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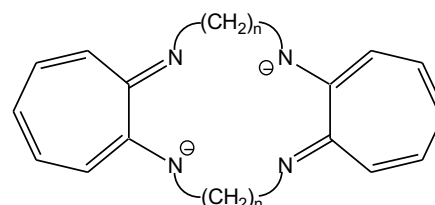
Singlet-triplet gaps of cobalt nitrosyls: Insights from tropocoronand complexes

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A DFT study of cobalt-nitrosyl [n,n]tropocoronand (TC-*n,n*) complexes has revealed a sharp reduction of singlet-triplet gaps as the structures change from near-square-pyramidal (for *n* = 3) to trigonal-bipyramidal with an equatorial NO (for *n* = 5, 6). For *n* = 6, low-energy triplet states may result in enhanced reactivity, which would account for the failure to isolate [Co(TC-6,6)(NO)] as a stable species.



Scheme 1. Dianion of an [n,n]tropocoronand (n,n-TC) ligand.

By varying the length of the alkyl linker chains, one can tune the tropocoronand ligands ([TC-*n,n*]²⁻; Scheme 1) to provide sterically constrained coordination environments which, for five-coordinate complexes, vary from square-pyramidal (SQP) to trigonal bipyramidal (TBP). Several of these complexes have unusual geometric and electronic structures.¹ Among these are [Fe(TC-5,5)(NO)],² which has an unusual linear {FeNO}⁷ unit, and the unique *S* = 1 {MNO}⁶ complex [Mn(TC-5,5)(NO)].³ The literature on {CoNO}⁸ tropocoronand complexes is also of interest. Whereas [Co(TC-3,3)(NO)] was reported to be paramagnetic,⁴ the analogous TC-4,4 and TC-5,5 complexes are diamagnetic, a more common situation for {CoNO}⁸ complexes. The hypothetical [Co(TC-6,6)(NO)] complex has thus far eluded isolation and characterization.⁵

In the present study, density functional theory (DFT) calculations⁶ were undertaken with the goal of contributing to our understanding of the divergent spin states and chemical behavior of {CoNO}⁸ tropocoronand complexes. The calculations showed, that the essentially SQP [Co(TC-3,3)(NO)] complex is *S* = 0, like other {CoNO}⁸ species,⁷ and was confirmed by experimental reinvestigation of the molecule. The calculations also revealed a decreasing singlet-triplet gap and low-energy triplet states as the coordination geometry changed from the nearly SQP TC-3,3 complex to the TBP TC-5,5 and TC-6,6 complexes. Thermally accessible triplet states are a distinct possibility for [Co(TC-6,6)(NO)], which would explain its apparent instability.

The lowest-energy singlet and triplet states of the [Co(TC-*n,n*)(NO)] complexes (*n* = 3-6) were optimized with the B3LYP, OLYP, and PW91 functionals and the 6-311G(d,p) basis set. In general, the hybrid functional B3LYP led to a broken-symmetry *M_S* = 0 solution as the ground state, whereas the pure functionals

PW91 and OLYP led to closed-shell ground states. Interestingly, depending on the starting point of the optimizations, two distinct triplet states, denoted T₁ and T₂ in the discussion below, could be obtained. The T₁ state may be described as low-spin *S* = ½ Co(II) ferromagnetically coupled to a NO radical, and the T₂ state may be described as a high-spin *S* = 2 Co(III) antiferromagnetically coupled to an *S* = 1 NO⁻ anion. Table 1 lists the energies of the triplet states, relative to the singlet ground state, for the different functionals.

The energetics of the T₁ and T₂ states are qualitatively consistent across the three functionals. As noted elsewhere,⁸ classic pure functional PW91 may have a certain bias in favor of the singlet state, whereas the hybrid functional B3LYP may have a similar bias in favor of the triplet states. In certain applications involving transition metal nitrosyls, OLYP was one of the least biased functionals vis-à-vis the issue of spin pairing.^{8c,d} This generalization may also apply to the present study. It is significant in this context that the three functionals examined predict singlet ground states for all the CoNO complexes, with the highest singlet-triplet (S-T) gap predicted for [Co(TC-3,3)(NO)], casting doubt on the original description of this compound as being paramagnetic.

A reinvestigation of [Co(TC-3,3)(NO)] was accordingly undertaken. Published procedures for the synthesis of both [Co(TC-3,3)(NO)] and its precursor [Co(TC-3,3)] are low-yielding and afford only small quantities of the desired materials. New synthetic procedures were therefore sought to improve the yield and scale of the older preparations. Reaction in THF of CoI₂ with Na₂[TC-3,3], prepared *in situ* by deprotonation of the free ligand with NaN(SiMe₃)₂, afforded [Co(TC-3,3)] in 69% yield after crystallization from toluene. The reported *S* = ½ ground state of [Co(TC-3,3)] was confirmed by solution

Table 1. Energies (eV) of the triplet states T_1 and T_2 , relative to the lowest-energy $M_S = 0$ state S_0 .^a

Complex	B3LYP/6-311G(d,p)		OLYP/6-311G(d,p)		PW91/6-311G(d,p)	
	T_1	T_2	T_1	T_2	T_1	T_2
[Co(TC-3,3)(NO)]	0.43	0.61	1.03 (1.00) ^b	0.78	1.09	1.06
[Co(TC-4,4)(NO)]	0.38	0.23	-	0.36	0.59	-
[Co(TC-5,5)(NO)]	0.21	0.21	0.29	0.27	0.35	-
[Co(TC-6,6)(NO)]	0.27	0.15	0.40 (0.22) ^b	0.16	0.30	-

^a The S_0 state corresponds to a broken-symmetry $M_S = 0$ calculation for B3LYP, but to closed-shell $M_S = 0$ calculations for the pure functionals PW91 and OLYP.

^b These values were obtained with a STO-TZP basis set.

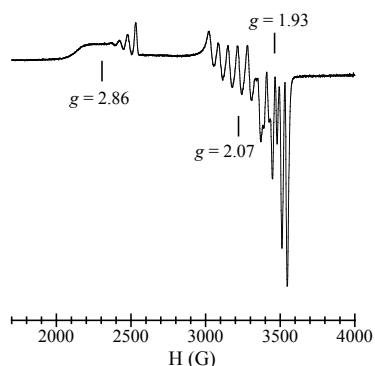


Figure 1. 9.335 GHz X-band EPR spectrum of [Co^{II}(TC-3,3)] recorded in a 2-MeTHF glass at 77 K. Instrument settings: 2.0 mW power, 100.0 KHz modulation frequency, 8.0 G modulation amplitude.

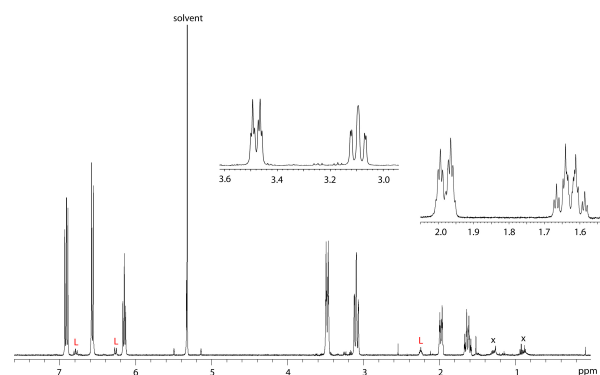


Figure 2. 500 MHz ¹H NMR spectrum of [Co(TC-3,3)(NO)] recorded in CD₂Cl₂. L represents peaks due to H₂(TC-3,3).

magnetic susceptibility measurements (Evan's method) and by EPR spectroscopy (Figure 1).^{1d} Preparation of [Co(TC-3,3)(NO)] from [Co^{II}(TC-3,3)] and NO gas proceeded smoothly in CH₂Cl₂ to afford the desired compound as brown microcrystals after precipitation at -30 °C. With this new synthetic procedure, [Co(TC-3,3)(NO)] could be obtained on scales of ca. 50 mg with reproducible yields exceeding 60%. Use of ¹⁵NO gas afforded the ¹⁵N-labeled analog in an identical fashion. The ¹H NMR spectrum of [Co(TC-3,3)(NO)] clearly demonstrates that the nitrosyl compound is diamagnetic, with apparent C_{2v} symmetry in solution (Figure 2), consistent with the DFT results. The low solubility of the complex in common organic solvents hindered attempts to collect ¹³C and ¹⁵N NMR spectra, although a weak resonance was identified in the 50.7

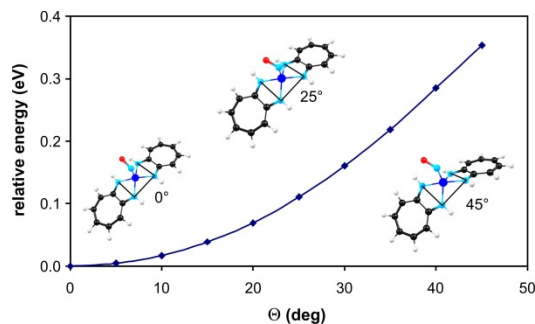


Figure 3. OLYP potential energy curve for TBP distortion of the model complex [Co(ATI)₂(NO)].

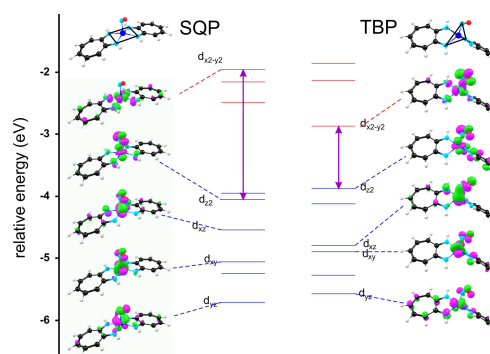


Figure 4. OLYP energy levels of the Co 3d-based MOs of limiting SQP and TBP forms of [Co(ATI)₂(NO)].

1040 MHz ¹⁵N NMR spectrum of [Co(TC-3,3)(¹⁵NO)] at 1040 ppm (vs NH₃). We tentatively assign this peak as the nitrosyl nitrogen atom based on its chemical shift, which is in the range commonly encountered for {Co-NO}⁸ species.⁹

Perhaps the most interesting conclusion from Table 1 is that the singlet-triplet gap of the complexes decreases monotonically as the linker length n increases from 3 to 6. Because the coordination geometry of the Co changes from nearly SQP for $n = 3$ to TBP for $n = 5, 6$, we chose to examine the energetics of the linker-free model complex [Co(ATI)₂(NO)] (ATI = dianion of aminotroponimine) as a function of the NNNN dihedral, Θ , defined as the dihedral angle between the two five-membered aminotroponimate chelate rings, shown in Figure 3. Figure 3 strongly indicates that, in the absence of steric constraints such as polymethylene linkers in tropocoronand ligands, {CoNO}⁸ complexes exhibit a distinct preference for SQP coordination.

Table 2. Selected optimized and experimental distances (Å) and angles (°).

Complex	Co-N				N-O				Co-N-O			
	B3LYP	PW91	OLYP	Exp	B3LYP	PW91	OLYP	Exp	B3LYP	PW91	OLYP	Exp
[Co(TC-3,3)(NO)]	1.844	1.722	1.778	1.785(6)	1.170	1.189	1.184	1.137(7)	122.2	122.9	123.4	127.3(6)
[Co(TC-4,4)(NO)]	1.824	1.747	1.746	1.779(6)	1.188	1.194	1.188	1.151(9)	132.3	131.6	133.0	128.9(6)
								1.18(2)				134.9(9)
[Co(TC-5,5)(NO)]	1.799	1.702	1.708	1.7856(17)	1.183	1.191	1.186	1.177(2)	137.5	140.7	139.5	129.48(13)
[Co(TC-6,6)(NO)]	1.804	1.709	1.708	-	1.185	1.191	1.186	-	137.0	139.3	139.6	-

Table 3. Selected Mulliken spin populations.

Complex	State	Co			N			O		
		B3LYP	PW91	OLYP	B3LYP	PW91	OLYP	B3LYP	PW91	OLYP
[Co(TC-3,3)(NO)]	T ₁	0.935	0.832	0.890	0.761	0.964	0.755	0.401	0.394	0.378
	T ₂	2.636	1.726	2.127	-0.581	-0.117	-0.299	-0.511	-0.147	-0.283
[Co(TC-4,4)(NO)]	T ₁	1.334	1.295	-	0.349	0.165	-	0.143	0.077	-
	T ₂	2.615	-	1.960	-0.600	-	-0.257	-0.510	-	-0.240
[Co(TC-5,5)(NO)]	T ₁	0.910	1.113	1.468	0.580	0.318	0.112	0.380	0.213	0.048
	T ₂	2.580	-	1.799	-0.583	-	-0.088	-0.478	-	-0.114
[Co(TC-6,6)(NO)]	T ₁	1.520	1.171	1.550	0.219	0.286	0.067	0.076	0.186	0.022
	T ₂	2.585	-	1.876	-0.570	-	-0.134	-0.471	-	-0.146

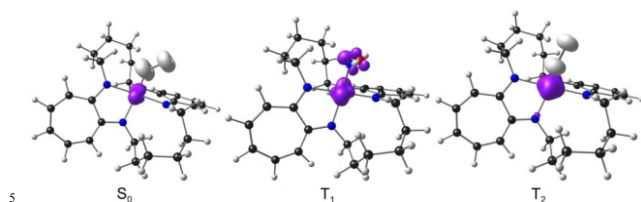
Figure 5. B3LYP/6-311G(d,p) spin density profiles (contour 0.03 e/Å³) for the S₀, T₁ and T₂ states of [Co(TC-6,6)(NO)]

Figure 4 compares the energy levels of the Co-3d-based molecular orbitals (MOs) for the limiting SQP and TBP geometries of this complex. For TBP geometry, the orbital energy of the d_{x²-y²} orbital is significantly lower than that of the SQP geometry, resulting in a lower HOMO-LUMO gap for the former structure. This MO picture thus provides a plausible explanation for decreasing S-T gaps with increasing linker lengths ($n = 3-6$) in CoNO tropocoronand complexes.

As shown in Table 2, the calculations do a fair job of reproducing the experimentally observed CoNO geometric parameters of [Co(TC- n,n)(NO)] for $n = 3-5$. The hybrid functional B3LYP overestimates the Co-N distance by up to 0.06 Å, whereas the pure functionals PW91 and OLYP underestimate this distance by up to 0.07 Å. For [Co(TC-5,5)(NO)], all three functionals appear to overestimate the CoNO angle by about 10°. Although these errors are slightly on the high side, they are still within acceptable limits, given that we have not made any attempt to model the solid-state environments of the molecules in question.

The twist angle Θ , (Figure 3) provides a measure of TBP distortion relative to a SQP base geometry. For the experimental [Co(TC- n,n)(NO)] structures, the Θ value indicated in Figure 3 is 0°, 34.4°, and 35.4° for $n = 3, 4$, and 5, respectively. For the B3LYP [Co(TC- n,n)(NO)] structures, Θ is 0°, 37.9°, 55.2°, and 53.5° for $n = 3, 4, 5$, and 6, respectively. Thus, the calculations do not reproduce the observed dihedrals in an entirely satisfactory manner. Nevertheless, the S-T gaps appear to correlate with the reactivity of the CoNO complexes.

The high S-T gap of [Co(TC-3,3)(NO)] appears consistent with its inertness toward NO. By contrast, the other [Co(TC- n,n)(NO)] ($n > 3$) complexes, with much lower S-T gaps, all

form {Co(NO)₂}¹⁰ complexes, and [Co(TC-6,6)(NO)], with the lowest S-T gap, appears not to exist as a stable molecule.⁵

Finally, a brief word is warranted on the open-shell states of the various complexes. Thus, Figure 5 depicts the B3LYP/6-311G(d,p) spin density profiles for the S₀, T₁ and T₂ states of [Co(TC-6,6)(NO)], which we chose as a representative example, and Table 3 presents the Mulliken spin populations for the T₁ and T₂ states of all four CoNO complexes. We encourage the interested reader to verify that spin populations in Table 3 are consistent with the qualitative descriptions of the T₁ and T₂ states given above.

Conclusions

In summary, we have confirmed that [Co(TC-3,3)(NO)] is not paramagnetic, as originally stated, but diamagnetic and $S = 0$ like other {CoNO}⁸ species. Our calculations do, however, raise the possibility of a low-energy $S = 1$ state for trigonal-bipyramidal {CoNO}⁸ complexes with an equatorial NO. For [Co(TC-6,6)(NO)], the S-T gap may be so low as to allow a thermally accessible triplet state. Such a state presumably enables reaction pathways that are energetically inaccessible for the other CoNO tropocoronand complexes.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Details of experimental procedures, spectra and computations. See DOI: XXXX.

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