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Synthesis and Characterization of $Mo_4Te_{16}(en)_4{}^{2-}$: A Molybdenum Telluride with Linked $Mo{\equiv}Mo^{6+}$ Subunits

Sir:

In contrast to the large number of discrete, metal-containing polysulfide complexes known,[1] there are few characterized transition-metal polytelluride complexes.[2-5] We have recently found that the ethylenediamine (en) extraction of certain ternary melts of composition $(M^1)_x(M^2)_yTe_z$ [M^1 = alkali metal, M^2 = Hg, Au, As] provides a convenient preparative route to a variety of structurally diverse polytelluride clusters and polymers such as $Hg_4Te_{12}{}^{4-}$,[6] $^{1}_{\infty}[Hg_2Te_5{}^{2-}]$,[6] $^{1}_{\infty}[K_2Au_4Te_4{}^{2-}\cdot 4solvent]$,[7] $KAu_9Te_7{}^{4-}$,[7] $Au_2Te_4{}^{2-}$,[8] and $As_{10}Te_3{}^{2-}$.[9] These compounds have no analogues in sulfur or selenium chemistry, suggesting that the transition-metal polytelluride systems may also be quite different from those of the other chalcogens. The solubility of polytelluride ions[10-12] such as $Te_5{}^{2-}$, $Te_4{}^{2-}$, and $Te_3{}^{2-}$ in en and DMF presents an attractive entry into transition-metal tellurium solution chemistry. The potential of this method is best illustrated by Kolis and co-workers' recent report[4] of $NbTe_{10}{}^{3-}$, formed in the reaction between $NbCl_5$ and polytelluride anions in DMF, in which the Nb atom is encapsulated in a "birdcage-like" Te sheath. We report here the synthesis and structural characterization of the unusual $Mo_4Te_{16}(en)_4{}^{2-}$ ion comprising two d^3–d^3 $Mo_2{}^{6+}$ subunits linked by a central $Te_2{}^{2-}$ ligand and two $Te_3{}^{2-}$ chains. These compounds, together with $[RbNbAs_8{}^{2-}]$[13] and $Sn_9Cr(CO)_3{}^{4-}$,[14] represent a new class of main-group cluster anions, namely those containing transition metals.

The reaction of 2–3 equiv of K_2Te_4 with $Mo_2(O_2CMe)_4$ in en results in the formation of black, crystalline $[K(crypt)]_2Mo_4Te_{16}(en)_4$ (**1**) in which all the acetate groups are replaced and the Mo_2 units are retained, albeit with changes of oxidation state and internuclear distance.[15] The best yield (ca. 40%) and product purity are obtained when 2.2 equiv of K_2Te_4 is used, although a balanced equation cannot be written under these conditions. The crystalline product will not redissolve in en or MeOH.

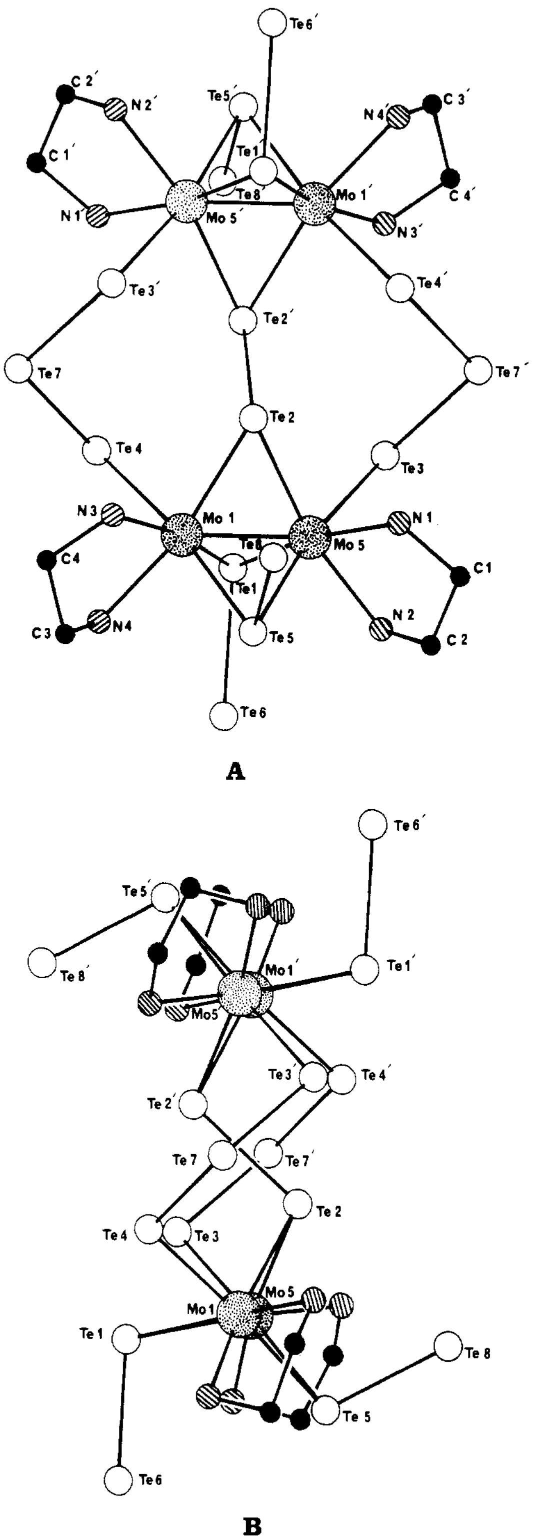

Figure 1. Two ball-and-stick representations of the $Mo_4Te_{16}(en)_4{}^{2-}$ ion: (A) front view showing the central Mo_4Te_2 core and the connectivity of the $Te_3{}^{2-}$ chains; (B) side view down the Mo–Mo bonds showing the conformation of the $Te_2{}^{2-}$ fragments relative to the M–M vectors.

The structure[16] of the anion in **1** (Figure 1) consists of two confacial bioctahedral d^3–d^3 $Mo_2{}^{6+}$ units with Mo–Mo bond distances of 2.469 (3) Å. Each Mo_2 dimer possesses two μ_2,η^1-$Te_2{}^{2-}$ ligands and two chelating en ligands. The two Mo_2

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(15) An en solution of $Mo_2(O_2CMe)_4$ was added dropwise to an en extract of a melt of nominal composition K_2Te_4. The purple color of the polytelluride solution turned dirty maroon-brown during the addition, and copious amounts of white precipitate were formed. The reaction mixture was stirred for 45 min and filtered. One equivalent of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (crypt) was added to each mole of K_2Te_4. Dark, well-formed crystals of **1** precipitated from solution after ≈24 h and were washed with en. Anal. Calcd for $K_2Mo_4C_{44}H_{104}N_{12}O_{12}Te_{16}$: C, 15.11; H, 3.00; N, 4.81; Mo, 10.97; Te, 58.38. Found: C, 14.42; H, 2.87; N, 4.83; Mo, 12.39; Te, 53.42.

(16) Crystal data for **1**: space group $P2_1/c$, with a = 15.720 (4) Å, b = 23.400 (4) Å, c = 12.955 (4) Å, β = 97.29 (2)°, V = 4726 (1) Å^3, and Z = 4. Final R values are R = 0.0397 and R_w = 0.0455.

fragments are joined by a common $\mu_2,\eta^1,\mu_2,\eta^1$-$Te_2^{2-}$ ligand and two Te_3^{2-} chains. The tetramolybdenum anion has virtual C_{2h} symmetry with a crystallographically imposed inversion center. The Te–Te distances of 2.74–2.84 Å are typical for single bonds [Te–Te distances in Te_4^{2-}·2MeOH are 2.76 (1) and 2.72 (1) Å;[11] elemental Te has a Te–Te contacts of 2.84 Å[17]] with the Te(2)–Te(2′) distance being the longest, 2.841 (2) Å. The Mo–Te bond distances range between 2.693 (2) and 2.796 (3) Å with the shortest being the Mo–Te(2) contacts.

The Mo–Mo distance in **1** is surprisingly short when compared with those in other face-sharing bioctahedral Mo_2^{III} species. Several studies[18] of $Mo_2Cl_9^{3-}$ salts with different cations have shown that the Mo–Mo distance is quite variable, ranging from 2.52 to 2.82 Å in 10 different compounds. Nonetheless, all of these are longer than the value found here. In five $Mo_2Br_9^{3-}$ compounds[18b] the Mo–Mo distance ranged from 2.57 to 3.12 Å, and in $Cs_3Mo_2I_9$ it is 3.07 Å. Since the telluride ions forming the bridges in these cases are more similar in size to I^- than to Cl^- or Br^-, the occurrence of such a short Mo–Mo distance is of even greater interest. However, the comparison of halide-bridged and chalcogen-bridged species may be misleading, if we note that in the $(Me_2S)Cl_2Mo(\mu\text{-}Cl)_2(\mu\text{-}Me_2S)MoCl_2(Me_2S)$ molecule the Mo–Mo distance, 2.462 (2) Å, is nearly 0.3 Å shorter than it is in the $[(Me_2S)Cl_2Mo(\mu\text{-}Cl)_3MoCl_2(Me_2S)]^-$ ion, 2.746 (9) Å.[19]

It is interesting to note that **1** is composed of Te_2^{2-} and Te_3^{2-} fragments when the polytelluride source was an extract of a melt of nominal composition K_2Te_4. Kolis and co-workers have shown that $M(Te_4)(CO)_4^{2-}$ [where M = Cr, Mo, W] could be synthesized from various polytelluride sources [Te_x^{2-} where x = 2, 3, or 4] under identical reaction conditions.[3] Presumably, a complex equilibrium of Te_x^{n-} species is established in solution[20] thus allowing the substrate to "choose" a telluride ion of a desired chain length. This phenomenon has been observed in the polysulfide and polyselenide systems[21] and is likely to be a recurring theme in polytelluride solution chemistry.

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Supplementary Material Available: Tables of crystal data, positional parameters, general displacement parameters, bond distances, and bond angles and an ORTEP drawing of the $[K(crypt)]^+$ ion (11 pages); a table of structure factors (14 pages). Ordering information is given on any current masthead page.

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Articles

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Novel C-2 Epimerization of Aldoses Promoted by Nickel(II) Diamine Complexes, Involving a Stereospecific Pinacol-Type 1,2-Carbon Shift

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The newly discovered C-2 epimerization of aldoses promoted by nickel(II) diamine complexes has been investigated in detail by using ^{13}C-enriched D-glucose, ^{13}C NMR spectroscopy, and EXAFS (extended X-ray absorption fine structure) analysis. Aldoses treated with nickel(II) diamine complexes (diamine = *N,N,N′*-trimethylethylenediamine (*N,N,N′*-Me_3en), *N,N,N′,N′*-tetramethylethylenediamine (*N,N,N′,N′*-Me_4en), etc.) in methanolic solutions were rapidly (60 °C, 3–5 min) epimerized at C-2 to give equilibrium mixtures where the ratio of C-2 epimers shifts to the side of the naturally rare mannose-type aldoses (having the cis arrangement of C-2 and C-3 hydroxyl groups) compared with those in the thermodynamic equilibrium states. The epimerization product of D-[1-^{13}C]glucose was exclusively D-[2-^{13}C]mannose, demonstrating that the reaction involves a stereospecific 1,2-shift of the carbon skeleton resulting in inversion of configuration at C-2. Furthermore, the absorption and circular dichroism spectra of the reaction solutions indicated the presence of an intermediate nickel(II) complex containing both diamine and sugar components, which was directly revealed by EXAFS analysis to be a mononuclear nickel(II) complex having octahedral coordination geometry. All these observations strongly suggest that the C-2 epimerization proceeds through an intermediate mononuclear nickel(II) complex, where the carbinolamine-like adduct of aldose with diamine in an open-chain form is epimerized at C-2 by a stereospecific rearrangement of the carbon skeleton or a pinacol-type rearrangement involving a cyclic transition state.

Introduction

Effective synthetic procedures for naturally rare carbohydrates are highly desirable in the fields of biochemistry and medicinal chemistry, and it is important to develop methods whereby metals promote transformation of sugars in bioinorganic chemistry. In a series of reports, Bilik et al. have shown that, in mildly acidic solutions of molybdate, aldoses epimerize at C-2 with the formation of a thermodynamic equilibrium mixture of the two epimers.[2-8]

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