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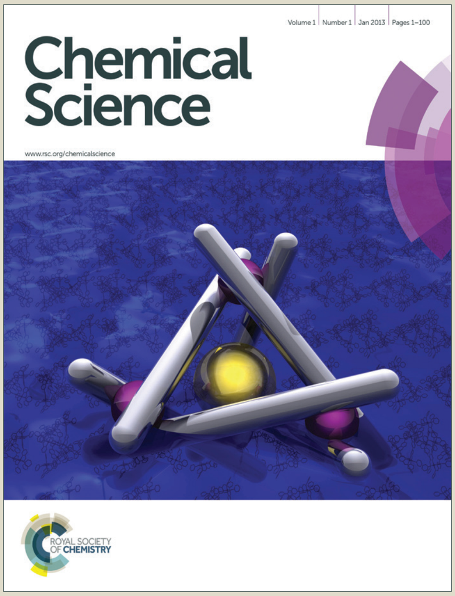

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Uptake of one and two molecules of CO_2 by the molybdate dianion: a soluble, molecular oxide model system for carbon dioxide fixation†‡

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Tetrahedral $[MoO_4]^{2-}$ readily binds CO_2 at room temperature to produce a robust monocarbonate complex, $[MoO_3(\kappa^2\text{-}CO_3)]^{2-}$, that does not release CO_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_2 binds to afford a pseudo-octahedral dioxo dicarbonate complex, $[MoO_2(\kappa^2\text{-}CO_3)_2]^{2-}$, the first structurally characterized transition-metal dicarbonate complex derived from CO_2. The monocarbonate $[MoO_3(\kappa^2\text{-}CO_3)]^{2-}$ reacts with triethylsilane in acetonitrile under an atmosphere of CO_2 to produce formate (69% isolated yield) together with silylated molybdate (quantitative conversion to $[MoO_3(OSiEt_3)]^{-}$, 50% isolated yield) after 22 hours at 85 °C. This system thus illustrates both the reversible binding of CO_2 by a simple transition-metal oxoanion and the ability of the latter molecular metal oxide to facilitate chemical CO_2 reduction.

Metal oxide catalysts for CO_2 transformations are advantageous based on considerations of cost, ease of re-use, and stability,[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_2 in a well-defined manner (e.g., Equation 1),[2–4] 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_2 (the second, reversibly) together with complete characterization including single-crystal X-ray diffraction studies of the resulting mono- and dicarbonate complexes.

$$L_nM{=}O + CO_2 \rightleftharpoons L_nM(CO_3) \qquad (1)$$

As our studies were in progress, it was reported that the related tungstate dianion indeed serves as a homogeneous catalyst for CO_2 fixation,[5] 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_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_2 to formate. The present work follows and improves upon our earlier report of titanium trisanilide oxoanion CO_2 binding[2] 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_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_2 reduction to CO at a niobium nitride binding site; that system represented our initial foray into ligand-based strategies for CO_2 conversion.[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_2 under aqueous conditions (as assessed by ^{95}Mo NMR spectroscopy).[7] In order to endow the molybdate dianion with solubility in organic media, we prepared $[PPN]_2[MoO_4]$ ($PPN^+ = (Ph_3P)_2N^+$) in one step from Ag_2MoO_4 and [PPN]Cl using a modified literature procedure.[8] Upon addition of CO_2 to a 0.04 M acetonitrile solution of $[PPN]_2[MoO_4]$ at room temperature, a new species quickly formed. The ^{95}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

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‡ CCDC 978136, 978137 and 981116 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via *www.ccdc.cam.ac.uk/data_request/cif*

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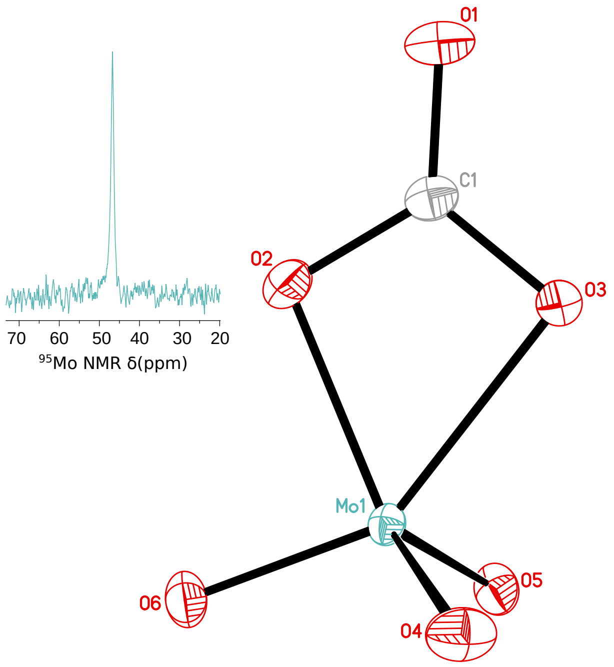

Fig. 1 Left: ^{95}Mo NMR resonance of $[MoO_3(\kappa^2\text{-}CO_3)]^{2-}$. Right: solid-state structure of $[NEt_4]_2[MoO_3(\kappa^2\text{-}CO_3)]$ (ellipsoids at the 50% probability level, cations omitted for clarity). Representative interatomic distances [Å] and angles [°]: C1–O1 1.2258(13), C1–O2 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–O3 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).

of $[Mo_2O_7]^{2-}$ by-product identified by a signal at −3.8 ppm.[9] A new characteristic carbonyl stretch at 1638 cm^{-1} could also be observed by IR spectroscopy.[10]

A preliminary X-ray crystal structure of the CO_2-addition product revealed a κ^2-bound carbonate moiety and enabled us to formulate the major product obtained as $[PPN]_2[MoO_3(\kappa^2\text{-}CO_3)]$. In the interest of obtaining high quality crystallographic data, $[NEt_4]_2[MoO_4]$ (previously reported in the literature and used to prepare examples of well-behaved and crystallographically characterized molybdenum complexes)[11] was used to obtain the $[MoO_3(\kappa^2\text{-}CO_3)]^{2-}$ dianion as its tetraethylammonium salt. Colorless crystals were grown by vapor diffusion of Et_2O into a CH_3CN solution of $[NEt_4]_2[MoO_3(\kappa^2\text{-}CO_3)]$, and the structure obtained in the ensuing crystallographic investigation is shown in Figure 1. The C–O distances are elongated from 1.162 Å in free CO_2[12] 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 $[MoO_4]^{2-}$.[13] 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)° and C1–O3–Mo1–O6 2.09(11)°) 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)°. This κ^2 binding mode is not surprising given the lack of steric bulk around the molybdenum center, in contrast to the arrangement in $[(\kappa^1\text{-}CO_3)TiX_3]^-$ (X = N[^{t}Bu](3,5-$Me_2C_6H_3$)) for which a combination of ancillary ligand steric bulk and external carbonate complexation by an alkali-metal counterion promotes κ^1-binding of $CO_3{}^{2-}$ to the titanium center.[2]

Solid $[PPN]_2[MoO_3(\kappa^2\text{-}CO_3)]$ 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, $[PPN]_2[MoO_3(\kappa^2\text{-}^{13}CO_3)]$ was heated to 56 °C without any observable loss of $^{13}CO_2$ 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 $[PPN]_2[MoO_3(\kappa^2\text{-}CO_3)]$. On the other hand, solid $[NEt_4]_2[MoO_3(\kappa^2\text{-}CO_3)]$ 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 $^{13}CO_2$, $[PPN]_2[MoO_3(\kappa^2\text{-}^{13}CO_3)]$ displays a sharp ^{13}C NMR resonance at 165.7 ppm, this being in a region of the spectrum that is characteristic for carbonates.[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 $[PPN][HCO_3]$[15] to a mixture of $[PPN]_2[MoO_3(\kappa^2\text{-}^{13}CO_3)]$ 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 $[MoO_4]^{2-}$ with $[MoO_3(\kappa^2\text{-}CO_3)]^{2-}$ to yield $[Mo_2O_7]^{2-}$ 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 disap-

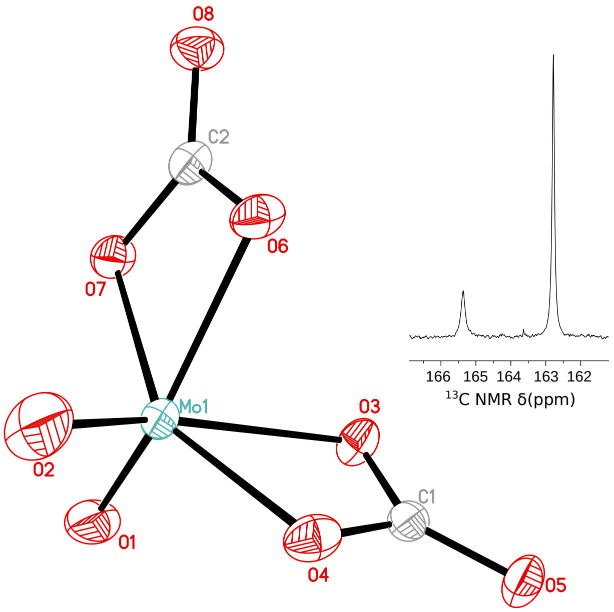

Fig. 2 Right: ^{13}C NMR spectrum showing the distribution of $[MoO_3(\kappa^2\text{-}CO_3)]^{2-}$ (165.4 ppm) and $[MoO_2(\kappa^2\text{-}CO_3)_2]^{2-}$ (162.8 ppm) at −19 °C under 1 atm of $^{13}CO_2$. Left: solid-state structure of $[PPN]_2[MoO_2(\kappa^2\text{-}CO_3)_2]$ (ellipsoids at the 50% probability level, cations and solvent molecules omitted for clarity). Representative interatomic distances [Å] and angles [°]: C1–O3 1.302(4), C1–O4 1.352(4), C1–O5 1.228(4), C2–O6 1.303(3), C2–O7 1.358(3), C2–O8 1.223(3), Mo1–O1 1.695(2), Mo1–O2 1.705(3), Mo1–O3 2.198(2), Mo1–O4 2.024(2), Mo1–O6 2.175(2), Mo1–O7 2.0145(19); O3–C1–O4 110.4(2), O6–C2–O7 109.9(2), O4–Mo1–O7 149.44(6), O3–Mo1–O2 152.29(10), O6–Mo1–O1 152.10(8), O1–Mo1–O2 104.86(18); C1–O3–Mo1–O2 18.3(2), C1–O4–Mo1–O6 −79.04(11), C1–O4–Mo1–O1 80.37(14), C2–O6–Mo1–O1 27.3(2), C2–O7–Mo1–O2 86.70(15), C2–O7–Mo1–O3 −76.00(12).

peared after degassing the sample. The ratio of the unknown species at 162.8 ppm to $[MoO_3(\kappa^2\text{-}^{13}CO_3)]^{2-}$ increases at higher pressure of $^{13}CO_2$ (3 atm), and at lower temperature (−31 °C). These data are indicative of additional reversible binding of $^{13}CO_2$ to the $[MoO_3(\kappa^2\text{-}^{13}CO_3)]^{2-}$ 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_3CN solution of $[PPN]_2[MoO_4]$ under an atmosphere of CO_2. In the solid state, both carbonate ligands are bound κ^2 (Figure 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 $[MoO_3(\kappa^2\text{-}CO_3)]^{2-}$ as the Mo–O π character is shared over fewer centers. The carbonate ligand binding mode is characterized by the same type of asymmetry as seen in $[MoO_3(\kappa^2\text{-}CO_3)]^{2-}$ due to the *trans* influence of the oxo ligands (O3–Mo1–O2 152.29(10)°, O6–Mo1–O1 152.10(8)°, C1–O3–Mo1–O2 18.3(2)°, C2–O6–Mo1–O1 27.3(2)°). While we were able to find several examples of κ^2-bound molybdenum carbonates reported in the Cambridge Structural Database,[16] this is the first example of a molybdenum complex with *two* κ^2-carbonates. To the best of our knowledge, $[PPN]_2[MoO_2(\kappa^2\text{-}CO_3)_2]$ is also the first transition-metal dicarbonate complex obtained directly from CO_2.[17]

In order to gain further insight into the energetics and potential energy landscape of this system, we turned to computational methods (Figure 3). Binding of the first CO_2 molecule is exothermic and exergonic with a $\Delta H°(298\ K) = -14.2$ kcal/mol and $\Delta G°(298\ K) = -5.2$ kcal/mol. The stability of the $[MoO_3(\kappa^2\text{-}CO_3)]^{2-}$ species is explained by the considerable activation energy of $\Delta G^{\ddagger}(298\ K) = 17.2$ kcal/mol 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 ($\Delta G°(298\ K) = 3.2$ kcal/mol), 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 $\Delta G°(298\ K) = 14.6$ kcal/mol, as well as $\Delta H° > 0$ and $\Delta S° < 0$. In contrast to the findings of Mizuno et al. who reported a calculated κ^1 structure for the related tungstate-CO_2

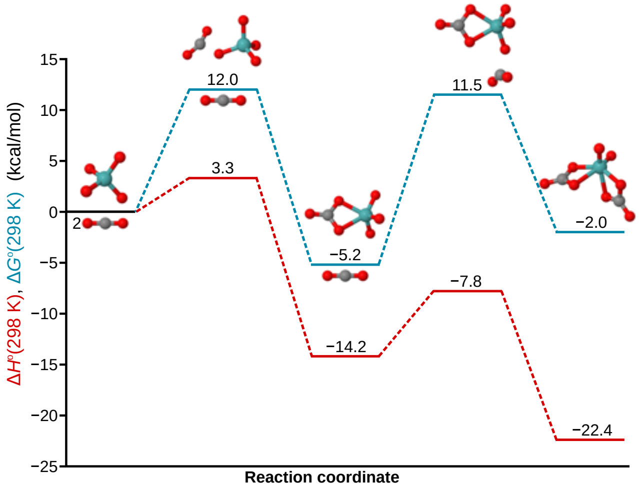

Fig. 3 Combined calculated potential energy diagram for the first and second CO_2 binding events. Electronic structure calculations were carried out using the M06[18] density functional with the Def2-QZVPP[19] basis set for molybdenum, incorporating the SDD[20] effective core potential, and 6-311+G(3df) for all other atoms as implemented in the Gaussian 09 suite of programs.[21] The CPCM model[22] for CH_3CN was used to describe solvation effects, and the final single-point energies were calculated with QCISD(T)[23] at the optimized M06 geometries.

adduct,[5] we were unable to locate minima corresponding to κ^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 $[PPN]_2[MoO_3(\kappa^2\text{-}CO_3)]$ 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 δ = 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 $[MoO_3(OSiMe_3)]^-$ anion.[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 complex $[MoO_3(\kappa^2\text{-}CO_3)]^{2-}$ or the dicarbonate complex $[MoO_2(\kappa^2\text{-}CO_3)_2]^{2-}$. After optimization, clean conversion to [PPN][OCHO] and $[PPN][MoO_3(OSiEt_3)]$ (Equation 2) as the sole products can be obtained after 22 h at 85 °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 $[PPN][MoO_3(OSiEt_3)]$ in 50% yield by taking advantage of their differential solubilities in THF.

$$\begin{array}{c}[PPN]_2[MoO_3(\kappa^2\text{-}CO_3)] + Et_3SiH \\ \downarrow \\ [PPN][MoO_3(OSiEt_3)] + [PPN][OCHO]\end{array} \qquad (2)$$

In summary, we have synthesized and characterized two molybdenum oxo carbonate species obtained from the uptake of CO_2 by the molybdate dianion and begun exploring their reactivity in the context of CO_2 reduction to formate.[25] ^{13}C-labeling experiments and computational analysis suggest that the first binding event to form $[MoO_3(\kappa^2\text{-}CO_3)]^{2-}$ is irreversible, while the second CO_2 molecule binds in a reversible process. We are currently investigating potential uses of $[MoO_4]^{2-}$ as a nucleophilic catalyst for CO_2 fixation[26] (encouraged by the methods already developed using the analogous tungstate dianion),[5] 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 CO_2 activation and conversion to formate in conjunction with a mild hydride source.

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