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Uptake of one and two molecules of CO\textsubscript{2} by the molybdate dianion: a soluble, molecular oxide model system for carbon dioxide fixation\textsuperscript{†}

Ioana Knopf,a Takashi Ono,a Manuel Temprado,b Daniel Tofana and Christopher C. Cummins\textsuperscript{a}

Tetrahedral [MoO\textsubscript{4}]\textsuperscript{2−} readily binds CO\textsubscript{2} at room temperature to produce a robust monocarbonate complex, [MoO\textsubscript{3}(k\textsuperscript{2}-CO\textsubscript{3})]\textsuperscript{2−}, that does not release CO\textsubscript{2} even at modestly elevated temperatures (up to 56 °C in solution and 70 °C in the solid state). In the presence of excess carbon dioxide, a second molecule of CO\textsubscript{2} binds to afford a pseudo-octahedral dioxo dicarbonate complex, [MoO\textsubscript{2}(k\textsuperscript{2}-CO\textsubscript{3})\textsubscript{3}]\textsuperscript{2−}, the first structurally characterized transition-metal dicarbonate complex derived from CO\textsubscript{2}. The monocarbonate [MoO\textsubscript{3}(k\textsuperscript{2}-CO\textsubscript{3})]\textsuperscript{2−} reacts with triethylsilane in acetonitrile under an atmosphere of CO\textsubscript{2} to produce formate (69% isolated yield) together with silylated molybdate (quantitative conversion to [MoO\textsubscript{2}(OSiEt\textsubscript{3})]\textsuperscript{−}, 50% isolated yield) after 22 hours at 85 °C. This system thus illustrates both the reversible binding of CO\textsubscript{2} by a simple transition-metal oxoanion and the ability of the latter molecular metal oxide to facilitate chemical CO\textsubscript{2} reduction.

Metal oxide catalysts for CO\textsubscript{2} transformations are advantageous based on considerations of cost, ease of re-use, and stability,\textsuperscript{1} but these advantages come at the expense of our ability to readily characterize such systems at a molecular level of detail. Intrigued by the paucity of soluble transition-metal oxide systems known to react with CO\textsubscript{2} in a well-defined manner (e.g., eqn (1)),\textsuperscript{2} we decided to investigate salts of the molybdate dianion in this respect, in order to determine the behavior and mode of reaction (if any) of a simple oxoanion with carbon dioxide as either the potential basis for a new homogeneous catalytic system or as a soluble model for known heterogeneous oxide catalysts. Accordingly, herein we report the finding that molybdate absorbs not just one but two equivalents of CO\textsubscript{2} (the second, reversibly) together with complete characterization including single-crystal X-ray diffraction studies of the resulting mono- and dicarbonate complexes.

\[
\text{L}_\text{m}M=O + \text{CO}_2 \rightleftharpoons \text{L}_\text{m}M(\text{CO}_3)^2
\]  

(1)

As our studies were in progress, it was reported that the related tungstate dianion indeed serves as a homogeneous catalyst for CO\textsubscript{2} fixation,\textsuperscript{3} but so far the reaction intermediates in that system have not been isolated. The structural, spectroscopic, and computational details we disclose herein form an excellent point of reference both for understanding tungstate-catalyzed CO\textsubscript{2} fixation processes and for developing analogous systems based upon molybdate. Toward the latter goal, we show herein the ability of molybdate to mediate the triethylsilane reduction of CO\textsubscript{2} to formate. The present work follows and improves upon our earlier report of titanium trisanilide oxoanion CO\textsubscript{2} binding\textsuperscript{4} in that the present system utilizes essentially non-interacting organic cations (in the earlier system oxophilic alkali-metal cations such as lithium were a necessary ingredient for CO\textsubscript{2} uptake) and in that the molybdate dianion is an entirely inorganic species well suited as a discrete, molecular analog of a solid-state metal oxide. Also serving as a precursor to the present work is our report of a cycle for CO\textsubscript{2} reduction to CO at a niobium nitride binding site; that system represented our initial foray into ligand-based strategies for CO\textsubscript{2} conversion.\textsuperscript{6}

We began our studies with the commercially available sodium molybdate, but soon determined that this organic-media insoluble salt does not react with CO\textsubscript{2} under aqueous conditions (as assessed by\textsuperscript{7}\textsuperscript{5}Mo NMR spectroscopy).\textsuperscript{7} In order to endow the molybdate dianion with solubility in organic media, we prepared [PPN\textsubscript{3}][MoO\textsubscript{4}] [PPN\textsuperscript{+} = (Ph\textsubscript{3}P)\textsuperscript{N\textsuperscript{+}}] in one step from Ag\textsubscript{2}MoO\textsubscript{4} and [PPN]Cl using a modified literature procedure.\textsuperscript{8} Upon addition of CO\textsubscript{2} to a 0.04 M acetonitrile solution of [PPN\textsubscript{3}][MoO\textsubscript{4}] at room temperature, a new species quickly formed. The \textsuperscript{5}Mo NMR spectrum of the isolated product exhibits a new resonance at +46.7 ppm, no unreacted starting material (+13.2 ppm), but also a small amount of [Mo\textsubscript{2}O\textsubscript{2}]\textsuperscript{2−}.

\textsuperscript{†}Electronic supplementary information (ESI) available: Full experimental, crystallographic, spectroscopic, and computational data. CCDC 978136, 978137 and 981116. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4sc00132j

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by-product identified by a signal at ~3.8 ppm. A new characteristic carbonyl stretch at 1638 cm$^{-1}$ could also be observed by IR spectroscopy.\textsuperscript{10}

A preliminary X-ray crystal structure of the CO$_2$-addition product revealed a $\kappa^2$-bound carbonate moiety and enabled us to formulate the major product obtained as [PPN]$_2$[MoO$_3$(k$^2$-CO$_3$)]. In the interest of obtaining high quality crystallographic data, [NET$_3$]$_2$[MoO$_4$] (previously reported in the literature and used to prepare examples of well-behaved and crystallographically characterized molybdenum complexes)\textsuperscript{11} was used to obtain the [MoO$_3$(k$^2$-CO$_3$)]$^{2-}$ dianion as its tetraethylammonium salt. Colorless crystals were grown by vapor diffusion of Et$_2$O into a CH$_3$CN solution of [NET$_3$]$_2$[MoO$_4$(k$^2$-CO$_3$)], and the structure obtained in the ensuing crystallographic investigation is shown in Fig. 1. The C–O distances are elongated from 1.162 Å in free CO$_2$\textsuperscript{11} to 1.2258(13) Å, 1.3048(13) Å, and 1.3357(14) Å in the carbonate unit. The average Mo–O distance is 1.739 Å for the three molybdenum oxo bonds, shorter than the average Mo–O distance of 1.776 Å in tetrahedral [MoO$_4$]$^{2-}$.\textsuperscript{11} The carbonate ligand is associated with longer Mo–O interatomic distances at 2.0674(9) and 2.2191(9) Å. The slight asymmetry of the carbonate binding mode is apparently induced by the trans influence of one of the molybdenum oxo ligands (O3–Mo1–O6 148.75(3)$^\circ$ and C1–O3–Mo1–O6 2.09(11)$^\circ$) as reflected in the Mo–O bond lengths that differ by approximately 0.15 Å, but also in the different Mo–O–C angles of 97.75(6) and 91.74(7)$^\circ$. This $\kappa^2$ binding mode is not surprising given the lack of steric bulk around the molybdenum center, in contrast to the arrangement in [k$^2$-CO$_3$]TIX$_2$ (X = N[3Bu(3,5-Me$_2$C$_6$H$_3$)]) for which a combination of ancillary ligand steric bulk and external carbonate complexation by an alkali-metal counterion promotes $\kappa^2$-binding of [CO$_3$]$^{2-}$ to the titanium center.\textsuperscript{2}

Solid [PPN]$_2$[MoO$_3$(k$^2$-CO$_3$)] is moderately stable in air, and does not lose CO$_2$ even after being heated at 70 °C under vacuum for 1 h. In solution, [PPN]$_2$[MoO$_3$(k$^2$-CO$_3$)] was heated to 56 °C without any observable loss of CO$_2$ as monitored by $^{13}$C NMR spectroscopy. However, this compound is moisture sensitive, undergoing conversion to [PPN]$_2$[MoO$_4$] when even a few equivalents of water are added to a solution of [PPN]$_2$[MoO$_3$(k$^2$-CO$_3$)]. On the other hand, solid [NET$_3$]$_2$[MoO$_3$(k$^2$-CO$_3$)] is hygroscopic and converts to molybdate and dimolybdate in ca. 15 minutes by absorbing moisture from the ambient atmosphere, as monitored by IR spectroscopy.

Prepared and isolated using $^{13}$CO$_2$, [PPN]$_2$[MoO$_3$(k$^{13}$-CO$_3$)] displays a sharp $^{13}$C NMR resonance at 165.7 ppm, this being in a region of the spectrum that is characteristic for carbonates.\textsuperscript{2,3,14} In its IR spectrum, an isotope-shifted carbonyl stretch is present at 1599 cm$^{-1}$, in good agreement with the theoretical 1602 cm$^{-1}$ predicted using the harmonic oscillator approximation. A small peak due to a minor impurity at 158.9 ppm could also be observed by $^{13}$C NMR spectroscopy, correlated with the trace dimolybdate by-product detected by $^{95}$Mo NMR spectroscopy. Adding [PPN][HCO$_3$]$^-$ to a mixture of [PPN]$_2$[MoO$_3$(k$^{13}$-CO$_3$)] and this unknown species yielded an increase in the intensity of the 158.9 ppm signal and no additional resonances, allowing us to conclusively assign the minor impurity as bicarbonate anion. The minor [HCO$_3$]$^-$ impurity may originate from the reaction of [MoO$_3$]$^{2-}$ with [MoO$_4$(k$^2$-CO$_3$)]$^{2-}$ to yield [MoO$_4$]$^{2-}$ and free [CO$_3$]$^{2-}$, the latter converting to bicarbonate upon protonation, presumably from adventitious water.

Under 1 atm of $^{13}$CO$_2$, the room temperature $^{13}$C NMR spectrum of a [PPN]$_2$[MoO$_4$] solution features two broad signals: one for the free $^{13}$CO$_2$ at 125.8 ppm, and one for the molybdenum carbonate at 165.3 ppm, the broad nature of the resonances suggesting that a chemical exchange is occurring on the NMR time scale. A new major resonance appeared at 162.8 ppm when acquiring the spectrum at ~19 °C, but disappeared after degassing the sample. The ratio of the unknown species at 162.8 ppm to [PPN]$_2$[MoO$_4$] is ca. 5:1 (Fig. 2), with Mo–O distances of 2.198(2) Å and free CO$_2$ (3 atm), and at lower temperature (~31 °C). These data are indicative of additional reversible binding of $^{13}$CO$_2$ to the [MoO$_4$(k$^{13}$-CO$_3$)]$^{2-}$ dianion.

The existence of a dicarbonate species was confirmed by X-ray crystallography, as colorless diffraction quality crystals were grown by slowly cooling a CH$_3$CN solution of [PPN]$_2$[MoO$_4$] under an atmosphere of CO$_2$. In the solid state, both carbonate ligands are bound $\kappa^2$ (Fig. 2), with Mo–O distances of 2.198(2) and 2.024(2), 2.175(2) and 2.0145(19) Å, respectively. The molybdenum oxo distances are 1.695(2) and 1.705(3) Å, shorter still than in [MoO$_4$(k$^2$-CO$_3$)]$^{2-}$ as the Mo–O $\pi$ character is shared over fewer centers. The carbonate ligand binding mode is characterized by the same type of asymmetry as seen in

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**Fig. 1** Left: $^{95}$Mo NMR resonance of [MoO$_3$(k$^2$-CO$_3$)]$^{2-}$. Right: solid-state structure of [NET$_3$]$_2$[MoO$_4$(k$^2$-CO$_3$)] (ellipsoids at the 50% probability level, cations omitted for clarity). Representative interatomic distances [Å] and angles [$^\circ$]: C1–O1 1.2258(13), C1–O2 1.3357(14), C1–O3 1.3048(13), Mo1–O2 2.0674(9), Mo1–O3 2.2191(9), Mo1–O4 1.7351(8), Mo1–O5 1.7390(8), Mo1–O6 1.7436(8); C1–O2–Mo1 97.75(6), C1–O3–Mo1 91.74(7), O6–Mo1–O5 148.75(3), O4–Mo1–O2 120.28(4), O5–Mo1–O2 121.93(4), O4–Mo1–O5 110.10(4), O4–Mo1–O6 105.15(4), O5–Mo1–O6 105.34(4); C1–O3–Mo1–O6 2.09(11), C1–O2–Mo1–O4 75.02(8), C1–O2–Mo1–O5 –71.35(8).
[MoO$_3$(k$^2$-CO$_3$)$_2$]$^{2-}$ due to the trans influence of the oxo ligands (O3–Mo1–O2 152.29(8)$^\circ$, O6–Mo1–O1 152.10(8)$^\circ$, O1–Mo1–O2 18.32(2)$^\circ$, C2–O6–Mo1–O1 27.3(2)$^\circ$). While we were able to find several examples of k$^2$-bound molybdenum carbonates reported in the Cambridge Structural Database,$^{21}$ this is the first example of a molybdenum complex with two k$^2$-carbonates. To the best of our knowledge, [PPN][MoO$_3$(k$^2$-CO$_3$)$_2$] is also the first transition-metal dicarbonate complex obtained directly from CO$_2$.$^{27}$

In order to gain further insight into the energetics and potential energy landscape of this system, we turned to computational methods (Fig. 3). Binding of the first CO$_2$ molecule is exothermic and exergonic with a $\Delta G^\circ$ (298 K) $= -14.2$ kcal mol$^{-1}$ and $\Delta G^\circ$ (298 K) $= -5.2$ kcal mol$^{-1}$. The stability of the [MoO$_3$(k$^2$-CO$_3$)$_2$]$^{2-}$ species is explained by the considerable activation energy of $\Delta G^\ddagger$ (298 K) $= 17.2$ kcal mol$^{-1}$ for regenerating the molybdate dianion with loss of CO$_2$. This is consistent with our inability to remove CO$_2$ under vacuum at room temperature from this material. As expected, binding of the second CO$_2$ is slightly endergonic ($\Delta G^\ddagger$ (298 K) $= 3.2$ kcal mol$^{-1}$), being favored at higher CO$_2$ pressures and lower temperatures as observed in our $^{13}$C-labeling experiments. The possibility of binding a third CO$_2$ molecule was also investigated. However, producing such a species is endergonic with a

$$\Delta G^\ddagger$$ (298 K) $= 14.6$ kcal mol$^{-1}$, as well as $\Delta H^\ddagger > 0$ and $\Delta S^\ddagger < 0$. In contrast to the findings of Mizuno et al., who reported a calculated k$^1$ structure for the related tungstate–CO$_2$ adduct,$^2$ we were unable to locate minima corresponding to k$^1$ structures for any of the molybdenum carbonate complexes studied herein.

Curious to see whether the new molybdenum carbonate complexes can serve as a source of activated CO$_2$, we subjected [PPN][MoO$_3$(k$^2$-CO$_3$)$_2$] to the mild hydride donor triethylsilane, which exhibits no background reactivity with CO$_2$ according to a control experiment.$^{24}$ A test reaction revealed a new resonance at $\delta = 8.73$ ppm ($^1$H NMR spectroscopy), this being located in a region characteristic for formyl protons, as well as a new molybdenum species having a $^{95}$Mo NMR signal at $-23.7$ ppm, a shift essentially identical to that reported for the [Mo$_2$(OSiMe$_3$)$_3$]$_2^-$ ion.$^9$ The production of formate improves from 16% to 71% if the reaction is run under an atmosphere of CO$_2$, raising the question of whether the active species facilitating CO$_2$ reduction is the monocarbonate [MoO$_3$(k$^2$-CO$_3$)$_2$]$^{2-}$ or the dicarbonate complex [MoO$_2$(k$^2$-CO$_3$)$_2$]$^{2-}$. After optimization, clean conversion to [PPN][OCHO] and [PPN][MoO$_2$(OSiEt$_3$)$_2$] (eqn (2)) as the sole products can be obtained after 22 h at 85 Â°C, as evidenced by the $^1$H NMR spectrum of the crude reaction mixture. We were able to isolate [PPN][OCHO] in 69% yield, along with [PPN][MoO$_2$(OSiEt$_3$)$_2$] in 50% yield by taking advantage of their differential solubilities in THF.

$$\text{[PPN][MoO}_3$(k$^2$-CO$_3$)$_2$] + \text{Et}_2\text{SiH} \downarrow \text{[PPN][MoO}_2$(OSiEt$_3$)$_2$] + \text{[PPN][OCHO]} \quad (2)$$

In summary, we have synthesized and characterized two molybdenum oxo carbonate species obtained from the uptake
of CO₂ by the molybdate dianion and begun exploring their reactivity in the context of CO₂ reduction to formate.¹
¹³C-labeling experiments and computational analysis suggest that the first binding event to form [MoO₃(k²-CO₃)₂]²⁻ is irreversible, while the second CO₂ molecule binds in a reversible process. We are currently investigating potential uses of [MoO₄]²⁻ as a nucleophilic catalyst for CO₂ fixation³⁰ (encouraged by the methods already developed using the analogous tungstate dianion),² while also making efforts to develop an improved mechanistic understanding of this rich, yet simple system. This work illustrates the finding that a discrete, soluble molecular metal oxide system unencumbered by organic spectator ligands and unobstructed by hydrogen bonding with water is sufficient for CO₂ activation and conversion to formate in conjunction with a mild hydride source.

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References

7 Sodium molybdate dihydrate (50 mg, 0.2 mmol, 1 equiv.) was dissolved in ca. 0.8 mL D₂O. Carbon dioxide (20 mL, 0.8 mmol, 4 equiv.) was bubbled through this solution, after which it was stirred for 10 min. The ⁹⁵Mo NMR spectrum of the resulting solution showed only the molybdate resonance at δ = 0 ppm and no other species.
21 M. J. Frisch, et al., Gaussian 09, Revision C.01, 2010.
24 Triethylsilane (23 mg, 0.2 mmol) was dissolved in ca. 1 mL CD₃CN and transferred to a Schlenk tube which was brought outside the glovebox. The solution was frozen using liquid nitrogen, the headspace was evacuated and the tube refilled with 1 atm of CO₂. The tube was sealed and heated at 85 °C overnight. The solution was analyzed by ¹H NMR spectroscopy, showing that no reaction had occurred.