermed.	Maximum
Cs(1)	0.193(7)	0.227(4)	0.227(4)
Cs(2)	0.161(5)	0.238(3)	0.238(3)
Mo	0.148(7)	0.203(4)	0.203(4)
Br(1)	0.152(9)	0.189(10)	0.317(8)
Br(2)	0.187(4)	0.237(6)	0.257(6)

TABLE VII

BOND ANGLES IN THE $Mo_2Br_8^{3-}$ ION, DEGREES

Mo - Br(1) - Mo'	54.3(2)
Br(1) - Mo - Br(1')	100.8(1)
Br(1) - Mo - Br(2)	83.90(6)
Br(1) - Mo - Br(2')	172.5(2)
Br(2) - Mo - Br(2')	90.8(1)

FIGURE 1

Glass crystallizing apparatus.
The interchangeable centerpiece
has a fritted disk (dotted line),
where the diffusion occured. Three
such center pieces were devised
with different porosity of the disk.
This apparatus was also used to
gain crystals for complexes described
in Chapter IV and V.

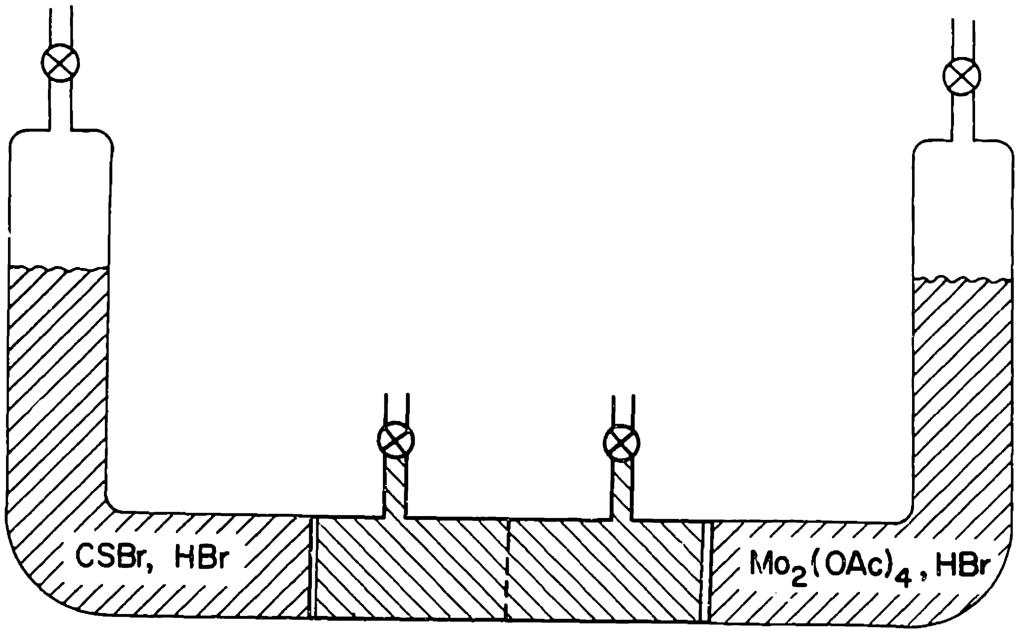
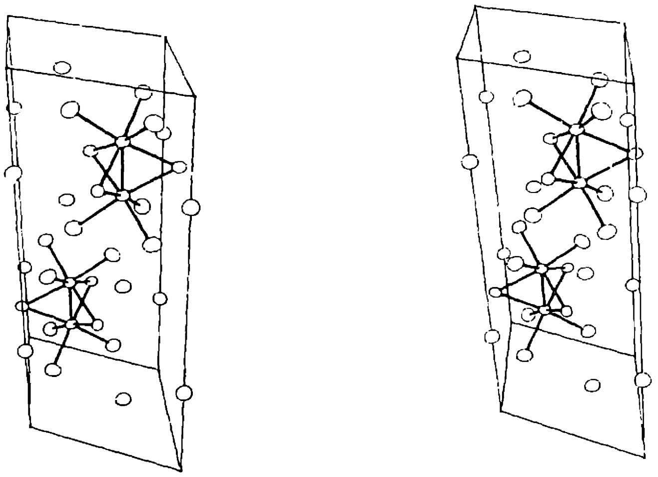

CSBr, HBr
Mo$_2$(OAc)$_4$, HBr

FIGURE 2.

The unit cell of $Cs_3Mo_2Br_8$ presented as a stereoscopic pair. The origin of the unit cell is the front, upper left-hand corner, with x pointing into the plane of the paper, y pointing to the right, z pointing downward.



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CHAPTER III

DIMOLYBDENUM TETRAACETATE

INTRODUCTION

Dimolybdenum tetraacetate is a compound of unique significance in the field of metal-to-metal multiple bonds, since it is the precursor of nearly all of the known compounds containing $\mathrm{Mo}\overset{4^\circ}{\text{----}}\mathrm{Mo}$ (quadruple) bonds. Its partial structure was reported by Lawton and Mason[1] (1965) nearly a decade ago, but many details were omitted and the accuracy was low by present standards. Two particulary important questions which remained unsettled by the published report are: (1) Is the Mo-Mo distance in this compound (reported as 2.11(1)Å) really different from that (2.090(4)Å) in $Mo_2(O_2CCF_3)_4$.[2] (2) Are the $Mo_2(O_2CCH_3)_4$ molecules packed so as to give slightly bonding intermolecular Mo•••O contacts, as in the case of $Mo_2(O_2CCF_3)_4$ where the distance is 2.72(1)Å and in $K_4(Mo_2(SO_4)_4)\cdot 2H_2O$ where it is 2.593Å.[3] A redetermination of the structure was undertaken to answer these questions and provide a complete set of structural parameters.

EXPERIMENTAL

Preparation. - The preparation of dimolybdenum tetraacetate[4] invariably provides microcrystalline material, but the size of the crystals are too small for the purpose of single-crystal investigations. Since dimolybdenum tetraacetate does not have any solvent in which it is capable to dissolve without chemical change, the usual recrystallization procedures fail. However, a very carefully controlled reaction following Wilkinson's method[4], where the reaction mixture after 4 hours reflux was slowly (one day) cooled down to room temperature, provided suitable crystals for single-crystal work. This material proved to be rather stable in air contrary to previous observations. The crystal selected for data collection did not show any significant change even after several months.

Collection of X-Ray Data. - A Syntex P$\bar{1}$ computer-controlled, four-circle diffractometer equipped with a graphite-crystal monochromator in the incident beam was used for data collection. A needle-shaped crystal with dimensions 0.045x0.0025x0.0021 cm was selected and a triclinic unit cell, similar to that previously reported, was obtained. Least-squares refinement of fifteen reflections provided the orientation matrix for data collection and resulted in the following cell parameters: $a = 8.418(2)$Å, $b = 5.500(1)$Å, $c = 7.529(1)$Å, $\alpha = 84.13(2)°$, $\beta = 105.24(2)°$, $\gamma = 106.00(2)°$, and $V = 323.15(1)$Å^3. For $Z = 1$ the calculated density is 2.20gcm^{-3}, in good agreement with the experimental value of 2.18 g cm^{-3} determined by flotation in a mixture of bromoform and cyclohexane.

Data were collected in the range of $0° < 2\theta° < 60°$ using Mo Kα radiation. The $\theta/2\theta$ scan technique with variable scan rate from 4°-24 °/min has been used. The scan range was from $2\theta(\text{MoK}\alpha_1) - 0.9°$ to $2\theta(\text{MoK}\alpha_2) + 0.9°$.

The stabilities of the crystal and the instrument were checked by periodic remeasurements of three standard reflections. No significant changes in these intensities were observed.

A total of 1909 reflections were collected and the usual data reduction procedures were applied. Computer programs used in data reduction, refinement, and interpretation of the structure were as follows: DATARED by Frenz for data reduction; FOURIER, by Robinson and Dellaca, based on FORDAP by Zalkin; the least-squares program NUCLS by Doedens and Ibers based on Busing and Levy's

ORFLS program; a local modification of Baur's SADIAN program for calculating atomic distances and angles; PERFACT by Frenz for analyzing structure factors; ORTEP by Johnson for illustrations; the function and error program ORFFE by Busing, Martin and Levy as modified by Brown, Johnson and Thiessen; and LIST by Snyder for listing the data. The parameter 'p' used in the calculation of standard deviations on intensities ($\sigma(F_o^2)$) was assigned the value 0.07.

Since the linear absorption coefficient was relaively low (μ= 19.17 cm^{-1}, MoKα) absorption corrections were omitted.

Solution and Refinement of the Structure. - A three-dimensional Patterson function was calculated and from this - assuming space group P$\bar{1}$ - one Mo and four oxygen atoms were immediately located. The structure was solved and refined by the usual combination of least-squares refinements and difference Fourier-syntheses. In the least-squares refinement only those 1526 reflections were employed for which $F_o^2 > 3\sigma(F_o^2)$. Three cycles of isotropic least-squares refinement of one molybdenum and four oxygen atoms resulted in $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o| =$ 0.159 and $R_2 = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2)^{\frac{1}{2}}$ = 0.215. A difference

Fourier synthesis then provided the locations of the carbon atoms. Five cycles of anisotropic refinement on all non-hydrogen atoms resulted in full convergence and gave $R_1 = 0.047$ and $R_2 = 0.062$. Parameter changes in the last cycle were all less than 0.05 times the estimated standard deviation of that parameter. There were only three pairs of parameters (all between the scale factor and β_{11}(Mo), β_{22}(Mo) and β_{33}(Mo)) where the correlation coefficients slightly exceeded 0.5. The standard deviation in an observation of unit weight was 1.18.

Of the 1526 reflections used in the least-squares refinement there were only 40 for which $||F_o| - |F_c||$ slightly exceeded $3\sigma(F_o^2)$. The $1\overline{21}$ reflection suffered from extinction.

In the final difference Fourier map the highest peak had a density of $1.67e\text{Å}^{-3}$ and there were four other peaks, with densities exceeding $1e\text{Å}^{-3}$. These 5 peaks appeared at distances of 0.8Å to 1.2Å from the Mo atom. Another difference Fourier map, where all reflections beyond $\sin\theta/\lambda = 0.35$ were excluded provided densities less than $0.8\ e\text{Å}^{-3}$. In this map there were peaks at locations reasonable for hydrogen atoms, but attempts at refinement failed.

Atomic scattering factors for Mo, C and O were taken from Cromer (1972)[5] and the anomalous dispersion corrections for Mo were obtained from Cromer and Liberman (1971)[6].

RESULTS

The positional, thermal parameters are reported in Table I and II. Figure 1 shows the structure and the atom numbering scheme. The bond distances (as well as the one important intermolecular contact) and the bond angles are listed in Table III and IV. The important least-squares planes are depicted in Table V. The observed and final calculated structure factors are reported in Table VI.

DISCUSSION

The structure found in this work is in very close agreement with that of $Mo_2(O_2CCF_3)_4$. The two Mo-Mo distances, 2.093(1) and 2.090(4) are the same to within $\pm$ 0.005A, despite the difference in the basicities of the CH_3COO^- and CF_3COO^- ligands. The average values of the other principal dimensions of this structure, viz., Mo-O, 2.12 ± 0.01Å; C-O, 1.280 ± 0.005Å; C-C, 1.151 ± 0.005Å; Mo-Mo-O, $91.8\pm0.8°$; O-C-O, $121.3\pm0.5°$, all agree closely with the corresponding dimensions of the $Mo_2(O_2CCF_3)_4$

structure. These dimensions would be suitable for use in molecular orbital calculations or vibrational analysis.

The $Mo_2(O_2CCH_3)_4$ molecules are strung together in infinite chains in essentially the same way as the $Mo_2(O_2CCF_3)_4$ molecules. The oxygen atoms O2 and O2' each make a contact that is essentially coaxial with the Mo-Mo bond to the closest Mo atom of the adjacent molecule. The O•••Mo distance in this case, 2.645(4)Å, is similar to those in $Mo_2(O_2CCF_3)_4$, 2.72(1)Å, and $K_4(Mo_2(SO_4)_4)\cdot 2H_2O$, 2.593Å.

The fact that the Mo-Mo distance in the two carboxylato compounds (2.092Å) is significantly (in a statistical sense) shorter than that (2.110(3)Å) in the $(Mo_2(SO_4)_4)^{4-}$ ion may be due to the smaller "bite" of the RCO_2^- ligand as compared to that of the SO_4^{2-} ligand. On the other hand, since Mo-Mo distances in various salts of the $Mo_2Cl_8^{4-}$ ion vary over a range of <u>ca</u>. 0.02Å, (cf. ref. 3), there may not be any such simple explanation.

TABLE I

POSITIONAL PARAMETERS FOR $Mo_2(O_2CCH_3)_4$[a]

[a] The numbers in parentheses in this and other tables are the estimated standard deviations in the least significant digits.

Atom	x	y	z
Mo	0.04395(6)	0.16735(8)	0.07307(6)
O1	-0.1754(6)	0.0809(8)	0.1772(6)
O2	-0.0766(5)	0.3644(7)	-0.1600(6)
O3	0.2687(6)	0.2754(8)	-0.0214(7)
O4	0.1697(6)	-0.0069(8)	0.3127(6)
C1	-0.2869(8)	-0.1273(13)	0.1296(9)
C2	-0.1561(8)	0.2426(11)	-0.3077(8)
C3	-0.4438(9)	0.1974(17)	0.2040(11)
C4	-0.2329(10)	0.3802(14)	-0.4760(9)

TABLE II

THERMAL PARAMETERS FOR $Mo_2(O_2CCH_3)_4$[a]

a) The anisotropic temperature parameters are of the form

$$\exp(-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}kh+2\beta_{13}hl+2\beta_{23}kl))$$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{13}
Mo	0.01016(8)	0.01295(16)	0.01091(9)	0.00340(8)	0.00134(6)	-0.00261(8)
O1	0.0128(7)	0.0240(15)	0.0146(8)	0.0051(8)	0.0045(6)	-0.0038(9)
O2	0.0127(7)	0.0166(13)	0.0125(8)	0.0046(8)	0.0015(6)	-0.0020(8)
O3	0.0115(7)	0.0221(15)	0.0166(9)	0.0018(8)	0.0028(6)	-0.0028(9)
O4	0.0152(8)	0.0180(14)	0.0128(8)	0.0068(8)	0.0003(6)	-0.0041(8)
C1	0.0119(10)	0.0292(23)	0.0157(12)	0.0083(13)	0.0028(9)	0.0019(13
C2	0.0122(9)	0.0233(20)	0.0123(10)	0.0059(11)	0.0034(8)	-0.0019(11)
C3	0.013(1)	0.046(3)	0.022(2)	0.055(2)	0.009(1)	-0.001(2)
C4	0.021(1)	0.029(2)	0.012(1)	0.012(1)	0.000(1)	-0.001(1)

TABLE III

BOND DISTANCES, Å

Mo-Mo	2.0934(8)
Mo-O1	2.110(4)
Mo-O2	2.137(4)
Mo-O3	2.107(5)
Mo-O4	2.121(4)
C1-O1	1.279(8)
C1-O3'	1.272(8)
C2-O4	1.273(7)
C2-O2'	1.284(7)
C1-C3	1.507(9)
C2-C4	1.496(9)

Intermolecular Distance, Å:

Mo-O2	2.645(4)

TABLE IV

BOND ANGLES, DEGREES

Mo'-Mo-O1	91.7(1)
Mo'-Mo-O2	90.4(1)
Mo'-Mo-O3	92.0(1)
Mo'-Mo-O4	93.2(1)

O1-Mo-O3	176.3(1)
O2-Mo-O4	176.5(2)

O1-Mo-O2	90.9(2)
O1-Mo-O4	89.2(2)
O2-Mo-O3	89.1(2)
O3-Mo-O4	90.6(2)

Mo-O1-C1	117.2(4)
Mo-O2-C2'	118.5(4)
Mo-O3-C1'	117.3(4)
Mo-O4-C2	117.1(4)

O1-C1-O3'	121.8(6)
O4-C2-O2'	120.8(5)
O1-C1-C3	118.7(6)
O2'-C2-C4	119.4(5)
O3'-C1-C3	119.5(5)
O4-C2-C4	119.4(5)

TABLE V

LEAST SQUARES PLANES[a]

[a] x, y and z are fractional triclinic coordinates.

A. Equations of Planes[a]

(1) 01, 03', 01', 03	$3.311x-2.873y+4.588z-0.=0$
(2) 02, 04, 02', 04'	$-7.642x+0.216y+4.151z-0.=0$
(3) 01, 02, 03, 04	$-0.321x+4.576y+3.762z-1.0916=0$

B. Dihedral Angles

Planes (1) and (2)	90.8°
Planes (1) and (3)	91.3°
Planes (2) and (3)	89.7°

TABLE VI

OBSERVED AND FINAL CALCULATED STRUCTURE FACTORS

AS $10|F_o|$ AND $10|F_c|$, IN ELECTRONS

H= 0

K	L	FOBS	FCALC
0	1	849	877
0	2	271	248
0	4	116	113
0	5	257	255
0	6	130	129
0	7	196	191
0	8	193	194
0	9	83	86
1	-10	91	90
1	-9	140	136
1	-8	201	189
1	-7	154	159
1	-5	102	97
1	-4	249	251
1	-3	546	514
1	-2	301	326
1	-1	369	350
1	0	539	548
1	1	446	371
1	2	395	369
1	3	332	325
1	4	481	467
1	5	409	338
1	6	247	242
1	7	51	51
1	9	94	90
1	10	108	113
2	-7	138	132
2	-6	214	205
2	-5	269	256
2	-4	241	237
2	-3	306	320
2	-2	181	179
2	-1	74	73
2	0	350	373
2	1	714	701
2	2	749	720
2	3	530	520
2	4	261	261
2	5	134	135
2	6	55	40
2	7	73	70
2	8	136	132
2	9	148	131
3	-8	123	116
3	-7	214	208
3	-6	271	278
3	-5	182	168
3	-4	119	119
3	-3	87	85
3	-2	259	255
3	-1	377	377
3	0	359	355
3	1	518	503
3	2	286	277
3	4	68	95
3	5	190	179
3	6	268	260
3	7	205	208
3	8	122	119
3	9	89	87
4	-8	88	71
4	-7	78	83
4	-5	93	95
4	-4	170	176
4	-3	155	156
4	-2	293	326
4	-1	263	282
4	0	197	187
4	1	76	72
4	2	124	111
4	3	476	458
4	4	415	396
4	5	260	256
4	6	184	173
4	7	87	81
5	-6	118	114
5	-5	208	219
5	-4	229	242
5	-3	152	155
5	-2	74	70
5	0	186	175
5	1	191	178
5	2	219	204
5	3	266	259
5	4	253	245
5	5	63	57
5	7	102	101
6	-5	77	89
6	-3	55	52
6	-2	133	121
6	-1	160	168
6	0	239	221
6	1	211	217
6	2	118	121
6	4	98	88
6	5	171	157
6	6	186	171
7	-3	171	171
7	-2	181	165
7	-1	161	144
7	0	75	80
7	2	71	62
7	3	102	95

H= 1

K	L	FOBS	FCALC
-7	-4	138	136
-7	-3	96	139
-7	-2	63	47
-7	0	134	123
-7	1	154	140
-7	2	167	169
-7	3	136	143
-6	-6	152	166
-6	-5	47	118
-6	-3	111	118
-6	-2	191	206
-6	-1	261	273
-6	0	172	176
-6	1	123	121
-6	4	87	78
-6	5	95	90
-5	-8	109	96
-5	-5	128	132
-5	-4	278	295
-5	-3	296	311
-5	-2	311	310
-5	-1	262	269
-5	0	103	94
-5	1	99	100
-5	2	93	98
-5	3	190	206
-5	4	208	225
-5	5	144	158
-5	6	56	58
-4	-7	145	137
-4	-6	166	171
-4	-5	183	190
-4	-4	346	377
-4	-3	293	292
-4	-2	60	78
-4	-1	75	85
-4	0	352	322
-4	1	402	469
-4	2	268	279
-4	3	108	113
-4	4	127	133
-4	6	73	75
-4	7	111	113
-4	8	98	109
-3	-9	126	124
-3	-8	166	163
-3	-7	244	260
-3	-6	166	172
-3	-5	48	49
-3	-4	82	89
-3	-3	177	185
-3	-2	427	483
-3	-1	397	419
-3	0	474	487
-3	1	427	490
-3	2	280	295
-3	4	113	122
-3	5	193	201
-3	6	225	233
-3	7	157	162
-3	8	82	90
-2	-10	128	136
-2	-9	160	158
-2	-8	131	142
-2	-7	65	62
-2	-5	139	154
-2	-4	220	224
-2	-3	539	589
-2	-2	625	696
-2	0	36	5
-2	1	196	216
-2	2	490	481
-2	3	276	292
-2	4	236	235
-2	5	170	177
-2	6	153	150
-2	7	49	41
-2	9	71	78
-1	-10	80	92
-1	-9	47	35
-1	-7	158	157
-1	-6	358	355
-1	-5	369	357
-1	-4	148	158
-1	-3	140	154
-1	-2	224	221
-1	-1	298	340
-1	0	500	484
-1	1	897	867
-1	2	892	911
-1	3	650	617
-1	4	74	82
-1	5	48	50
-1	6	103	99
-1	7	169	167
-1	8	145	161
-1	9	78	89
0	-9	151	146
0	-8	231	234
0	-7	178	179
0	-6	264	265
0	-5	198	208
0	-4	44	45
0	-3	188	168
0	-2	136	114
0	-1	754	734
0	0	925	938
0	1	493	484
0	2	443	419
0	4	362	356
0	5	333	330
0	6	152	153
0	7	213	210
0	8	137	124
1	-10	84	73
1	-9	154	158
1	-8	198	182
1	-7	100	99
1	-6	96	101
1	-5	183	188
1	-4	522	493
1	-3	451	441
1	-2	257	234
1	-1	108	90
1	0	199	181
1	1	332	303
1	2	354	351
1	3	419	413
1	4	563	554
1	5	421	426
1	6	180	174
1	9	112	103
2	-7	156	152
2	-6	264	254
2	-5	357	360
2	-4	345	337
2	-3	340	321
2	-2	74	74
2	-1	42	21
2	0	403	388
2	1	639	610
2	2	647	655
2	3	328	323
2	4	138	147
2	5	63	64
2	6	112	110
2	7	131	126
2	8	131	129
2	9	133	124
3	-9	57	61
3	-8	115	116
3	-7	164	180
3	-6	182	180
3	-5	137	134
3	-3	245	252
3	-2	354	353
3	-1	272	268
3	0	227	214
3	1	358	344
3	2	147	138
3	4	199	183
3	5	344	332
3	6	365	354
3	7	186	175
3	8	136	106
4	-8	68	68
4	-6	59	57
4	-5	170	178
4	-4	193	190
4	-3	300	294
4	-2	377	369
4	-1	214	212
4	0	73	79
4	2	201	191
4	3	332	330
4	4	243	231
4	5	246	230
4	6	161	151
4	8	66	64
5	-6	127	132
5	-5	224	215
5	-4	206	209
5	-3	80	92
5	-1	157	144
5	0	235	222
5	1	200	188
5	2	195	190
5	3	229	214
5	4	109	104
5	7	152	145
6	-3	77	74
6	-2	185	171
6	-1	242	222
6	0	279	254
6	1	184	165
6	2	92	89
6	4	117	102
6	5	165	158
7	-2	138	127
7	-1	107	106
7	2	80	88

H= 2

K	L	FOBS	FCALC
-7	-5	149	152
-7	-4	116	112
-7	-3	72	80
-7	-1	85	104
-7	0	156	158
-7	1	165	154
-7	2	149	157
-7	3	71	80
-6	-7	123	127
-6	-6	101	105
-6	-5	59	53
-6	-3	143	161
-6	-2	268	312
-6	-1	310	324
-6	0	210	210
-6	1	100	103
-6	3	66	64
-6	4	79	95
-6	5	94	94
-5	-8	64	67
-5	-6	74	71
-5	-5	206	221
-5	-4	207	217
-5	-3	195	213
-5	-2	252	266
-5	-1	249	276
-5	1	105	106
-5	2	192	210
-5	3	254	277
-5	4	188	207
-5	5	68	80
-4	-8	112	110
-4	-7	164	177
-4	-6	182	185
-4	-5	211	238
-4	-4	241	281
-4	-2	73	88
-4	-1	207	239
-4	0	394	416
-4	1	448	474
-4	2	212	228
-4	3	206	213
-4	4	102	97
-4	6	97	95
-4	7	84	91
-4	8	114	126
-3	-10	83	73
-3	-9	143	133
-3	-8	251	246
-3	-7	275	282
-3	-6	140	139
-3	-4	91	94
-3	-3	232	254
-3	-2	362	427
-3	-1	324	383
-3	0	540	529
-3	1	343	342
-3	2	63	66
-3	3	167	172
-3	4	168	168
-3	5	240	251
-3	6	160	168
-3	7	98	107
-2	-10	91	101
-2	-9	135	128
-2	-8	96	99
-2	-7	64	59
-2	-6	116	114
-2	-5	199	216
-2	-4	326	353
-2	-3	385	409
-2	-2	334	377
-2	-1	237	252
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-2	1	409	377
-2	2	640	666
-2	3	497	492
-2	4	344	350
-2	5	176	172
-2	6	77	82
-2	9	103	98
-1	-8	86	82
-1	-7	294	287
-1	-6	417	413
-1	-5	403	398
-1	-4	183	186
-1	-3	185	179
-1	-2	297	265
-1	-1	260	238
-1	0	136	119
-1	1	399	427
-1	2	816	798
-1	3	430	456
-1	4	150	143
-1	5	53	44
-1	6	225	227
-1	7	209	208
-1	8	117	121
-1	9	72	74
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0	-8	189	187
0	-7	207	205
0	-6	294	291
0	-5	49	53
0	-4	164	159
0	-3	248	253
0	-2	373	397
0	-1	998	897
0	0	271	249
0	1	91	72
0	2	49	23
0	3	222	222
0	4	410	408
0	5	252	244
0	6	253	257
0	7	221	219
0	8	73	89
1	-10	65	66
1	-9	98	101
1	-8	97	102
1	-6	93	91
1	-5	357	345
1	-4	694	669
1	-3	521	500
1	-2	280	278
1	-1	188	203
1	0	178	141
1	1	243	242
1	2	240	235
1	3	512	518
1	4	497	483
1	5	272	275
1	8	107	99
1	9	95	99
2	-8	93	98
2	-7	131	134
2	-6	207	197
2	-5	254	252
2	-4	348	338
2	-3	221	215
2	-1	267	255
2	0	448	436
2	1	417	396
2	2	337	323
2	3	213	209
2	4	94	96
2	5	138	131
2	6	185	181
2	7	205	213
2	8	153	159
2	9	139	117
3	-9	82	81
3	-8	121	129
3	-7	165	161
3	-6	79	91
3	-5	47	43
3	-4	168	162
3	-3	367	350
3	-2	428	417
3	-1	340	329
3	0	363	350
3	1	174	177
3	4	146	142
3	5	289	288
3	6	278	263
3	7	156	154
3	8	102	87
4	-6	65	62
4	-5	132	135
4	-4	194	188
4	-3	354	352
4	-2	287	279
4	-1	122	117
4	1	136	121
4	2	328	315
4	3	252	238
4	4	166	164
4	5	149	142
4	6	79	62
4	7	60	45
5	-6	115	118
5	-5	150	139
5	-4	114	108
5	-3	53	60
5	-1	245	229
5	0	272	256
5	1	245	236
5	2	233	216
5	3	186	176
5	6	100	97
6	-3	72	85
6	-2	150	142
6	-1	216	202
6	0	213	200
6	1	115	109
6	3	81	80
6	4	140	121

H= 3

K	L	FOBS	FCALC
-7	-5	73	89
-7	-1	166	170
-7	0	195	202
-7	1	196	216
-7	2	138	142
-6	-7	129	138
-6	-4	111	115
-6	-3	180	184
-6	-2	246	280
-6	-1	190	226
-6	0	191	197
-6	1	93	91
-6	3	108	120
-6	4	109	111
-6	5	117	127
-5	-6	152	160
-5	-5	237	261
-5	-4	166	187
-5	-3	139	164
-5	-2	148	168
-5	-1	68	59
-5	0	118	114
-5	1	130	128
-5	2	280	282
-5	3	278	292
-5	4	177	188
-4	-8	128	138
-4	-7	211	213
-4	-6	234	249
-4	-5	299	337
-4	-4	147	161
-4	-3	46	49
-4	-2	94	124
-4	-1	298	310
-4	0	491	479
-4	1	356	343
-4	2	176	176
-4	3	145	155
-4	5	76	81
-4	6	90	98
-4	7	82	92
-3	-10	102	91
-3	-9	118	123
-3	-8	209	228
-3	-7	207	202
-3	-6	101	118
-3	-4	164	177
-3	-3	309	374
-3	-2	185	215
-3	-1	250	254
-3	0	374	351
-3	1	262	247
-3	2	79	77
-3	3	236	254
-3	4	347	349
-3	5	288	311
-3	6	151	154
-2	-10	104	91
-2	-9	99	80
-2	-7	59	53
-2	-6	197	200
-2	-5	311	308
-2	-4	521	550
-2	-3	454	487
-2	-2	297	305
-2	-1	68	55
-2	0	120	121
-2	1	382	362
-2	2	295	303
-2	3	362	369
-2	4	312	324
-2	5	206	210
-2	8	96	96
-1	-8	119	115
-1	-7	313	311
-1	-6	411	397
-1	-5	315	321
-1	-4	223	212
-1	-2	480	400
-1	-1	202	217
-1	0	291	276
-1	1	415	410
-1	2	405	383
-1	3	47	49
-1	4	41	41
-1	5	152	158
-1	6	235	242
-1	7	207	209
-1	8	111	108
-1	9	78	90
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0	-9	123	122
0	-8	63	64
0	-7	156	151
0	-6	172	169
0	-4	244	233
0	-3	500	477
0	-2	963	901
0	-1	757	737
0	0	146	166
0	1	162	153
0	2	52	53
0	3	315	312
0	4	330	337
0	5	213	213
0	6	261	255
0	7	121	124
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1	-9	91	89
1	-7	86	90
1	-6	119	120
1	-5	332	329
1	-4	421	406
1	-3	406	399
1	-2	356	321
1	-1	222	199
1	0	213	199
1	1	199	197
1	2	194	198
1	3	371	363
1	4	334	336
1	5	156	156
1	7	84	95
1	8	165	164
1	9	114	114
2	-8	112	108
2	-7	147	145
2	-6	190	191
2	-5	165	171
2	-4	156	156
2	-2	178	171
2	-1	490	473
2	0	557	549
2	1	475	465
2	2	215	208
2	3	110	108
2	5	86	80
2	6	133	136
2	7	187	175
2	8	163	161
3	-9	87	97
3	-8	122	123
3	-7	105	104
3	-6	79	79
3	-4	177	179
3	-3	326	320
3	-2	373	365
3	-1	352	338
3	0	306	291
3	1	49	38
3	3	107	110
3	4	205	204
3	5	243	244
3	6	132	135
3	7	108	97
4	-6	98	99
4	-5	74	76
4	-4	154	141
4	-3	236	229
4	-2	174	165
4	-1	68	60
4	0	85	86
4	1	299	291
4	2	364	360
4	3	203	210
4	4	183	168
4	5	106	105
5	-6	143	141
5	-5	111	112
5	-2	100	99
5	-1	186	175
5	0	197	191
5	1	222	212
5	2	211	203
5	3	91	87
6	-3	116	103
6	-2	135	135
6	-1	168	162
6	0	115	107
6	2	62	59
6	3	133	128

H= 4

K	L	FOBS	FCALC
-7	-5	86	74
-7	-2	83	98
-7	-1	155	156
-7	0	205	182
-7	1	238	209
-7	2	121	115
-6	-7	123	114
-6	-5	62	76
-6	-4	149	161
-6	-3	222	249
-6	-2	197	218
-6	-1	128	125
-6	0	80	76
-6	2	77	75
-6	3	123	122
-6	4	119	125
-6	5	141	147
-5	-6	230	246
-5	-5	235	267
-5	-4	194	224
-5	-3	161	188
-5	-2	118	139
-5	-1	69	70
-5	0	143	122
-5	1	235	215
-5	2	324	312
-5	3	236	243
-5	4	102	97
-4	-9	102	93
-4	-8	126	128
-4	-7	165	161
-4	-6	256	261
-4	-5	303	323
-4	-4	49	66
-4	-3	66	69
-4	-2	191	217
-4	-1	322	323
-4	0	339	330
-4	1	146	141
-4	2	184	187
-4	3	65	71
-4	4	88	88
-4	5	148	160
-4	6	126	134
-4	7	130	137
-3	-10	101	94
-3	-9	157	150
-3	-8	176	167
-3	-7	73	76
-3	-5	125	129
-3	-4	268	301
-3	-3	401	427
-3	-2	308	313
-3	-1	345	339
-3	0	189	181
-3	1	44	37
-3	2	124	125
-3	3	171	168
-3	4	305	317
-3	5	244	249
-3	6	144	158
-2	-10	76	77
-2	-7	94	84
-2	-6	199	192
-2	-5	402	406
-2	-4	518	536
-2	-3	427	437
-2	-2	172	172
-2	-1	92	91
-2	0	325	305
-2	1	392	381
-2	2	204	213
-2	3	205	206
-2	4	137	137
-2	5	78	79
-2	7	59	60
-2	8	117	129
-1	-9	59	60
-1	-8	167	162
-1	-7	200	190
-1	-6	200	186
-1	-5	167	168
-1	-4	216	208
-1	-3	201	200
-1	-2	495	452
-1	-1	492	463
-1	0	506	495
-1	1	520	505
-1	2	202	203
-1	3	41	47
-1	4	48	52
-1	5	231	238
-1	6	214	236
-1	7	142	148
-1	8	89	86
0	-10	137	129
0	-9	138	132
0	-8	98	98
0	-7	103	107
0	-5	107	105
0	-4	147	148
0	-3	371	375
0	-2	805	802
0	-1	526	497
0	0	255	247
0	2	189	182
0	3	276	272
0	4	139	140
0	5	206	202
0	6	202	199
0	7	67	69
1	-10	104	96
1	-9	80	74
1	-7	70	82
1	-6	199	194
1	-5	326	328
1	-4	235	229
1	-3	137	140
1	-2	70	74
1	-1	59	58
1	0	337	324
1	1	306	298
1	2	414	411
1	3	342	336
1	4	194	193
1	7	104	104
1	8	136	126
2	-9	94	81
2	-8	128	121
2	-7	146	150
2	-6	143	143
2	-5	165	158
2	-4	117	114
2	-2	250	247
2	-1	498	493
2	0	492	499
2	1	371	357
2	2	160	153
2	4	103	106
2	5	105	102
2	6	130	135
2	7	119	122
2	8	105	105
3	-8	121	117
3	-7	57	65
3	-5	96	94
3	-4	167	159
3	-3	170	163
3	-2	172	174
3	-1	264	264
3	0	152	155
3	2	130	123
3	3	227	227
3	4	274	274
3	5	212	199
3	6	102	106
3	7	62	65

K	L	FOBS	FCALC
4	-7	80	80
4	-6	127	125
4	-5	134	136
4	-4	201	193
4	-3	117	125
4	0	104	100
4	1	288	279
4	2	265	259
4	3	197	194
4	4	146	139
4	5	58	44
5	-6	120	121
5	-5	75	81
5	-2	143	137
5	-1	149	146
5	0	142	144
5	1	152	144
5	2	117	109
6	-3	124	109
6	-2	136	130
6	-1	130	127
6	0	86	75
6	2	83	84

H= 5

K	L	FOBS	FCALC
-7	-2	141	147
-7	-1	158	147
-7	0	181	162
-7	1	125	114
-6	-7	61	61
-6	-5	112	120
-6	-4	212	224
-6	-3	277	295
-6	-2	179	182
-6	-1	123	113
-6	1	65	58
-6	2	147	133
-6	3	117	120
-6	4	141	145
-5	-7	124	124
-5	-6	199	211
-5	-5	174	196
-5	-4	214	230
-5	-3	188	214
-5	-2	60	58
-5	-1	125	119
-5	0	114	110
-5	1	242	234
-5	2	258	244
-5	3	166	164
-5	6	69	82
-4	-9	108	111
-4	-8	128	132
-4	-7	142	141
-4	-6	199	213
-4	-5	88	105
-4	-3	127	140
-4	-2	330	319
-4	-1	435	414
-4	0	262	244
-4	1	90	90
-4	2	106	105
-4	4	70	79
-4	5	114	123
-4	6	129	138
-3	-10	116	103
-3	-9	161	150
-3	-8	112	100
-3	-6	63	57
-3	-5	172	162
-3	-4	365	372
-3	-3	367	367
-3	-2	385	377
-3	-1	329	309
-3	0	133	125
-3	1	102	97
-3	2	176	172
-3	3	214	221
-3	4	213	217
-3	5	122	121
-3	6	77	67
-2	-7	116	110
-2	-6	129	124
-2	-5	257	263
-2	-4	324	310
-2	-3	305	309
-2	-2	55	48
-2	-1	233	219
-2	0	511	501
-2	1	381	375
-2	2	278	278
-2	3	180	184
-2	4	102	105
-2	6	53	58
-2	7	109	107
-1	-9	116	118
-1	-8	233	232
-1	-7	221	214
-1	-6	95	100
-1	-4	50	48
-1	-3	231	225
-1	-2	194	194
-1	-1	409	398
-1	0	584	567
-1	1	451	444
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-1	4	121	129
-1	5	196	193
-1	6	164	170
-1	7	86	99
-1	8	83	83
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0	-8	131	133
0	-7	87	88
0	-6	54	48
0	-5	141	135
0	-4	206	211
0	-3	421	409
0	-2	372	364
0	-1	94	107
0	0	68	68
0	1	133	133
0	2	321	317
0	3	281	286
0	4	150	155
0	5	187	189
0	6	95	97
1	-8	77	65
1	-7	126	126
1	-6	238	241
1	-5	241	231
1	-4	171	170
1	-3	132	133
1	-2	78	79
1	-1	177	177
1	0	311	301
1	1	358	362
1	2	408	405
1	3	280	278
1	4	100	99
1	7	107	114
2	-9	77	80
2	-8	120	123
2	-7	165	167
2	-6	136	136
2	-5	97	88
2	-3	51	53
2	-2	180	175
2	-1	261	258
2	0	319	315
2	1	220	220
2	2	91	85
2	3	94	96
2	4	154	153
2	5	160	156
2	6	139	146
2	7	110	116
3	-8	67	67
3	-7	50	39
3	-5	177	171
3	-4	225	224
3	-3	189	195
3	-2	135	144
3	-1	113	116
3	2	108	115
3	3	238	232
3	4	245	257
3	5	140	146
3	6	84	87
4	-7	81	83
4	-6	105	104
4	-5	147	155
4	-4	159	177
4	-3	93	99
4	-1	56	49
4	0	163	166
4	1	221	216
4	2	146	139
4	3	122	121
4	4	68	63
5	-3	91	95
5	-2	144	137
5	-1	124	126
5	0	128	128
5	1	123	125
5	2	64	54

H= 6

K	L	FOBS	FCALC
-7	-3	129	119
-7	-2	174	177
-7	-1	189	171
-7	0	173	157
-6	-5	128	126
-6	-4	200	230
-6	-3	231	241
-6	-2	169	168
-6	-1	94	95
-6	1	100	87
-6	2	106	112
-6	3	118	108
-6	4	135	137
-5	-8	88	71
-5	-7	185	181
-5	-6	141	162
-5	-5	130	131
-5	-4	131	136
-5	-3	95	104
-5	-2	75	68
-5	-1	133	123
-5	0	222	197
-5	1	278	261
-5	2	178	179
-5	3	61	63
-4	-9	126	113
-4	-8	121	118
-4	-7	131	148
-4	-6	164	163
-4	-4	66	77
-4	-3	233	227
-4	-2	393	371
-4	-1	378	379
-4	0	182	172
-4	1	137	134
-4	3	88	82
-4	4	112	107
-4	5	71	88
-4	6	127	115
-3	-9	139	139
-3	-8	58	56
-3	-6	99	98
-3	-5	140	143
-3	-4	203	198
-3	-3	215	199
-3	-2	324	313
-3	-1	208	209
-3	1	204	203
-3	2	239	236
-3	3	281	282
-3	4	169	172
-3	5	103	91
-2	-8	106	93
-2	-7	171	170
-2	-6	249	250
-2	-5	231	225
-2	-4	118	115
-2	-3	40	29
-2	-2	53	57
-2	-1	220	214
-2	0	368	362
-2	1	335	325
-2	2	294	300
-2	3	158	159
-2	6	56	52
-2	7	128	115
-1	-9	158	148
-1	-8	201	200
-1	-7	187	186
-1	-6	122	126
-1	-5	66	69
-1	-4	162	159
-1	-3	236	227
-1	-2	195	193
-1	-1	261	261
-1	0	317	312
-1	1	153	141
-1	3	84	74
-1	4	208	217
-1	5	192	190
-1	6	113	110
-1	7	66	68
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0	-6	102	105
0	-5	162	157
0	-4	239	237
0	-3	360	365
0	-2	203	201
0	-1	98	107
0	1	235	235
0	2	324	335
0	3	212	222
0	4	190	201
0	5	151	151
1	-8	69	67
1	-7	153	153
1	-6	255	262
1	-5	214	215
1	-4	125	117
1	-3	42	34
1	-1	98	100
1	0	121	114
1	1	264	270
1	2	294	292
1	3	187	180
1	5	55	61
1	6	119	126
1	7	117	113
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2	-8	92	98
2	-7	101	102
2	-6	97	94
2	-4	64	73
2	-3	192	201
2	-2	269	275
2	-1	210	217
2	0	136	144
2	3	94	92
2	4	126	126
2	5	176	165
2	6	138	138
3	-6	71	79
3	-5	162	165
3	-4	199	193
3	-3	183	187
3	-2	184	180
3	-1	68	75
3	2	130	133
3	3	170	182
3	4	142	145
3	5	82	82
4	-6	81	70
4	-5	119	127
4	-4	90	98
4	-1	97	100
4	0	180	184
4	1	150	154
4	2	118	116
4	3	92	88
5	-3	118	115
5	-2	131	134
5	-1	122	124
5	0	107	105
5	1	76	72

H= 7

K	L	FOBS	FCALC
-7	-3	146	126
-7	-2	181	158
-7	-1	202	180
-7	0	134	123
-6	-6	104	103
-6	-5	160	158
-6	-4	206	195
-6	-3	115	123
-6	-2	102	95
-6	0	76	58
-6	1	135	121
-6	2	108	101
-6	3	130	117
-5	-8	130	112
-5	-7	168	166
-5	-6	133	119
-5	-5	129	119
-5	-4	111	105
-5	-2	135	129
-5	-1	165	150
-5	0	283	263
-5	1	259	241
-5	2	127	132
-4	-9	120	111
-4	-8	130	133
-4	-7	158	160
-4	-6	57	52
-4	-5	54	56
-4	-4	84	78
-4	-3	177	172
-4	-2	280	267
-4	-1	235	222
-4	0	139	139
-4	1	107	100
-4	2	66	61
-4	3	124	121
-4	4	128	127
-4	5	108	109
-3	-9	102	80
-3	-7	65	64
-3	-6	163	153
-3	-5	239	248
-3	-4	174	175
-3	-3	130	120
-3	-2	106	101
-3	-1	66	59
-3	0	59	55
-3	1	170	161
-3	2	250	253
-3	3	261	255
-3	4	141	143
-3	5	65	62
-2	-8	108	104
-2	-7	170	173
-2	-6	258	262
-2	-5	223	226
-2	-4	155	150
-2	-2	167	159
-2	-1	276	277
-2	0	209	203
-2	1	184	186
-2	2	152	150
-2	3	86	81
-2	6	79	91
-1	-9	115	113
-1	-8	123	131
-1	-7	116	116
-1	-6	84	72
-1	-4	193	192
-1	-3	150	154
-1	-2	201	204
-1	-1	264	268
-1	0	207	211
-1	3	176	179
-1	4	219	223
-1	5	159	167
0	-6	99	109
0	-5	201	206
0	-4	325	329
0	-3	267	261
0	-2	74	72
0	-1	44	42
0	0	49	42
0	1	158	150
0	2	179	184
0	3	150	158
0	4	179	183
0	5	75	79
1	-8	73	74
1	-7	138	141
1	-6	143	157
1	-5	123	130
1	-4	83	81
1	-2	151	152
1	-1	190	190
1	0	155	166
1	1	171	174
1	2	133	135
1	3	60	63
1	5	70	75
1	6	131	128
2	-4	91	105
2	-3	209	218
2	-2	243	252
2	-1	224	232
2	0	124	134
2	2	72	65
2	3	89	90
2	4	95	101
2	5	113	111
3	-5	98	105
3	-4	121	128
3	-3	128	135
3	-2	103	96
3	1	84	89
3	2	156	146
3	3	136	153
3	4	83	90
4	-2	72	61
4	-1	147	150
4	0	172	177
4	1	111	114
4	2	84	85

H= 8

K	L	FOBS	FCALC
-6	-6	114	113
-6	-5	164	167
-6	-4	166	144
-6	-3	98	86
-6	-1	58	43
-6	0	107	106
-6	1	131	127
-6	2	126	115
-5	-7	141	142
-5	-6	122	117
-5	-5	91	94
-5	-4	60	43
-5	-2	77	68
-5	-1	142	132
-5	0	227	221
-5	1	186	177
-5	2	77	75
-4	-8	112	111
-4	-7	128	119
-4	-5	80	83
-4	-4	179	174
-4	-3	236	220
-4	-2	189	174
-4	0	62	67
-4	2	72	68
-4	3	124	115
-4	4	114	119
-3	-7	83	83
-3	-6	166	161
-3	-4	204	198
-3	-3	186	183
-3	-2	78	74
-3	0	135	139
-3	1	153	149
-3	2	188	190
-3	3	138	135
-3	4	85	82
-2	-8	65	71
-2	-7	150	147
-2	-6	179	182
-2	-5	135	142
-2	-4	69	57
-2	-3	69	68
-2	-2	181	176
-2	-1	226	218
-2	0	170	171
-2	1	162	164
-2	2	79	78
-2	5	82	81
-1	-9	84	87
-1	-5	112	107
-1	-4	191	186
-1	-3	207	210
-1	-2	231	235
-1	-1	188	195
-1	0	78	75
-1	3	137	150
-1	4	163	163
-1	5	116	115
0	-7	73	67
0	-6	100	97
0	-5	153	159
0	-4	216	237
0	-3	142	148
0	-2	55	58
0	-1	57	55
0	0	164	164
0	1	172	179
0	2	99	91
0	3	84	96
0	4	71	94
1	-7	96	103
1	-6	98	98
1	-5	73	66
1	-3	61	58
1	-2	150	159
1	-1	178	183
1	0	215	222
1	1	188	185
1	2	93	95
1	5	70	84
2	-4	81	86
2	-3	150	161
2	-2	163	175
2	-1	129	142
2	0	64	58
2	2	70	75
2	3	88	83
2	4	108	101
3	-6	79	90
3	-5	73	78
3	-3	59	70
3	0	75	76
3	1	130	131
3	2	139	145
4	-2	62	66
4	-1	117	122

H= 9

K	L	FOBS	FCALC
-6	-5	175	158
-6	-4	92	92
-6	-3	71	56
-6	0	92	87
-5	-7	103	88
-5	-6	101	101
-5	-5	54	78
-5	-3	117	107
-5	-2	100	98
-5	-1	162	146
-5	0	129	125
-4	-8	102	83
-4	-5	101	93
-4	-4	195	187
-4	-3	246	234
-4	-2	166	158
-4	-1	66	60
-4	1	66	65
-4	2	82	84
-4	3	80	86
-3	-7	72	63
-3	-6	128	131
-3	-5	146	149
-3	-4	151	149
-3	-3	110	112
-3	-1	62	63
-3	0	127	126
-3	1	158	161
-3	2	152	155
-3	3	83	83
-2	-8	87	84
-2	-7	91	94
-2	-6	79	69
-2	-5	58	62
-2	-3	129	124
-2	-2	224	222
-2	-1	185	184
-2	0	139	145
-2	1	100	97
-1	-5	108	120
-1	-4	99	109
-1	-3	149	159
-1	-2	196	198
-1	-1	138	134
-1	2	103	108
-1	3	120	120
-1	4	65	85
0	-6	68	78
0	-5	143	144
0	-4	120	133
0	-1	94	93
0	0	176	176
0	1	168	173
0	2	127	119
0	3	99	104
1	-7	66	82
1	-3	60	53
1	-2	95	108
1	-1	132	143
1	0	153	161
1	1	110	116
2	-5	71	68
2	-4	90	56
2	-3	73	91
2	-2	87	90
2	1	62	64
2	2	82	90
3	-4	73	76

H= 10

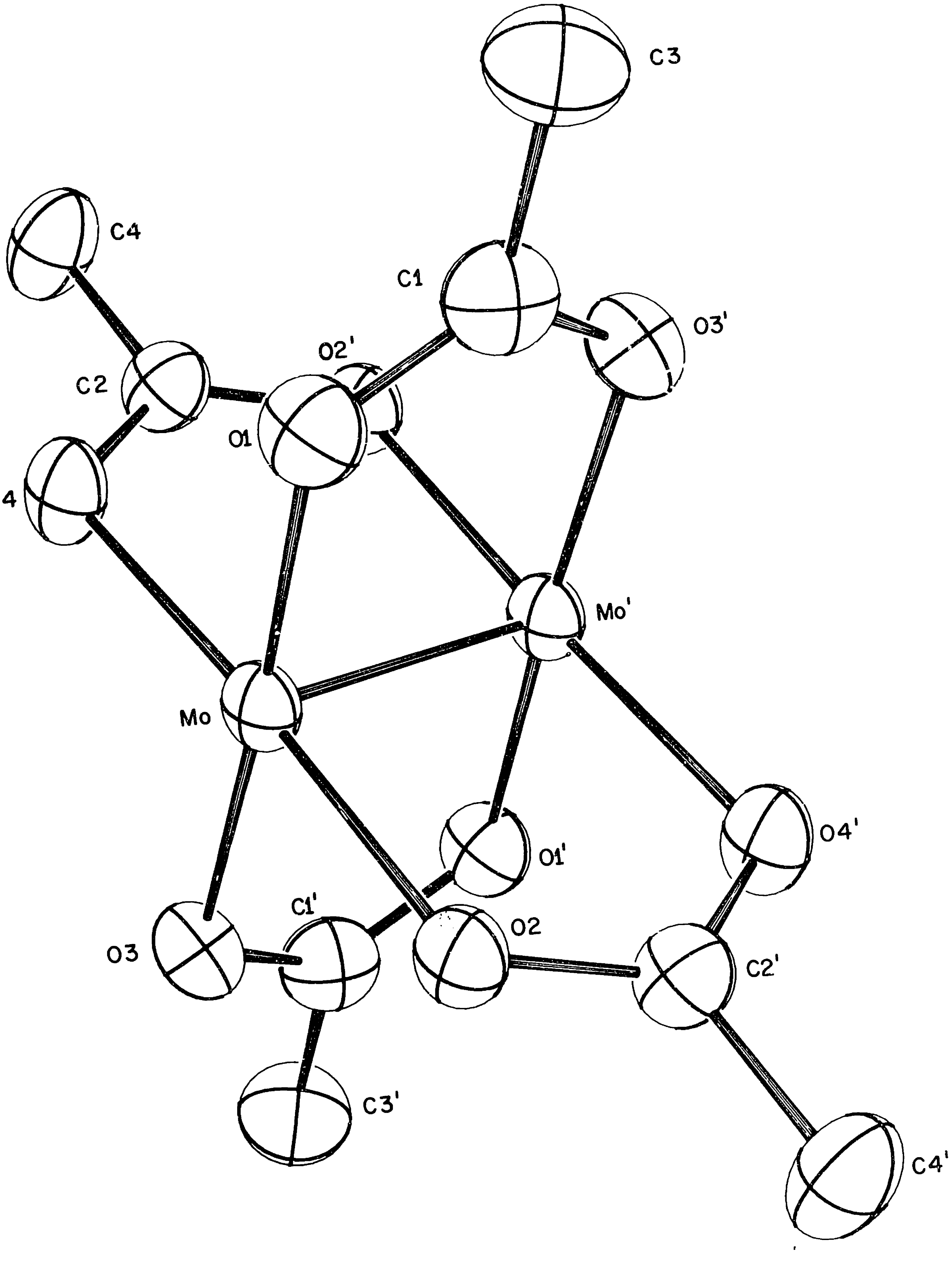
K	L	FOBS	FCALC
-5	-3	93	89
-5	-2	144	136
-5	-1	188	169
-5	0	117	104
-4	-5	90	87
-4	-4	163	153
-4	-3	170	161
-4	-2	96	87
-4	-1	68	61
-4	1	63	66
-4	2	96	85
-3	-7	88	87
-3	-6	82	88
-3	-5	75	63
-3	-4	64	73
-3	-1	98	112
-3	0	136	134
-3	1	141	144
-3	2	94	95
-2	-7	101	98
-2	-6	64	55
-2	-4	55	63
-2	-3	106	122
-2	-2	139	150
-2	-1	146	139
-2	0	122	126
-1	-6	68	53
-1	-5	80	75
-1	-4	78	86
-1	-3	108	122
-1	-2	114	112
-1	-1	48	37
-1	1	70	70
-1	2	130	141
-1	3	132	123
0	-7	80	80
0	-6	86	93
0	-5	86	97
0	-1	64	87
0	0	132	132
0	1	101	106
0	2	86	97
1	-3	79	76
1	-2	65	66
1	-1	74	83
1	0	89	87
1	1	63	52
2	-4	94	105
2	-3	96	98

H= 11

K	L	FOBS	FCALC
-4	-5	90	86
-4	-4	86	95
-3	-6	98	95
-3	-5	71	66
-3	-1	86	95
-3	0	120	119
-3	1	104	114
-2	-3	91	103
-2	-2	98	94
-2	-1	84	90
-2	0	68	62
-1	-6	95	91
-1	-5	69	74
-1	-4	63	70
-1	-3	76	75
-1	1	78	78
0	-5	84	89

FIGURE 1

An ORTEP drawing of the $Mo_2(O_2CCH_3)_4$ structure. Each atom is represented by its ellipsoid of thermal motion drawn to enclose 30% of the electron density. The molecule has a center of inversion, $\bar{1}$, and the primed and corresponding unprimed atoms are related by $\bar{1}$.


C3
C4
C1
O2'
O3'
C2
O1
O4
Mo'
Mo
O4'
O1'
C1'
O2
O3
C2'
C3'
C4'

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CHAPTER IV

COPPER(I) AND COPPER(II) COMPLEXES OF TETRAMETHYLDIPHOSPHINEDISULFIDE I. STRUCTURAL CHARACTERIZATION OF THE DINUCLEAR, MOLECULAR COMPLEX OF COPPER(I) CHLORIDE

INTRODUCTION

Despite the fact that, on the one hand, sulfur as a ligand atom is of major, widespread importance and, on the other, phosphine oxides, and P = O groups in other compounds, are also important ligands, the literature on complexes containing P = S groups as ligands is remarkably sparse. Indeed the first coordination compound containing such a ligand, Ph_3PS, was reported only in 1960.[1] In that limited investigation only the palladium complex, $PdCl_2(Ph_3PS)_2$, its Ph_3PSe analog and $SnCl_4(Ph_3PSe)_2$ were reported. An attempt to prepare $SnCl_4(Ph_3PS)_2$, as well as attempts to prepare Ph_3PS complexes of BF_3, Co^{2+}, Hg^{2+} and Cu^{2+} were unsuccessful.

This work implied that the prospects for obtaining an extensive series of phosphine sulfide (or selenide) complexes seemed doubtful.

Subsequently, however, there have been many further reports.[2-11] Of special interest there are certain results of Meek and Nicpon.[12,13] These workers have shown that Me_3PS is a better ligand than Ph_3PS. They then extended their studies to the potentially bidentate ligands, $Me_2P(S)-P(S)Me_2$ and its tetraethyl analog. They found these diphosphine disulfides to be good ligands for Cu(I); these complexes were prepared by reactions of the ligands with Cu(II) compounds, specifically, $Cu(ClO_4)_2$ and $CuCl_2$. From the perchlorate, compounds with the composition $(R_4P_2S_2)_2CuClO_4$ were obtained. Conductance data led Meek and Nicpon to conclude that these compounds are uni-univalent electrolytes. Thus, the ability of the $R_4P_2S_2$ ligand to function as a bidentate chelating ligand was indicated. The product obtained with $Me_4P_2S_2$ and $CuCl_2$, of composition $(Me_4P_2S_2)CuCl$, was formulated as $((Me_4P_2S_2)_2Cu)(CuCl_2)$ on the basis of electrolytic conductance data.

Aside from a general interest in the ligand properties of the $R_4P_2S_2$ molecules, our interest in the particular compound $(Me_4P_2S_2)CuCl$ was aroused because of the plausible suggestion that it might contain the $CuCl_2^-$ ion. Although this linear ion has often been postulated, there is only one report of direct evidence for its existence[14] and an additional documented example would have been of interest. An attempt was therefore made to prepare the compound in crystalline form and ascertain its structure by X-ray crystallography. That attempt was successful and is described herein. In the course of preparing the substance in a form suitable for crystallographic investigation we observed that the white substance was not the sole product of the reaction, but that a brown product could be obtained in small quantities and in crystalline form. Nicpon[13] made a similar observation, however, he did not characterize that product either. That substance was also identified and structually characterized, as described in the following chapter.[15]

EXPERIMENTAL

Preparation. - Copper(II) chloride dihydrate (0.5g) was dissolved in 70 ml absolute ethanol. Separately, an equimolar solution of $Me_4P_2S_2$ (0.55g) in 50 ml tetrahydrofuran plus 20 ml CH_2Cl_2 was prepared. These solutions were poured into the two sides of a U-tube having a medium porosity sintered glass disk at its midpoint. The solutions were able to mix slowly, at 22°, through the disk. After about an hour a mixture of brown crystals and white crystals had formed on the disk, the white crystals being far more abundant. Further observation showed that when the brown substance remained in contact with the reaction mixture, it was converted into a white material in a few hours. Crystals of both the brown and the white substances were separated by filtration, dried by brief pumping and mounted in capillaries for X-ray study.

Collection of X-ray Data. - A crystal of dimensions 0.010x 0.0047 x 0.050 cm was selected and mounted on a Syntex P$\bar{1}$ computer-controlled, four-circle diffractometer, equipped with a graphite-crystal monochromator in the incident beam. The unit cell was found to be monoclinic and least-squares refinement of fifteen centered reflections produced the orientation matrix for data collection and gave the following unit cell dimensions: a = 7.998(1)Å; b = 9.688(2)Å; c = 14.473(3)Å; β = 104.90(1)° ; V = 1083.7(3)$Å^3$. Systematic absences subsequently evident in the set of intensity data indicated that the space group is $P2_1/n$, a nonstandard setting of $P2_1/c$.

The calculated density is 1.747gcm^{-3} if the cell is assumed to contain four formula units, $(CH_3)_4P_2S_2CuCl$; this agrees well with a density of 1.752gcm^{-1} measured by flotation.

Intensity data were collected in the range $0° < 2\theta \leq 55°$ using Mo K$\bar{\alpha}$ radiation. The θ-2θ scan technique with a variable scan rate from 4-24°/min was used. The scan range was from 2θ(Mo Kα_1) $-0.9°$ to 2θ(Mo Kα_2) $+ 0.9°$. Additional details about data collection have been described elsewhere.[16] In order to check the stability of the crystal and the X-ray diffractometer, four reflections were selected as standards and their intensities were recorded periodically. No significant variations in these intensities were observed.

A total of 3242 reflections were collected and the usual data reduction procedures[17] were applied. The parameter p, used in the calculation of standard deviations on intensities ($\sigma(F_o^2)$), was assigned the value 0.06. Although the linear absorbtion coefficient is not especially high (μ= 29.24cm^{-1} for Mo K$\bar{\alpha}$ radiation), in order to get the most accurate atomic parameters, absorption corrections have been made. The faces of the crystal were identified by the indices $0\bar{1}0$, $\bar{1}01$,

$10\bar{1}$, 101, $\bar{1}0\bar{1}$, $11\bar{1}$ and $\bar{1}11$. A numerical correction gave transmission factors varying from 73% to 91% with an average of 85%.

Solution and Refinement of the Structure.[17]

A Patterson function was calculated and the copper atom was located on the Harker plane of 1/2-2X; 1/2; 1/2-2Z. The structure was solved by the usual combination of least-squares refinements and difference Fourier syntheses. In the least-squares refinements only those 1488 reflections were used for which $F_o^2 \geq 3\sigma(F_o^2)$. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and the weight w is $4F_o^2/\sigma^2(F_o^2)$. Scattering factors were taken from the International Tables[18] and anomalous dispersion corrections[19] were included for all atoms except carbon and hydrogen atoms.

After all nonhydrogen atoms in the asymmetric unit, i.e., Cu, Cl, 2S 2P and 4C atoms, had been located, anisotropic refinement was carried out, which resulted in the following discrepancy indices: $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.065$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.11$. A difference electron density map then revealed some of the hydrogen atoms, namely two on C(1), two on C(2), one on C(3) and one on C(4). The position of the remaining six hydrogen atoms were calculated assuming tetrahedral geometry about the carbon atoms and C-H bond lengths of 0.95Å.

Two more cycles of refinement were carried out in which all nonhydrogen atoms were refined anisotropically and the positional coordinates of the hydrogen atoms were refined, while the temperature parameter for each hydrogen atom was fixed at an isotropic value of 5.0$Å^2$. This lead to the discrepancy indicates $R_1 = 0.041$ and $R_2 = 0.052$. Finally, two cycles, in which the isotropic thermal parameters for the hydrogen atoms were also allowed to vary, were carried out; in these cycles there was a total of 139 variable parameters so that the ratio of data to variables was slightly greater than 10. The final R values were: $R_1 = 0.040$ and $R_2 = 0.051$. For only three parameter pairs (all on the chlorine atom) did the correlation coefficients slightly exceed 0.5. Parameter changes in the final cycle were all less than 0.25 times the esd of the parameter.

A final difference map, calculated using all the reflections included in the refinement, had no peak with a density in excess of 0.5e$Å^{-3}$ with the exception of one maximum with a density of 1.7e$Å^{-3}$ at a distance of 0.92Å from the Cu atom and trans to a trigonal sulfur atom.

This peak had roughly twice the density of peaks due to the hydrogen atoms that were found. However, on a difference map calculated using only the 126 reflections for which $\lambda^{-1}\sin\theta \leq 0.250$ this peak disappeared while the peaks due to the hydrogen atoms remained. We conclude that this peak is an artifact.

Of the 1488 reflections used in the refinement, there were only 20 for which $||F_o| - |F_c||$ slightly exceeded $3\sigma(F_o^2)$. No dependence of the $\Sigma w(|F_o| - |F_c|)^2$ values on the indices, on $(\sin\theta)/\lambda$ or on $|F_o|$ was noted. The standard deviation in an observation of unit weight was 1.11.

A table of the F_o and the final F_c values are presented in Table I. The final refined positional and thermal parameters are listed in Table II and in Table III.

RESULTS

The structure is made up of dinuclear molecules, one of which is shown in Figure 1. These dinuclear units lie on crystallographic inversion centers; there are two of them in each unit cell. Table IV presents interatomic distances and Table V gives bond angles. Table VI gives the equations of some mean planes and the dihedral angles between them.

DISCUSSION

The $Me_4P_2S_2$ molecules in this compound serve as chelating, bidentate ligands. They form puckered five-membered rings including the copper atoms.

Each copper(I) atom achieves a coordination number of four with distorted tetrahedral geometry of the surrounding ligands. This is possible because one sulfur atom in each $Me_4P_2S_2$ molecule serves as a bridge between two copper atoms. The bonds from the copper atoms to the bridging sulfur atoms are considerably longer ($\sim$0.15Å) than those to the nonbridging sulfur atoms.

The central four-membered ring consisting of alternating Cu and S atoms is rigorously planar because of the crystallographic inversion center. There is a slight distortion from full rhombic (C_{2h}) symmetry because the Cu-S2 and Cu-S2' are not quite equal.

It is notable that there is still only one proven example for the existence of the $CuCl_2^-$ ion. Though its presence had been suggested to account for the electrolytic conductance of this compound, it is not present in the crystalline substance.

TABLE I

THE OBSERVED AND FINAL CALCULATED STRUCTURE FACTORS, LISTED AS $10|F_o|$ AND $10|F_c|$, IN ELECTRONS.

H= 0

K	L	FOBS	FCALC
0	2	514	503
0	4	284	275
0	6	707	701
0	8	322	327
0	10	179	181
0	14	505	511
1	1	1183	1125
1	4	517	501
1	5	214	230
1	6	770	758
1	7	498	522
1	8	426	441
1	9	425	428
1	12	248	254
1	14	226	226
1	15	422	416
1	16	173	175
2	0	514	504
2	1	190	198
2	3	519	558
2	4	859	826
2	5	109	115
2	6	464	479
2	7	309	319
2	8	563	568
2	9	198	221
2	10	177	181
2	11	223	207
2	12	221	226
2	13	318	310
2	15	173	143
2	16	277	291
3	1	359	337
3	2	1507	1465
3	4	875	864
3	6	341	344
3	7	317	324
3	8	103	97
3	9	402	403
3	10	271	282
3	11	159	173
3	12	566	579
4	0	365	351
4	1	567	574
4	2	249	233
4	3	1571	1622
4	4	191	198
4	6	305	304
4	8	391	376
4	9	199	216
4	10	296	305
4	11	480	490
4	12	120	102
4	13	230	233
4	16	169	159
5	1	479	473
5	2	141	125
5	3	405	407
5	4	516	510
5	5	907	905
5	6	346	357
5	7	156	150
5	9	512	511
5	10	102	107
5	11	140	153
5	12	337	330
5	14	111	109
5	15	108	121
5	16	260	262
6	0	1094	1074
6	1	760	743
6	2	403	413
6	4	207	205
6	5	133	137
6	6	221	223
6	7	353	339
6	8	235	242
6	10	227	244
6	11	191	190
6	12	122	114
6	14	265	262
6	15	328	330
7	1	773	752
7	3	195	195
7	4	94	98
7	6	148	133
7	7	321	325
7	8	445	437
7	9	105	107
7	11	172	164
7	12	127	120
7	13	130	120
7	14	190	192
7	15	218	188
8	0	469	474
8	2	149	160
8	6	243	227
8	7	578	582
8	8	330	326
8	13	134	126
9	2	601	597
9	3	196	199
9	4	133	151
9	5	138	125
9	6	155	143
9	7	166	154
9	8	254	264
9	9	304	306
9	11	109	102
9	12	152	137
10	1	378	369
10	2	171	170
10	3	289	309
10	4	572	576
10	5	229	238
10	6	117	131
10	7	122	127
10	10	178	177
11	1	142	138
11	4	151	146
11	5	358	356
11	6	159	146
12	4	218	225

H= 1

K	L	FOBS	FCALC
0	-17	283	288
0	-13	154	165
0	-11	478	495
0	-9	815	411
0	-7	198	188
0	-5	533	532
0	-3	1568	1479
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H= 4

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1	-14	321	313
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6	-12	166	200
6	-11	206	227
6	-10	151	145
6	-9	155	152
6	-6	131	142
6	-5	189	191
6	-4	193	201
6	-3	350	366
6	-1	156	154
6	0	613	657
6	1	381	386
6	2	381	392
6	5	176	183
6	11	245	245
6	12	156	140
7	-15	119	102
7	-14	128	139
7	-13	321	326
7	-11	115	115
7	-10	203	207
7	-8	345	347
7	-7	149	147
7	-6	391	373
7	-5	104	128
7	-3	134	134
7	-2	143	137
7	-1	402	420
7	0	178	173
7	1	649	673
7	3	109	86
7	4	112	93
7	8	223	255
8	-11	126	139
8	-10	179	182
8	-9	134	104
8	-7	599	588
8	-5	261	261
8	-1	191	192
8	2	131	135
8	4	363	352
8	5	232	196
8	6	137	106
8	7	326	330
9	-4	103	171
9	-2	127	132
9	0	256	266
9	1	166	167
9	2	111	129
9	3	237	232
9	4	111	94
9	5	170	190
9	6	150	132
9	7	129	127
10	-5	173	177
10	-4	128	96
10	-1	324	333
10	0	181	180
10	2	121	109
10	3	186	177
10	5	133	129
10	6	130	131
11	-7	227	223
11	-5	317	318
11	-4	120	139
11	-2	163	168
11	-1	122	95

H= 5

K	L	FOBS	FCALC
0	-15	109	90
0	-13	91	86
0	-9	320	313
0	-7	278	261
0	-5	239	241
0	-3	413	436
0	1	857	950
0	3	351	357
0	5	220	219
0	9	164	160
1	-17	167	167
1	-15	167	162
1	-14	149	158
1	-13	228	218
1	-10	183	160
1	-9	320	332
1	-8	512	531
1	-6	86	49
1	-2	197	195
1	-1	651	670
1	0	657	678
1	1	179	175
1	2	197	191
1	4	273	265
1	5	328	316
1	6	242	257
1	7	115	125
1	9	178	168
1	10	114	121
1	11	122	105
2	-15	225	230
2	-12	329	310
2	-11	276	298
2	-10	295	320
2	-9	467	467
2	-8	164	191
2	-7	521	535
2	-6	353	360
2	-3	235	233
2	-2	170	169
2	-1	419	453
2	0	108	104
2	1	110	90
2	2	255	254
2	4	360	347
2	5	204	199
2	6	106	87
2	7	146	143
2	8	197	130
3	-16	173	177
3	-15	107	136
3	-13	139	97
3	-12	146	160
3	-11	334	337
3	-9	190	168
3	-7	167	161
3	-6	174	173
3	-5	326	353
3	-4	444	460
3	-3	153	137
3	-2	125	143
3	-1	643	645
3	1	151	163
3	2	133	130
3	3	576	671
3	4	136	129
3	5	122	142
3	6	197	191
3	7	459	418
3	13	155	172
4	-12	135	331
4	-10	94	96
4	-9	116	135
4	-7	393	406
4	-5	234	206
4	-3	133	120
4	-2	107	110
4	0	241	271
4	1	152	151
4	2	120	111
4	4	294	287
4	5	269	266
4	6	245	279
4	7	264	258
4	8	277	280
4	12	155	169
5	-16	263	241
5	-15	168	143
5	-14	157	149
5	-12	136	126
5	-11	270	272
5	-9	289	284
5	-8	118	124
5	-7	102	104
5	-6	111	152
5	-5	216	227
5	-3	254	234
5	-2	158	159
5	-1	462	490
5	2	115	100
5	3	131	330
5	5	171	176
5	6	290	290
5	9	127	116
5	11	145	126
6	-13	169	181
6	-12	124	138
6	-11	175	110
6	-10	199	197
6	-9	243	253
6	-8	351	348
6	-6	186	225
6	-3	296	307
6	-2	209	198
6	-1	109	106
6	0	302	313
6	1	458	462
6	2	154	152
6	3	136	136
6	4	304	290
6	9	165	160
7	-12	107	109
7	-10	252	266
7	-9	174	196
7	-8	139	135
7	-7	311	305
7	-4	206	292
7	-2	190	207
7	-1	121	126
7	0	353	373
7	1	143	129
7	2	330	325
7	3	100	74
7	5	150	171
7	7	259	298
7	10	120	99
8	-11	117	136
8	-10	291	271
8	-7	113	110
8	-6	196	183
8	-5	193	187
8	-3	126	136
8	-1	125	122
8	3	204	205
8	4	163	156
8	7	139	136
8	8	289	299
9	-8	236	249
9	-6	173	166
9	-4	275	287
9	-2	240	238
9	-1	188	180
9	2	150	142
9	6	237	210
10	-8	191	169
10	-5	170	170
10	-2	166	178
10	0	236	214
11	-4	230	222
11	-2	179	130

H= 6

K	L	FOBS	FCALC
0	-12	242	205
0	-10	569	544
0	-8	162	163
0	-7	625	657
0	0	85	69
0	2	254	261
0	4	249	245
0	12	192	146
1	-17	117	124
1	-16	167	175
1	-9	427	409
1	-7	129	164
1	-6	140	135
1	-5	100	100
1	-4	351	375
1	-3	246	256
1	0	243	235
1	4	362	359
1	5	136	133
1	6	272	276
1	7	211	226
1	8	140	124
2	-11	142	131
2	-10	215	233
2	-8	352	357
2	-7	146	109
2	-5	421	429
2	-3	142	118
2	-2	112	113
2	0	220	225
2	1	367	374
2	4	296	202
2	5	120	156
2	6	526	532
2	8	176	174
2	9	137	138
2	10	157	145
3	-16	153	152
3	-15	119	124
3	-13	160	158
3	-12	279	251
3	-8	212	142
3	-7	97	104
3	-5	394	400
3	-4	482	536
3	-2	133	171
3	-1	117	116
3	0	231	251
3	2	215	212
3	6	151	154
3	7	204	195
3	10	192	195
3	11	[illegible]	161
4	-13	212	171
4	-12	138	128
4	-11	[illegible]	[illegible]
4	-10	151	174
4	-9	322	301
4	-7	195	192
4	-5	269	285
4	-4	296	281
4	-3	238	247
4	-2	280	292
4	-1	223	219
4	2	241	247
4	3	126	120
4	5	196	117
4	6	205	202
4	7	137	102
4	8	176	159
4	9	133	119
5	-15	154	132
5	-8	102	121
5	-6	316	312
5	-5	152	134
5	-4	100	79
5	-1	229	200
5	0	207	198
5	1	111	116
5	3	193	185
5	4	312	305
5	5	170	108
5	6	197	179
5	7	199	196
6	-13	138	144
6	-11	109	112
6	-10	292	264
6	-9	128	147
6	-8	191	203
6	-5	216	200
6	-3	131	140
6	-2	303	314
6	-1	168	173
6	3	256	260
6	4	165	151
6	5	165	164
7	-11	137	107
7	-10	187	203
7	-7	111	113
7	-5	131	135
7	-3	270	277
7	-2	261	254
7	-1	268	258
7	3	143	126
7	4	117	101
8	-12	169	142
8	-9	256	269
8	-8	137	123
8	-3	148	165
8	-1	200	201
8	5	312	305
8	6	189	197
9	-4	184	149
9	-1	153	160
10	-5	129	122
10	-3	207	226
10	-1	129	116

H= 7

K	L	FOBS	FCALC
0	-15	171	142
0	-13	195	199
0	-9	375	347
0	-7	179	171
0	-3	254	250
0	-1	143	149
0	1	331	340
0	5	256	247
1	-11	220	217
1	-7	213	201
1	-6	135	118
1	-4	98	83
1	-3	298	297
1	-2	350	378
1	1	233	244
1	2	142	148
1	3	239	252
1	5	162	152
1	6	204	196
2	-13	250	246
2	-12	111	135
2	-11	146	165
2	-9	112	126
2	-6	284	275
2	-5	285	271
2	-3	304	313
2	-2	126	96
2	0	141	147
2	1	166	182
2	2	115	111
2	3	210	225
2	5	122	130
3	-15	113	118
3	-11	216	195
3	-6	200	195
3	-5	172	194
3	-4	128	135
3	-3	177	223
3	2	109	113
3	3	192	193
3	4	120	119
3	5	237	243
3	9	222	227
4	-13	135	119
4	-12	207	214
4	-9	113	97
4	-8	177	135
4	-7	97	98
4	-6	151	127
4	-5	232	214
4	-2	193	130
4	3	272	269
4	6	132	146
4	8	132	117
5	-11	191	194
5	-9	192	91
5	-7	138	114
5	-6	170	126
5	-5	261	259
5	-4	310	277
5	-3	255	230
5	1	254	258
5	4	165	152
6	-13	164	134
6	-12	196	201
6	-10	193	192
6	-9	126	113
6	-6	204	214
6	-3	150	141
6	-2	103	75
6	-1	153	162
6	2	229	218
6	3	109	93
6	5	120	128
7	-10	109	70
7	-9	168	191
7	-6	118	95
7	-2	220	215
7	-1	130	144
7	4	184	179
7	5	167	192
8	-6	130	129
8	-5	153	149
8	-3	115	127
8	-2	159	147
8	1	136	144
8	2	157	132
[illegible]	[illegible]	163	164
[illegible]	[illegible]	203	198

H= 8

K	L	FOBS	FCALC
0	-14	206	165
0	-12	336	327
0	-6	231	197
0	-4	129	131
0	0	244	251
0	2	142	176
0	4	105	64
1	-14	153	135
1	-12	107	94
1	-11	144	160
1	-7	139	109
1	-6	339	328
1	-3	141	129
1	-2	100	[illegible]
1	1	106	80
1	2	199	198
1	4	114	107
2	-12	113	137
2	-10	113	119
2	-8	104	96
2	-5	117	114
2	-4	204	199
2	-3	142	109
2	-2	133	144
2	1	157	174
2	2	130	127
2	4	210	212
3	-14	203	239
3	-9	117	110
3	-6	170	212
3	-4	114	122
3	0	269	277
3	1	119	197
4	-12	149	142
4	-11	123	95
4	-8	171	122
4	-4	216	205
4	-3	131	124
4	-1	161	145
4	1	164	166
5	-9	149	112
5	-6	164	171
5	-5	233	191
5	-3	146	132
5	-2	133	125
5	2	191	225
6	-5	111	106
6	-3	118	119
6	1	138	151
6	2	142	142
6	3	152	155
7	-7	160	150
7	-6	132	124
7	1	142	154
8	-5	142	138

H= 9

K	L	FOBS	FCALC
0	-13	112	75
0	-9	176	154
0	-7	233	226
0	1	274	245
0	3	152	167
1	-9	228	233
1	-5	146	144
1	-1	125	137
1	0	154	140
1	2	124	86
1	4	126	126
2	-8	137	127
2	-7	231	225
2	-5	146	150
2	-1	149	134
3	-8	111	117
3	-5	144	138
3	-1	148	140
3	1	135	148
4	-7	188	140
4	-4	122	95
4	-2	117	95
4	0	179	161
5	-9	163	196
5	-8	126	112
5	-7	111	116
5	-5	111	66
5	-3	111	90

H= 10

K	L	FOBS	FCALC
0	-8	172	156
0	-2	177	181
1	-8	147	160
1	-4	116	86
2	-2	147	164
3	-2	134	161

TABLE II

POSITIONAL PARAMETERS FOR $((Me_4P_2S_2)CuCl)_2$[a]

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[a] Numbers in parentheses in this and all other tables are estimated standard deviations in the last significant digit.

Atom	x	y	z
Cu	-0.0295(1)	0.08567(8)	0.09733(6)
Cl	-0.1073(3)	0.3029(2)	0.1204(1)
S1	0.0053(2)	-0.0434(1)	0.2353(1)
S2	-0.2195(2)	-0.0580(1)	-0.0256(1)
P1	-0.0263(2)	-0.2314(1)	0.18115(9)
P2	-0.2455(2)	-0.2237(1)	0.05140(9)
C1	-0.0822(9)	-0.3578(7)	0.2586(5)
C2	0.1526(9)	-0.2968(8)	0.1437(6)
C3	-0.250(1)	-0.3827(7)	-0.0122(5)
C4	-0.4339(9)	-0.2156(9)	0.0966(6)
H1	-0.119(8)	-0.430(6)	0.228(4)
H2	-0.176(8)	-0.324(6)	0.277(4)
H3	0.019(9)	-0.368(7)	0.313(5)
H4	0.180(9)	-0260(8)	0.092(5)
H5	0.148(9)	-0.391(9)	0.137(5)
H6	0.262(9)	-0.277(7)	0.187(6)
H7	-0.143(9)	-0.386(7)	-0.044(4)
H8	-0.345(9)	-0.386(7)	-0.052(5)
H9	-0.259(8)	-0.457(6)	0.029(4)
H10	-0.417(9)	-0.137(9)	0.139(6)
H11	-0.444(9)	-0.285(7)	0.130(5)
H12	-0.518(9)	-0.211(7)	0.045(5)

TABLE III

THERMAL PARAMETERS FOR $((Me_4P_2S_2)CuCl)_2$[a]

a) The form of the thermal ellipsoid is
$\exp(-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl))$

Atom	B iso-tropic	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu		0.0340(3)	0.00583(5)	0.00450(4)	0.0019(1)	0.00244(8)	0.00049(5)
Cl		0.0373(5)	0.0061(1)	0.0069(1)	0.0032(2)	0.0100(2)	0.0008(1)
S1		0.0209(3)	0.0057(1)	0.00283(7)	-0.0018(1)	0.0006(1)	-0.00029(8)
S2		0.0120(1)	0.0059(1)	0.00322(7)	0.0000(1)	0.0003(1)	0.00122(8)
P1		0.0096(2)	0.0050(1)	0.00241(6)	0.0006(1)	0.0008(1)	0.00042(7)
P2		0.0091(2)	0.0047(1)	0.00282(6)	-0.0003(1)	0.0006(1)	0.00022(7)
C1		0.018(1)	0.0070(7)	0.0037(3)	-0.0013(8)	0.0018(6)	0.0014(4)
C2		0.14(1)	0.0122(9)	0.0053(4)	0.0048(9)	0.0032(6)	0.0007(5)
C3		0.026(2)	0.0066(7)	0.0035(3)	-0.0035(9)	0.0001(6)	-0.0009(4)
C4		0.011(1)	0.014(1)	0.0059(4)	0.0009(9)	0.0023(6)	0.0024(6)
H1	3(1)						
H2	3(1)						
H3	4(1)						
H4	5(2)						
H5	6(2)						
H6	6(2)						
H7	4(1)						
H8	5(2)						
H9	4(1)						
H10	7(2)						
H11	4(1)						
H12	5(2)						

TABLE IV

BOND DISTANCES, ANGSTROMS

		Average Value
Cu-Cl	2.244(2)	
Cu-S1	2.311(2)	
Cu-S2	2.453(2)	
Cu-S2'	2.486(2)	
P1-S1	1.973(2)	
P2-S2	1.995(2)	
P1-P2	2.217(2)	
Cu-Cu'	3.406(2)	
P1-C1	1.772(7)	1.787(3)
P1-C2	1.792(6)	
P2-C3	1.790(6)	
P2-C4	1.793(7)	
C1-H1	0.84(6)	0.92(2)
C1-H2	0.92(6)	
C1-H3	0.98(7)	
C2-H4	0.91(7)	
C2-H5	0.91(9)	
C2-H6	0.96(8)	
C3-H7	1.07(7)	
C3-H8	0.82(9)	
C3-H9	0.96(6)	
C4-H10	0.96(8)	
C4-H11	0.86(6)	
C4-H12	0.86(8)	

TABLE V

BOND ANGLES, DEGREES

C1-Cu-S1	110.81(7)
C1-Cu-S2	119.76(8)
C1-Cu-S2'	116.48(7)
S1-Cu-S2	103.52(6)
S1-Cu-S2'	111.79(7)
S2-Cu-S2'	92.82(5)
P1-S1-Cu	100.48(7)
Cu-S2-Cu'	87.18(5)
P2-S2-Cu	100.71(7)
P2-S2-Cu'	110.87(7)
S1-P1-P2	107.32(8)
C1-P1-S1	114.2(3)
C1-P1-P2	106.4(2)
C1-P1-C2	107.4(4)
C2-P1-S1	114.8(3)
C2-P1-P2	106.1(3)
P1-P2-S2	109.09(8)
C3-P2-P1	108.2(3)
C3-P2-S2	113.4(2)
C3-P2-C4	108.5(4)
C4-P2-P1	104.4(3)
C4-P2-S2	112.8(3)
H1-C1-P1	110(4)
H2-C1-P1	107(4)

H3-C1-P1	106(4)
H1-C1-H2	104(5)
H1-C1-H3	117(5)
H2-C1-H3	112(5)
H4-C2-P1	120(5)
H5-C2-P1	112(5)
H6-C2-P1	114(5)
H4-C2-H5	109(7)
H4-C2-H6	95(6)
H5-C2-H6	106(7)
H7-C3-P2	110(4)
H8-C3-P2	107(6)
H9-C3-P2	108(4)
H7-C3-H8	113(6)
H7-C3-H9	117(5)
H8-C3-H9	102(7)
H10-C4-P2	106(5)
H11-C4-P2	113(4)
H12-C4-P2	103(5)
H10-C4-H11	106(6)
H10-C4-H12	117(7)
H11-C4-H12	111(7)

TABLE VI

LEAST SQUARES PLANES[a]

a) x, y and z are fractional monoclinic coordinates.

Plane	Atoms	Equation	Dihedral Angle	
1	Cu,S1,S2,P1,P2	$-7.269x+2.716y+7.554z-1.3089=0$	1 and 2	11.7°
			1 and 3	6.1
			1 and 4	101.5°
2	Cu,S1,S2	$-7.006x+4.306y+5.797z-1.1397=0$	2 and 3	17.3°
			2 and 4	113.2°
3	S1,S2,P1,P2	$-7.455x+1.707y+7.744z-1.5244=0$	3 and 4	96.6°
4	Cu,S2,Cu',S2'	$1.217x-7.782y+7.218z=0$	----	

B. Distances (Å) of Atoms from Least Squares Planes

Plane 1

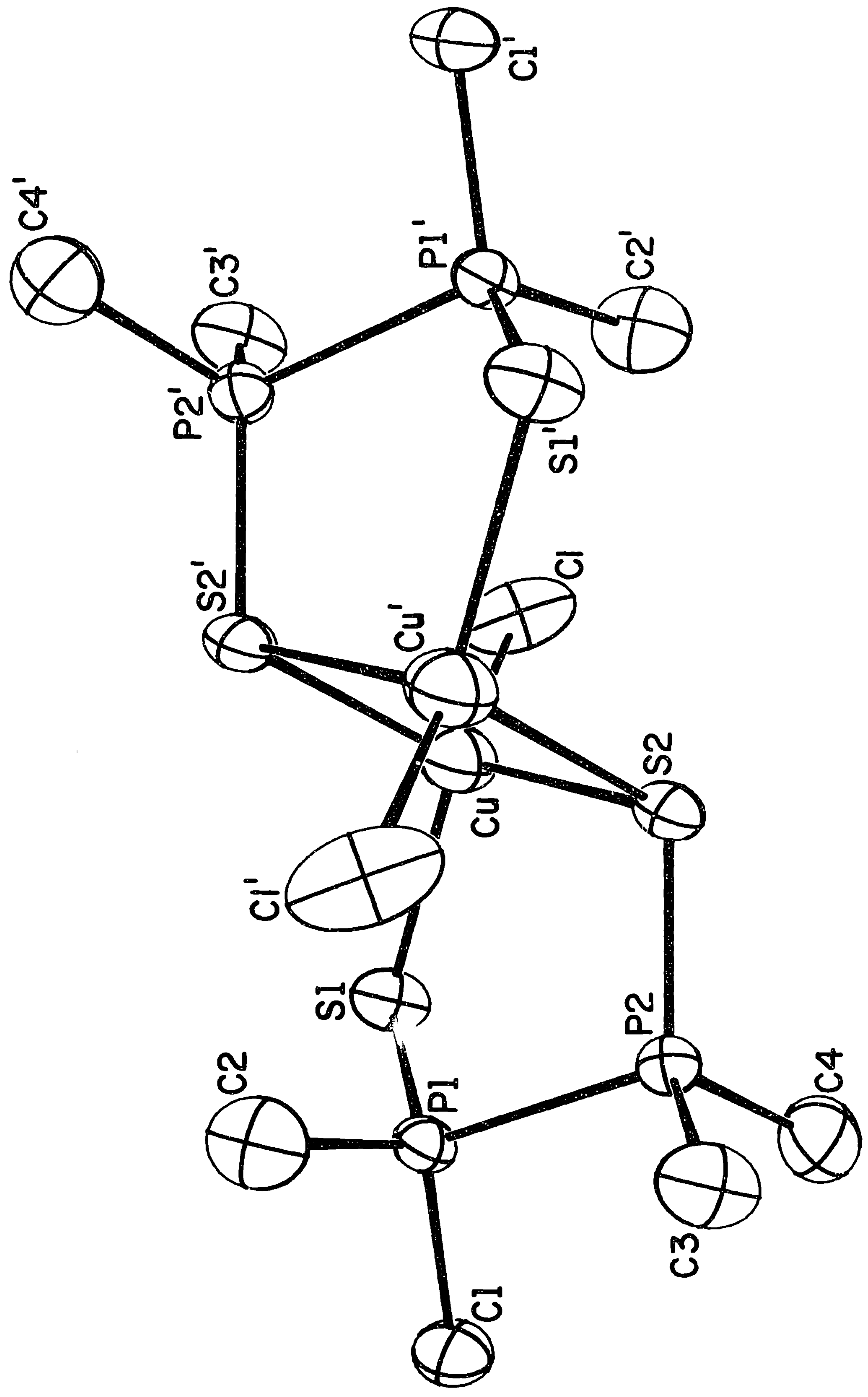
Cu	-0.127
S1	0.313
S2	-0.064
P1	-0.379
P2	0.257
Cl	1.207
C1	0.271
C2	-2.145
C3	-0.626
C4	1.996

Plane 3

S1	0.185
S2	-0.186
P1	-0.322
P2	0.323
C1	0.482
C2	-2.062
C3	-0.411
C4	2.096

FIGURE 1

The structure of the centrosymmetric dinuclear molecule showing the atom numbering scheme. Atoms with primed labels are related by the inversion center to those with the corresponding unprimed numbers. Each atom is represented by its thermal ellipsoid, scaled to enclose 50% of the electron density.


C1'
C4'
C3'
P1'
C2'
P2'
S1'
S2'
Cl
Cu'
Cu
S2
Cl'
S1
P2
C2
P1
C4
C3
C1

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CHAPTER V

COPPER(I) AND COPPER(II) COMPLEXES OF TETRAMETHYLDIPHOSPHINEDISULFIDE. II. ISOLATION AND CHARACTERIZATION OF A POLYMERIC COPPER(II) PRECURSOR, $(Me_4P_2S_2)CuCl_2$, TO THE ULTIMATE COPPER(I) PRODUCT, $((Me_4P_2S_2)CuCl)_2$.

INTRODUCTION

Meek and Nicpon[1,2] have described the reactions of the tetramethyl- and tetraethyldiphosphinedisulfides with various copper(II) salts, the products of which were found to be copper(I) complexes of the $R_4P_2S_2$ ligands. Their observations were that the copper(II) was consistently reduced, rapidly and completely, to copper(I) under the conditions they employed. In contrast to this, it has been reported[3] that the compounds $(Me_4P_2S_2)CuX_2$, X=Cl,Br, can be isolated. However, no details of their preparation were given and only the Cu and X analyses along with their IR spectra were reported.

As described in the preceding chapter[4], we conducted a reinvestigation of one of the compounds described by

Meek and Nicpon,[1,2] viz., the compound of empirical composition $((CH_3)_4P_2S_2)CuCl$, preparing it under conditions explicitly designed to yield useful single crystals. Under these conditions we obtained, in addition to the desired white cuprous compound, a crystalline brown product. This brown substance was obtained in only about 10% the yield of the white substance and was observed to decompose to produce the white substance if left in contact with the reaction mixture for several hours. These observations led us to hypothesize that the brown compound might be a copper(II) precursor to the final, white copper(I) product, perhaps even the substance formulated as $(Me_4P_2S_2)CuCl_2$ Beg and his coworkers.[3] Since the brown substance made itself available conveniently in the nature of well formed single crystals, its identity and structure were investigated by X-ray crystallography.

EXPERIMENTAL

The preparation of the brown compound has been described in the preceding chapter.

Collection of X-Ray Data. - A crystal of approximate dimensions 0.3x0.1x0.1 mm was placed in a glass capillary and mounted on a Syntex P$\bar{1}$ computer-controlled, four-circle diffractometer, equipped with a graphite-crystal monochromator in the incident beam. The crystal was found to belong to the monoclinic system. Least-squares refinement of fifteen carefully centered reflections produced the orientation matrix required to control data collection and afforded the following unit cell dimensions: $a = 6.138(1)$Å; $b = 15.452(5)$Å; $c = 12.465(7)$Å; $\beta = 93.30(4)°$; $V = 1180.1(8)$Å^3. Assuming a value of Z equal to 4, the reasonable density 1.81 gcm^{-1} can be calculated. Attempts to measure the density were unsuccessful because of the chemical instability of the compound.

Data were collected in the range of $0° < 2\theta \leq 30°$ using Mo Kα radiation. The θ-2θ scan technique with a variable scan rate from 4.0 to 24.0 deg/min was used. The scan range was from 2θ(Mo Kα_1) $-0.9°$ to 2θ(Mo Kα_2) $+ 0.9°$. In order to check the stability of the measurement three reflections were selected as standards and their intensities were recorded periodically throughout data collection. Data collection beyond $2\theta=30°$ failed due to an abrupt decrease of intensities. A total of 583 reflections were collected and the usual data reduction procedures were applied.[5] The parameter p used in the calculation of standard deviations on the intensities ($\sigma(F_o^2)$) was assigned the value 0.05. The linear absorption coefficient was 29.12 cm^{-1} (Mo $K\alpha$). As the conditions of the measurement did not permit an accurate determination of crystal dimensions, an absorption correction was not feasible.

Solution and Refinement of the Structure. - Systematic extinctions of $l = 2n+1$ for $h0l$ and $k = 2n+1$ for $0k0$ are consistent with space group $P2_1/c$. The copper atom was immediately located in a three-dimensional Patterson map. The solution and the refinement of the structure was carried out by the usual sequence of difference Fourier syntheses and full-matrix least-squares refinements. In the refinement only those 386 reflections were used for which $F_o^2 > 3\sigma(F_o^2)$ and the quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, and $w = 4F_o^2/\sigma^2(F_o^2)$.

Because of the small data set no attempt was made to locate the hydrogen atoms. The Cu, 2Cl, 2S and 2P atoms were refined anisotropically and the four carbon atoms isotropically (a total of 80 varied parameters).

Final discrepancy indices of $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.039$ and $R_2 = (\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.049$ were reached at convergence. No parameter changed by more than 0.01 times its standard deviation in the final cycle of refinement. The error in an observation of unit weight was 1.47 and the final difference Fourier map had no peak with an electron density greater than 0.38 $e\text{Å}^{-3}$.

A list of the observed and final calculated structure factors is given in Table I.

The positional and thermal parameters are listed in Table II and in Table III.

RESULTS

The structure consists of infinite chains running parallel to the y axis, as shown in Figure 1. The $Me_4P_2S_2$ ligands are extended in an anti-rotational conformation with each sulfur atom bonded to a different copper atom. Each copper atom is surrounded by a very distorted tetrahedral array of two chlorine atoms and two sulfur atoms. Interatomic distances and angles of greatest interest are listed in Table IV and Table V.

DISCUSSION

The structure reveals, that the tetramethyldiphosphinedisulfide ligand essentially retained its original anti-rotational conformation assumed as a free ligand.[6] The copper(II) atom has a coordination geometry which is one of its most common ones, namely a flattened tetrahedron, the Cl(1)-Cu-Cl(2) angle being 142° and the S1-Cu-S2 angle being 137 °, respectively. Due to the formation of the copper-sulfur bond, the P-S bond length (1.993Å) in the complex is significantly greater, than in the free ligand (1.960Å). The comparison of the P-P bond lengths in the complex and in the free ligand is somewhat obscure. In the free ligand two significantly different phosphorus-phosphorus bond lengths (2.245Å and 2.161Å) have been established[6], while the same distance (2.220Å) in the complex seems to fall almost exactly between these values. This bond length is twice as long as the single bond covalent radius of the phosphorus atom[7], suggesting the presence of a P-P single bond.

The instability of the complex is evidently of chemical rather than structural origin. It can be ascribed to the ability of the phophine sulfide ligand to reduce Cu(II) to Cu(I).

TABLE I

OBSERVED AND FINAL CALCULATED STRUCTURE FACTORS, $10|F_o|$ and $10|F_c|$, FOR $((Me)_4P_2S_2CuCl_2)$, IN ELECTRONS

L= -8

K	H	FOBS	FCALC
-4	-1	378	393
-3	-1	255	275
-2	-1	512	485
-1	-1	543	520

L= -7

K	H	FOBS	FCALC
-6	-1	616	625
-4	-1	309	311
-3	-1	544	573
-2	-2	202	182
-2	-1	821	836
-1	-2	182	183

L= -6

K	H	FOBS	FCALC
-7	-1	255	247
-6	-1	268	277
-5	-2	261	254
-4	-1	909	902
-3	-2	162	122
-3	-1	563	538
-2	-1	472	462
-1	-2	708	729
0	-3	812	803
0	-2	1198	1188
0	-1	1353	1359

L= -5

K	H	FOBS	FCALC
-8	-1	358	357
-7	-2	704	725
-6	-2	1060	1115
-6	-1	1101	1076
-5	-2	919	919
-4	-2	259	253
-4	-1	245	240
-3	-2	334	367
-3	-1	962	955
-2	-3	190	196
-2	-2	485	514
-2	-1	1451	1449
-1	-3	869	852
-1	-2	483	498

L= -4

K	H	FOBS	FCALC
-9	-1	495	512
-8	-2	244	258
-8	-1	1580	1624
-7	-2	279	290
-7	-1	258	254
-6	-1	191	194
-5	-3	566	595
-5	-2	724	702
-4	-3	300	284
-4	-2	697	671
-3	-3	270	220
-3	-2	368	387
-3	-1	302	311
-2	-3	196	187
-2	-2	165	183
-2	-1	198	214
-1	-3	492	465
-1	-2	1210	1232
-1	-1	203	177
0	-3	959	976
0	-2	1636	1689
0	-1	1670	1615

L= -3

K	H	FOBS	FCALC
-10	-1	575	595
-9	-2	280	273
-9	-1	423	410
-8	-2	200	196
-7	-3	574	566
-7	-2	1180	1128
-7	-1	298	300
-6	-3	321	282
-6	-2	506	453
-6	-1	209	217
-5	-3	394	411
-5	-2	270	266
-4	-3	172	212
-4	-1	239	271
-3	-3	416	399
-3	-2	155	168
-3	-1	626	608
-2	-3	647	673
-2	-2	300	275
-2	-1	471	496
-1	-3	1148	1116
-1	-2	605	617

L= -2

K	H	FOBS	FCALC
-9	-2	324	306
-9	-1	179	168
-8	-2	811	781
-8	-1	984	957
-7	-2	406	424
-7	-1	433	446
-6	-3	293	310
-5	-3	985	889
-5	-2	220	259
-4	-2	433	426
-4	-1	1310	1239
-3	-2	331	304
-2	-2	218	191
-1	-3	469	462
-1	-2	871	859
0	-3	1170	1185
0	-1	332	342

L= -1

K	H	FOBS	FCALC
-10	-1	379	352
-9	-2	340	330
-9	-1	233	243
-8	-3	202	192
-8	-2	348	353
-8	-1	244	233
-7	-3	269	220
-7	-2	998	1032
-7	-1	522	517
-6	-3	1021	1050
-6	-2	579	597
-6	-1	403	357
-5	-3	339	343
-5	-2	193	155
-5	-1	650	622
-3	-2	201	172
-2	-3	630	646
-2	-2	1252	1201
-2	-1	1403	1319
-1	-4	277	249
-1	-3	265	277
-1	-2	573	545
-1	-1	746	789

L= 0

K	H	FOBS	FCALC
-10	-2	196	184
-9	-2	259	255
-9	-1	296	330
-8	-3	550	539
-8	-2	1137	1174
-8	-1	1173	1206
-7	-3	185	243
-7	-2	788	810
-7	-1	626	615
-6	-3	307	292
-6	-1	139	189
-5	-3	539	593
-5	-2	174	137
-5	-1	714	682
-4	-3	809	795
-4	-2	270	249
-4	-1	888	881
-3	-2	645	676
-1	-4	445	441
-1	-2	572	548
-1	-1	1023	1063
0	-4	488	491
0	-3	1231	1202
0	-2	1293	1173

L= 1

K	H	FOBS	FCALC
-10	-2	602	636
-10	-1	450	424
-10	-1	450	424
-10	0	868	838
-9	-2	530	549
-9	-1	318	331
-9	0	224	234
-8	-1	236	242
-8	0	357	351
-7	-3	568	582
-7	-2	818	805
-7	-1	832	845
-7	0	517	535
-6	-3	760	740
-6	-1	696	670
-6	0	2028	2019
-5	-3	573	582
-5	-2	169	180
-5	-1	863	856
-5	0	384	374
-4	-1	149	182
-3	-2	936	973
-3	-1	208	271
-3	0	235	204
-2	-3	890	925
-2	-2	400	330
-2	-1	2059	2141
-2	0	547	576
-1	-4	478	492
-1	-2	699	661
-1	-1	1219	1239
-1	0	206	207

L= 2

K	H	FOBS	FCALC
-9	-2	612	651
-9	-1	526	529
-9	0	195	162
-8	-3	346	345
-8	-2	189	144
-8	-1	680	737
-8	0	291	278
-7	-3	193	154
-7	-2	574	569
-7	-1	263	264
-7	0	331	326
-5	-3	690	713
-5	-2	274	276
-5	-1	970	979
-4	-3	737	772
-4	-2	784	812
-4	-1	2180	2051
-4	0	217	129
-3	-3	307	320
-3	-2	1093	1119
-3	-1	344	354
-3	0	222	140
-2	-1	237	224
-1	-4	381	359
-1	-2	559	547
-1	-1	1374	1385
0	-4	579	555
0	-3	189	140
0	0	2321	2374

L= 3

K	H	FOBS	FCALC
-10	-1	265	257
-10	0	386	387
-7	-3	339	335
-7	-2	548	515
-7	-1	727	754
-7	0	885	876
-6	-3	287	252
-6	-2	167	166
-6	-1	467	427
-6	0	656	662
-5	-3	565	597
-5	-1	720	712
-5	0	305	305
-4	-2	160	167
-3	-3	281	315
-3	-2	1438	1434
-3	0	282	287
-2	-3	249	213
-2	-1	333	333
-2	0	219	307
-1	-2	218	240
-1	-1	845	863
-1	0	425	483

L= 4

K	H	FOBS	FCALC
-10	0	208	210
-9	-1	491	504
-9	0	298	289
-8	-1	721	723
-8	0	336	351
-7	-3	209	190
-7	-1	193	243
-7	0	801	807
-6	0	285	262
-5	-3	631	645
-5	-2	206	213
-5	-1	880	855
-5	0	183	172
-4	-3	520	513
-4	-2	399	402
-4	0	238	236
-3	-2	986	963
-3	0	402	390
-2	-2	283	295
-2	-1	198	210
-1	-1	1081	1073
-1	0	506	486
0	-4	410	425
0	-3	505	487
0	-2	354	414
0	-1	1793	1753

L= 5

K	H	FOBS	FCALC
-9	-1	208	187
-9	0	242	229
-8	-1	256	254
-7	-2	185	202
-7	0	653	680
-6	-2	945	925
-6	-1	478	501
-6	0	533	520
-5	-1	932	905
-5	0	194	174
-4	-3	243	241
-4	-1	237	205
-4	0	319	293
-3	-2	1013	1017
-3	0	410	417
-2	-3	1022	1029
-2	-3	1022	1029
-2	-2	814	827
-2	-1	235	292
-2	0	563	600
-1	-3	204	195
-1	-2	161	155
-1	-1	497	533
-1	0	413	393

L= 6

K	H	FOBS	FCALC
-8	-1	355	331
-8	0	409	421
-7	-1	290	273
-7	0	555	551
-6	-1	263	274
-6	0	291	288
-5	-2	173	142
-5	-1	846	816
-5	0	403	425
-4	-3	810	762
-4	-2	1300	1322
-4	0	1765	1742
-3	-3	382	355
-3	-2	848	859
-3	-1	345	323
-3	0	220	223
-2	-2	370	371
-1	-3	214	198
-1	-1	533	558
-1	0	352	380
0	-2	1101	1033
0	-1	224	201
0	0	698	659

L= 7

K	H	FOBS	FCALC
-7	0	593	590
-6	-1	297	273
-6	0	483	485
-5	-1	706	717
-5	0	184	148
-4	0	469	492
-3	-2	338	338
-3	-1	546	520
-3	0	636	639
-2	0	1059	1081
-1	-1	466	510

L= 8

K	H	FOBS	FCALC
-5	-1	629	634
-4	-1	353	309
-4	0	746	729
-3	-1	248	248
-3	0	415	386
-2	0	176	149
-1	-2	267	263
-1	0	512	519
0	-2	280	234
0	-1	932	956

TABLE II

POSITIONAL PARAMETERS FOR $(Me_4P_2S_2)CuCl_2$[a]

a) Numbers in parentheses in this and all other tables are estimated standard deviations in the last significant digit.

Atom	x	y	z
Cu	0.1323(5)	-0.1290(2)	0.2309(2)
Cl(1)	-0.1369(9)	-0.1382(4)	0.1038(5)
Cl(2)	0.1968(9)	-0.1216(4)	0.4067(4)
S1	0.216(1)	0.0084(4)	0.1700(5)
S2	0.230(1)	-0.2714(4)	0.1945(5)
P1	0.424(1)	0.0658(4)	0.2766(5)
P2	0.439(1)	-0.3212(4)	0.3063(5)
C1	0.663(4)	0.002(1)	0.322(2)
C2	0.303(3)	0.112(1)	0.393(2)
C3	0.323(3)	-0.363(1)	0.425(1)
C4	0.679(4)	-0.256(1)	0.348(2)

TABLE III

THERMAL PARAMETERS FOR $(Me_4P_2S_2)CuCl_2$[a]

a) The form of the thermal ellipsoid is
$\exp(-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}\ell^2+2\beta_{12}hk+2\beta_{13}h\ell+2\beta_{23}k\ell))$

Atom	Isotropic B	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu		0.024(1)	0.0024(2)	0.0043(3)	-0.0001(4)	-0.0013(4)	0.0000(2)
Cl(1)		0.027(3)	0.0032(4)	0.0056(6)	-0.0017(9)	-0.001(1)	0.0002(4)
Cl(2)		0.035(3)	0.0035(3)	0.0043(6)	0.001(1)	-0.001(1)	-0.0003(4)
S1		0.033(4)	0.0023(4)	0.0041(7)	-0.0012(9)	-0.001(1)	0.0002(3)
S2		0.029(4)	0.0020(4)	0.0060(6)	0.0010(8)	-0.002(1)	-0.0002(4)
P1		0.023(3)	0.0018(4)	0.0035(6)	0.0000(9)	-0.001(1)	0.0004(4)
P2		0.019(3)	0.0022(4)	0.0036(7)	-0.0001(8)	-0.001(1)	-0.0002(4)
C1	2.5(6)						
C2	2.3(5)						
C3	2.2(5)						
C4	3.1(6)						

TABLE IV

BOND DISTANCES, Å

		Average values
Cu-Cl(1)	2.225(6)	2.215±0.010
Cu-Cl(2)	2.206(6)	
Cu-S1	2.322(7)	2.327±0.005
Cu-S2	2.332(7)	
S1-P1	1.995(9)	1.993±0.002
S2-P2	1.991(9)	
P1-C1	1.83(2)	1.82±0.02
P1-C2	1.81(2)	
P2-C3	1.80(2)	
P2-C4	1.84(4)	
P1-P2	2.220(8)	

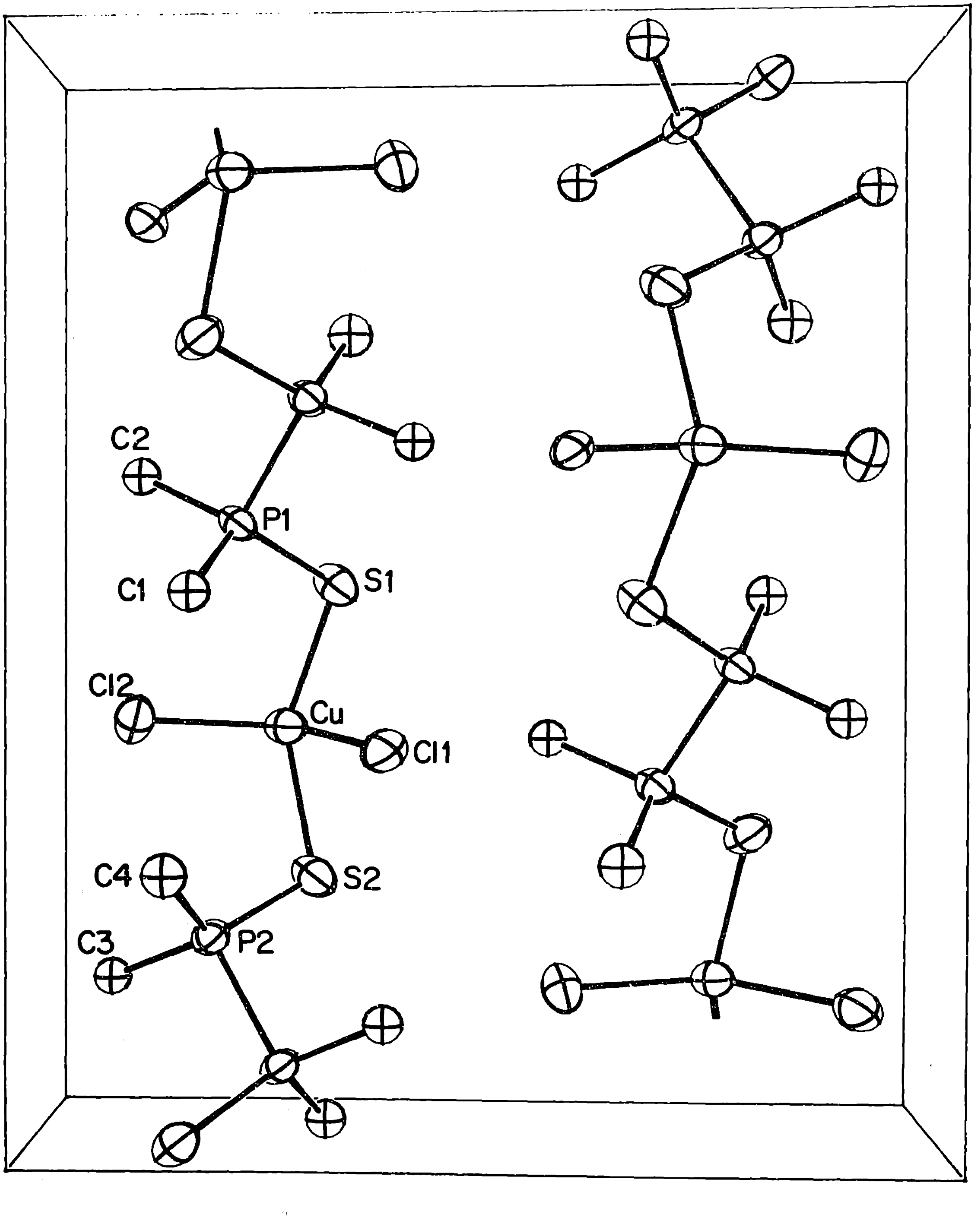
TABLE V

BOND ANGLES, DEGREES

Cl(1)-Cu-Cl(2)	142.4(3)
S1-Cu-S2	137.3(2)
Cl(1)-Cu-S1	89.7(2)
Cl(1)-Cu-S2	89.5(3)
Cl(2)-Cu-S1	104.3(3)
Cl(2)-Cu-S2	102.1(3)
P1-S1-Cu	109.5(3)
P2-S2-Cu	113.1(3)
C1-P1-S1	115.9(7)
C1-P1-P2	104.2(7)
C1-P1-C2	108.9(9)
C2-P1-S1	115.6(8)
C2-P1-P2	104.3(7)
S1-P1-P2	106.6(4)
C3-P2-S2	116.4(7)
C3-P2-P1	106.1(7)
C3-P2-C4	108.3(9)
C4-P2-S2	117.2(7)
C4-P2-P1	104.3(7)
S2-P2-P1	103.0(3)

FIGURE 1

An ORTEP projection of the contents of one unit cell in the x direction. (The origin of the unit cell is at the lower left corner, X axis is directed backward, Y axis upward and Z axis to the right, providing a right handed system). The atom numbering scheme used in the tables is shown. Each atom is represented by its thermal vibration ellipsoid scaled to enclose 50% of the electron density.


C2
P1
C1
S1
Cl2
Cu
Cl1
C4
S2
C3
P2

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BIOGRAPHICAL NOTE

The author was born on March 29, 1940 in Budapest, Hungary. Due to political reasons his family was deported by the communist regime in 1951 to a remote part of Hungary, where the whole family spent two years under most primitive circumstances. Altough the author finished high-school with highest distinctions in 1958, was still considered as "undesireable element" and was not admitted to the university, but was forced to work as a laborer in a steel factory. In 1959 was admitted to the Technical University of Budapest and in 1964 graduated as a Diploma Chemical Engineer. Between 1964 and 1968 he was employed by the same university as an instructor at the Inorganic Chemistry Department.

In 1968 he defected to the west, entered the U.S.A. in 1969 and started his studies in the same year toward the degree of Doctor of Phylosophy in the Department of Chemistry at M.I.T. He married the former Julie Molnar of Burlington, Massachusetts in 1970 and now have a daughter, Katalin, born February 23, 1974. They moved to College Station, Texas in 1972 where the author completed his research. Upon graduation, the author accepted a position in the Technical Center of Union Carbide in Charleston, West Virginia.