Table I. Rotational Correlation Times for ^{2}H in AK·AMPPCP Complexes

complex	line width (Hz)	τ_c (ns)
AK·AMPPCD$_2$P	367 ± 15	6.5 ± 0.5[a]
AK·MgAMPPCD$_2$P	660 ± 50	16 ± 1[a]
AK·[8-^{2}H]AMPPCP	1250 ± 150	27 ± 4[a]
AK		75[b]

[a] Calculated from line widths as described in ref 6 and 7. [b] Calculated from the Stokes–Einstein equation assuming that AK is a rigid sphere.[10]

at the same magnetic field (46.1 MHz) and from line width measurements at a different magnetic field (78.7 MHz).

The τ_c values reported in Table I indicate that the adenine ring of bound AMPPCP is motionally rigid[9] and is close to the overall τ_c of AK.[10] The β–γ region of the phosphonate chain possesses considerable local mobility.[9] This motional freedom is greatly reduced upon the binding of Mg^{2+} (ATP and MgATP have been shown[11] to bind to the same site of AK).

While it is difficult to quantitatively dissect the overall AK·ATP binding energy to contributions by the various local segments of ATP/MgATP[2,12] qualitative observations can be made regarding the relationship between local binding energy and local motion. Mg^{2+} appears to make very little contribution to the overall binding energy since MgATP and ATP bind to AK with nearly equivalent affinities, as do MnPPPi and PPPi.[13] However, our ^{2}H NMR results with AMPPCP indicate that Mg^{2+} does induce a significant increase in the τ_c of the phosphate chain.[3] Furthermore, the adenine ring of bound ATP is held rigidly compared to the triphosphate moiety, but the dissociation constant for adenosine binding to the ATP site of AK has been reported to be greater than 20 mM (compared to the value of 0.1 mM for ATP).[14] Thus, it appears that there is no correlation between local substrate dynamics and local binding energy.

Our results suggest the following important points. (a) Thermodynamically "tight" local binding does not necessarily imply local motional rigidity for the bound substrate (and vice versa). (b) Since AK is known to be more specific for ATP in catalysis than in binding (based on the k_{cat} and K_m values of ATP and its analogues)[13,15] and since the adenine ring is rigid at the ground state, the additional binding energy expressed at the transition state should be used primarily to increase the specificity not to rigidize the adenine ring. (c) Binding of Mg^{2+} may serve, among other functions, to immobilize and properly orient the γ-phosphate in preparation for the transition state. (d) Although the relatively large local freedom of the triphosphate moiety of AK·ATP has been revealed qualitatively by ^{31}P NMR (very narrow signals of bound ATP)[16] and ^{17}O NMR (relatively small increases in $\Delta\nu_{1/2}$ upon binding),[17] we have demonstrated that ^{2}H NMR can provide a comparison of relative local motional freedom in a straightforward way.

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(9) Although the τ_c obtained from ^{2}H NMR are only effective values ($1/\tau_{c,eff} = 1/\tau_{c,overall} + 1/\tau_{c,internal}$),[24] differences in $\tau_{c,eff}$ determined for the various species can be used to compare the local, internal dynamics of the different groups since $1/\tau_{c,overall}$ can be assumed to be similar for the three species since it is dictated by protein motion.

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Synthesis and Structural Characterization of a Thiolate Coordination Complex of a Mixed-Valence Mo(V)/Mo(VI) Polyoxomolybdate, $[Mo_{10}O_{28}(SCH_2CH_2O)_2(HOCH_3)_2]^{4-}$, and of Its Decomposition Product $[Mo_4O_6(SCH_2CH_2O)_5]^{2-}$

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Coordination compounds of isopolyoxomolybdate anions are of fundamental chemical interest as models for the interactions of substrates with metal oxide surfaces.[1] As a consequence of the development of polyoxoanions soluble in organic solvents, the synthetic chemistry of isopolyoxomolybdates has been extended beyond Bronsted acid-base chemistry to include a variety of complexes incorporating oxygen-[2-7] or nitrogen-containing[8-15] organic ligands. However, the coordination chemistry of polyoxometalates in general with sulfur-containing ligands remains undeveloped,[16] with the exceptions of a number of sulfido-polyoxometalate species[17,18] and a single example of a polyoxomolybdate ligated to an organodisulfide group.[19]

The notable absence of thiolate-containing isopolymolybdate

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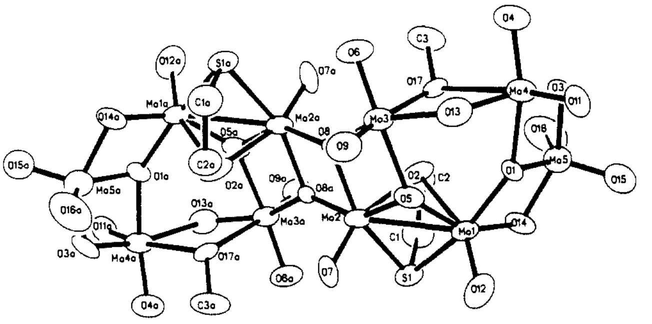

Figure 1. ORTEP view of the structure of $[Mo_{10}O_{28}(SCH_2CH_2O)_2(HOCH_3)_2]^{4-}$ (I), showing the atom-labeling scheme. Selected bond lengths (Å) and angles (°) are as follows: Mol–S1, 2.495 (1); Mol–O1, 1.978 (3); Mol–O2, 2.287 (3); Mo2–S1, 2.467 (1); Mol–O2, 2.199 (4); Mo2–O8, 2.011 (3); Mo3–O8, 2.055 (3); Mo3–O13, 1.858 (4); Mo3–O17, 2.555 (4); Mo4–O13, 1.951 (4); Mo4–O17, 2.569 (4); Mo5–O1, 2.059 (4); Mol–Mo2, 2.693 (1); S1–Mol–O14, 133.1 (1); S2–Mo2–O8, 113.0 (1); O3–Mo5–O14, 146.5 (2); O1–Mo5–O16, 136.2 (2). Average molybdenum–oxo distances: Mo–O(terminal), 1.676 (8); Mo–O(doubly bridging), 1.924 (8); Mo–O(triply bridging), 2.042 (9).

species is a consequence of the tendency of thiolate ligands to reduce Mo(VI) to Mo(V) to yield thiolate-bridged oligomers of Mo(V), under the reaction conditions of large excess of thiolate to the $[MoO_4]^{2-}$ precursor generally employed. However, in the course of our investigations of the chemistry of methanolic solutions of isopolymolybdate anions, we have found that under appropriate conditions thiolate complexes of mixed valence Mo(V)/Mo(VI) polyoxomolybdate anions may be isolated. In this paper, we describe the synthesis and structural characterization of the decanuclear polyoxomolybdate complex $(NBu_4)_4[Mo_{10}O_{28}(SCH_2CH_2O)_2(HOCH_3)_2]\cdot 2CH_3OH$ (I) and the tetranuclear molybdenum(V)-oxo species $(NBu_4)_2[Mo_4O_6(SCH_2CH_2O)_5]$ (II), isolated by acid decomposition of I.

Reaction of 1 equiv of $(NBu_4)_4[Mo_8O_{26}]$[20] with 2 equiv of 2-mercaptoethanol in rigorously dried and degassed methanol yields a bright yellow solution from which large yellow rhomboids of $(NBu_4)_4[Mo_{10}O_{28}(SCH_2CH_2O)_2(HOCH_3)_2]\cdot 2CH_3OH$ (I) crystallize upon standing for 3 weeks. The complexity of the infrared spectrum in the 750–950-cm^{-1} region indicated a number of unique terminal and bridging molybdenum–oxo units, while the elemental analysis confirmed the presence of the thiolate group in a ratio of 1 ligand to 5 Mo centers.[21]

The structure of I, illustrated in Figure 1, is seen to consist of discrete decanuclear anionic units $[Mo_{10}O_{28}(SCH_2CH_2O)_2(HOCH_3)_2]^{4-}$, with a center of symmetry at the midpoint of the Mo2–Mo2a vector relating the crystallographically unique halves of the tetraanion. The structure is a unique example of a polyoxomolybdate incorporating a thiolate ligand and presents a number of unusual structural features.

The Mo centers coordinated to the mercaptoethanolate ligands are clearly identified as reduced Mo(V), exhibiting a short Mol–Mo2 distance of 2.693 (1) Å and the triply bridged geometry through S1 and O2 of the mercaptoethanolate ligand and oxo group O5, characteristic of binuclear Mo(V) species.[22,23] Although a variety of mixed-valence isopolyoxomolybdate and heteropolyoxomolybdate anions have been structurally characterized,[24,25] electron delocalization in these species prevents assignment of unique Mo(V) centers. Ligand coordination in I localizes the reduced centers to the metal–thiolate coordination sites, as might be anticipated. The complex may thus be described as a class I mixed-valence compound with coupled binuclear Mo(V) centers.[26]

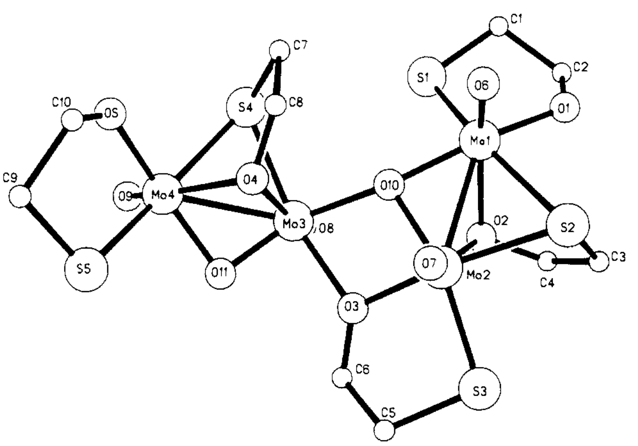

Figure 2. ORTEP view of the structure of $[Mo_4O_6(SCH_2CH_2O)_5]^{2-}$ (II), showing the atom-labeling scheme. Selected bond lengths (Å) and angles (deg) are as follows: Mol–Mo2, 2.681 (1); Mo3–Mo4, 2.640 (1); Mo2–Mo3, 3.110 (1); Mol–S1, 2.304 (3); Mo–S2, 2.526 (2); Mol–O1, 2.099 (5); Mol–O2, 2.206 (5); Mo2–S2, 2.460 (2); Mo2–3, 2.391 (2); Mo2–O3, 2.053 (5); Mo3–S4, 2.470 (2); Mo3–O3, 2.146 (5); Mo3–O4, 2.180 (4); Mo4–54, 2.496 (2); Mo4–S5, 2.431 (2)′; Mo4–O4, 2.246 (4); Mo4–O5, 2.020 (5); S1–Mol–O1, 81.4 (1); S2–Mol–O2, 69.0 (1); S2–Mo2–O2, 70.9 (1); S3–Mo2–O3, 80.4 (1); S4–Mo3–O4, 70.4 (1); S4–Mo4–O4, 68.9 (1); S5–Mo4–O5, 95.5 (1). Average molybdenum–oxo distances: Mo–O(terminal), 1.669 (10); Mo–O(doubly bridging), Mo–O(doubly bridging), 1.868 (8); Mo–O(triply bridging), 2.027 (10).

Although a number of the "conventional" molybdenum–oxo sites display $[MoO_6]$ coordination geometry, the Mo5 and Mo5a centers exhibit five coordinate pseudosquare-pyramidal geometry, an unusual feature in polyoxomolybdate structural chemistry. Furthermore, the $[MoO_6]$ centers, Mo3, Mo4, Mo3a, and Mo4a, incorporate bridging methanol ligands, whose identity is confirmed by the unusually long Mo–O17 distances (2.56 Å, av) and the charge requirements of the cluster. The Mo–O(methanol) distances may be compared to Mo–O(methoxy) bridge distances in similar complexes of 2.10–2.20 Å.

The isolation of complex I depends critically upon reaction conditions and stoichiometry. Addition of excess ligand yields exclusively the triply-bridged binuclear species $(NBu_4)[Mo_2O_2(SCH_2CH_2O)_3(SCH_2CH_2OH)]$, while an insufficient amount of ligand precludes the required reduction to the Mo(V) state followed by complexation of the ligand equivalents not consumed in disulfide formation. In effect, the synthesis of I exploits the ability of $[Mo_xO_y]^{n-}$ units to function as chelating ligands and to aggregate in methanolic solution so as to bridge the pair of $[Mo_2O_3(SCH_2CH_2O)]^{2+}$ fragments.

A common feature of the coordination complexes of polyoxomolybdates is the presence of weak Mo-bridging oxo-group interactions, allowing the extrusion of the Mo ligand core from the polyoxomolybdate framework.[27] Thus, treatment of I with a small amount of chloroacetic acid in methanol, in the presence of 2 equiv of mercaptoethanol, yielded clear orange crystals of $(NBu_4)_2[Mo_4O_6(SCH_2CH_2O)_5]$ (II), whose structure is shown in Figure 2.[28] The tetranuclear dianion consists of two triple-bridged $[Mo_2O_3(SCH_2CH_2O)_2]^0$ units, sharing an edge defined by O3 of

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a mercaptoethanolate ligand and the triply bridging O10. The most unusual feature of the structure is the presence of three distinct ligand geometries for the mercaptoethanolate groups: two terminal chelating, two doubly bridging through both the sulfur and oxygen donors, and one with a terminal sulfur donor and a doubly bridging oxygen donor. Further treatment of II with acid or recrystallization from wet methanol yields the binuclear species $(NBu_4)_4[Mo_2O_2(SCH_2CH_2O_3)(SCH_2CH_2OH)]$.[23]

The characterization of complexes I and II further demonstrates the ability of polyoxomolybdates to undergo chemical transformations characteristic of metal–ligand coordination chemistry[1] and suggests a rich and previously unsuspected molybdenum–oxo–thiolate cluster chemistry.

Acknowledgment. This research was supported by a grant from the National Science Foundation (CHE 8514634).

Supplementary Material Available: Tables of atomic positions, bond lengths and angles, anisotropic temperature factors, and calculated hydrogen atom positions for I and II (12 pages). Ordering information is given on any current masthead page.

A Novel n-Doped Metallomacrocyclic Conductor

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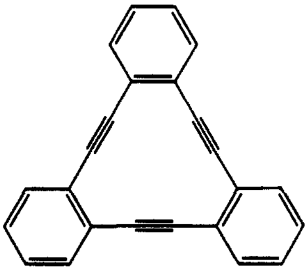
We have previously reported the synthesis of a Ni(0) macrocyclic complex (Ni(TBC))[1] in which the nickel atom resides in the cavity of the 12-membered ring of TBC[2] equally bound to all three alkynes. We now report the reduction of Ni(TBC) and the preparation of an n-doped metallomacrocycle conductor based upon Ni(TBC). Metallomacrocycles based on porphyrin and phthalocyanine type ligands have been studied as precursors for one-dimensional conductors.[3] The ligands of these molecules are planar, have an extended π-system, bind the metal through relatively hard nitrogen atoms, and have a formal negative charge. The resultant metallomacrocycle contains the metal in a positive oxidation state. The properties of Ni(TBC) parallel and contrast those of the nitrogen-based metallomacrocycles. The TBC ligand is also planar and has an extended π-system; however, TBC is neutral and can bind a metal via three soft, polarizable alkyne donors.[1,4] This allows the formation of complexes with a formal zero oxidation state for the metal.



TBC

The slipped stack arrangement of Ni(TBC)[1] is similar to that observed in TTF, TCNQ, and unoxidized Ni(Pc) (Pc = phthalocyanato).[5,3a] Oxidative doping of nickel phthalocyanine results in metal-over-metal stacking.[3a] Experiments on doping Ni(TBC) with iodine give decomposition of the complex yielding TBC and probably NiI_2. The cyclic voltammetry of Ni(TBC) in THF shows two consecutive quasi-reversible waves at strongly reducing potentials which suggests the consecutive formation of a monoanion and a dianion. An oxidizing potential gives decomposition, consistent with the experiments with I_2.[6] The monoanion and the dianion are formed when Ni(TBC) is reduced with lithium, sodium, or potassium. As with the stoichiometric reductions of transition-metal alkene and alkyne complexes,[7] solvated complexes are produced in these solution phase reductions. Without the aid of chelating agents for the alkali metal cation the solids are unstable, especially to dissolution. Several combinations of alkali metals and sequestering agents have been examined. Cryptand-(2.2.2) (C222) with potassium in THF gives the best yields of the dianion.[8] The reduction of Ni(TBC) is sequential. Formation of the red-brown dianion from blue Ni(TBC) occurs via formation of the intermediate purple monoanion. A trace of the monoanion is usually present in the dianion. The alkyne stretching frequency in the IR spectrum decreases from 1983 and 1957 cm^{-1} for Ni(TBC) (C_s symmetry in the solid state) to 1873 and 1834 cm^{-1} for the monoanion and dianion, respectively. The monoanion is EPR active (seven line spectra with $g_{iso} = 2.001$, $a_{iso} = 1.28$ G), consistent with a planar monoanion. The diamagnetic dianion shows an NMR spectrum similar in pattern but slightly shifted downfield from that of Ni(TBC).[1]

By combining Ni(TBC) and Ni(TBC)$^{2-}$ in various ratios n-doped Ni(TBC) has been obtained.[9] A two probe powder conductivity study of the resultant powders gave a conductivity of 2×10^{-3} (Ω-cm)$^{-1}$ at 0.5 e$^-$/Ni(TBC) (1:3 ratio of Ni(TBC)$^{2-}$ to Ni(TBC)). A plot of conductivity versus number of electrons per Ni(TBC) is shown in Figure 1. The insulator Ni(TBC) becomes conducting upon partial reduction. Upon further reduction the conductivity again decreases. The results set a lower limit to the conductivity of n-doped Ni(TBC) since measurements by two-probe powder compaction methods typically yield values that are 10^2–10^3 smaller than the corresponding four-probe values.[10] We have examined only a limited number of doping levels and have not determined the ideal doping level. The intensity of the $C\equiv C$ band for Ni(TBC) decreases monotonically with in-

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(8) Reduction of Ni(TBC) with potassium and cryptand(C222): rigorous air sensitive procedures were used throughout.[12] A mixture of Ni(TBC) (2.78×10^{-4} mol), C222 (5.58×10^{-4} mol), potassium (6.90×10^{-4} mol), and THF (70 mL) was stirred for 24 h. The mixture was filtered and concentrated to 3–4 mL. The precipitate was washed with THF and dried in vacuo: yield 0.252 g (76%) of a black-brown solid, $[K(C222)]_2[Ni(TBC)]$; IR (Nujol) 1873 w, 1834 ms.

(9) Doping of Ni(TBC) with $[K(C222)]_2[Ni(TBC)]$: the quantities of Ni(TBC) and $[K(C222)]_2[Ni(TBC)]$ used were calculated based on ~50 mg of doped Ni(TBC). The mixture of solids was dissolved in 20 mL THF and stirred for 10–15 min, and THF was removed in vacuo at room temperature. Each sample was measured for conductivity and an IR (Nujol) spectrum recorded. A control sample of only $[K(C222)]_2[Ni(TBC)]$ indicated slight decomposition when treated as above.

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