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Hydrothermal Synthesis of a New Molybdenum Hollandite Containing Tetranuclear Metal Atom Clusters. X-ray Crystal Structure of $K_2Mo_8O_{16}$

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Hydrothermal reaction of KOH/K_2MoO_4 solutions with molybdenum metal at 500–700 °C (3 kbar) gives black, columnar crystals of $K_2Mo_8O_{16}$. The tunnellike structure of this new compound is closely related to the mineral hollandite, $BaMn_8O_{16}$. Monoclinic lattice parameters for $K_2Mo_8O_{16}$ are a = 10.232 (3) Å, b = 10.286 (4) Å, c = 5.758 (1) Å, and γ = 90.14 (3)° in space group $P2/n$. Single-crystal X-ray data have shown this phase to be essentially isostructural with $Ba_{1.14}Mo_8O_{16}$. The structure displays two types of infinite chains built from Mo_4O_{16} groups via the sharing of oxygen atoms. Molybdenum–molybdenum bond lengths indicate different electron occupations for the orbitals of the planar Mo_4 groups in the two kinds of Mo_4O_{16} clusters. The possible role of Mo–O π bonding within the clusters is discussed.

Introduction

Recently, there has been an increasing interest in solid-state compounds containing discrete transition-metal atom clusters and condensed transition-metal atom clusters that form chain and sheet structures. A large fraction of these compounds exists in sulfur, selenium, tellurium, and halogen systems.[2,3] However, discrete and condensed clusters in *oxide* systems are relatively few in number. Dimeric molybdenum atom units are found in rutile-related MoO_2.[4] Triangular molybdenum atom clusters are present as Mo_3O_{13} moieties in the compounds $A^{II}_2Mo_3O_8$ (A = Mg, Mn, Fe, Co, Ni, Zn, Cd),[5] $LiRMo_3O_8$ (R = Sc, Y, In, Sm, Gd, Tb, Dy, Ho, Er, Yb),[6] and the recently synthesized $LiZn_2Mo_3O_8$,[7] $ScZnMo_3O_8$,[7] and $Zn_3Mo_3O_8$.[7] Tetranuclear metal atom clusters in an oxide were first found in $Ba_{1.14}Mo_8O_{16}$.[8] This hollandite-related phase displays two types of discrete planar Mo_4 units differing in the number of cluster bonding electrons and resulting Mo–Mo bond distances. The only oxide compound reported to contain discrete octahedral metal atom clusters is $Mg_3Nb_6O_{11}$.[9] Condensed cluster arrangements have been recently reported for the oxides $NaMo_4O_6$,[10] $Ba_{0.62}Mo_4O_6$,[8] $Sc_{0.75}Zn_{1.25}Mo_4O_7$,[11] and $Ti_{0.5}Zn_{1.5}Mo_4O_7$.[11] These compounds all contain infinite chains of edge-sharing molybdenum atom octahedra but differ in the manner in which the chains are interconnected and in the number of electrons available to the chains for Mo–Mo bonding.

All of the oxides above were prepared at high temperatures (>1000 °C) in sealed containers of fused quartz or molybdenum. We have investigated the use of hydrothermal techniques in the synthesis of low-valent molybdenum oxides and have prepared several new phases. Two of these, M_xMoO_2 (M = Li, Na; $x \sim 0.5$), have a layered monoclinic structure related to $NaFeO_2$ (rock salt superstructure) and will be discussed at another time. This paper describes the synthesis, single-crystal structure, and bonding of the new compound $K_2Mo_8O_{16}$. It is the second example of an oxide containing tetranuclear metal atom clusters and is another example of a hollandite-type tunnel structure. This phase is essentially isostructural with $Ba_{1.14}Mo_8O_{16}$ but displays Mo–Mo bond lengths that indicate different electron occupations for the metal atom cluster orbitals.

The crystal structure of the mineral hollandite, $BaMn_8O_{16}$,[12] and related phases[13] consists of an octahedral framework forming large channels parallel with the c axis in which large cations (e.g., K^+, Rb^+, Cs^+, Ba^{2+}) reside. A synthetic hollandite, $BaAl_2Ti_6O_{16}$, is one of the phases in SYNROC, a synthetic rock developed for the immobilization of radioactive wastes.[14] Nonstoichiometric phases can be prepared such as $Ba_x(Ti_{8-x}Mg_x)O_{16}$[15] with $0.80 < x < 1.33$, which exhibit incommensurate superlattice ordering of the tunnel cations. Superlattice formation is often indicated by partial occupation and disorder of the large cations in the tunnel sites of the subcell. Such a situation was observed in $Ba_{1.14}Mo_8O_{16}$. When all tunnel sites are fully occupied, no large-cation superlattice is observed. This appears to be the case for the group 6A hollandites $K_2Mo_8O_{16}$, reported in this paper, and $M_2Cr_8O_{16}$ (M = K, Rb).[16,17] However, the chromium hollandites display no metal–metal bonding, with the shortest Cr–Cr distances being 2.94 Å.

Experimental Section

Synthesis. Hydrothermal reaction of KOH/K_2MoO_4 solutions (molar ratio 0 to 3.4) with Mo metal at 500–700 °C (3 kbar) gives black, columnar crystals of $K_2Mo_8O_{16}$. A typical charge would consist of MoO_3 (4 mmol), Mo foil (5 mmol), and 1.5 mL of 11.3 M KOH solution (17 mmol) in a sealed gold tube. Reactions were heated for 12–16 h and then quenched or slowly cooled (25°/h) to 300 °C. The crystalline product was washed with distilled water, rinsed with acetone, and dried in air. Stoichiometry was established from single-crystal X-ray diffraction data.

X-ray Structure Determination.[18] A single crystal of $K_2Mo_8O_{16}$ in the form of a thin needle with dimensions 0.014 × 0.016 × 0.330 mm was mounted with its long dimension parallel with the φ axis on an Enraf-Nonius CAD4 X-ray diffractometer equipped with monochromatic Mo Kα radiation. After careful crystal alignment, 25 diffraction maxima were located and used to obtain cell parameters and an orientation matrix. The reflections indexed in a monoclinic

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Table I. Positional Parameters for the Atoms of $K_2Mo_8O_{16}$[a]

atom	*x*	*y*	*z*
Mo1	0.1021 (1)	0.9207 (1)	0.8455 (2)
Mo2	0.0825 (1)	0.9273 (1)	0.4015 (2)
Mo3	0.5767 (1)	0.0994 (1)	0.8351 (2)
Mo4	0.4301 (1)	0.9196 (1)	0.6144 (2)
K1	0.7500	0.7500	0.6437 (10)
K2	0.7500	0.7500	0.1290 (10)
O1	0.1165 (10)	0.0795 (9)	0.6217 (19)
O2	0.0941 (10)	0.0535 (10)	0.1170 (20)
O3	0.0818 (9)	0.7798 (9)	0.6246 (19)
O4	0.5817 (10)	0.2896 (10)	0.8794 (19)
O5	0.4192 (10)	0.1183 (10)	0.6133 (20)
O6	0.5572 (10)	0.9036 (10)	0.8839 (20)
O7	0.7189 (10)	0.0827 (10)	0.6157 (19)
O8	0.2878 (9)	0.9178 (10)	0.8845 (19)

[a] Space group *P*2/*n* (*c* unique).

Table II. Comparison of Bond Distances (Å) within the Cluster Units of $K_2Mo_8O_{16}$ and $Ba_{1.14}Mo_8O_{16}$

	$K_2Mo_8O_{16}$		$Ba_{1.14}Mo_8O_{16}$[a]	
atoms[b]	regular clusters	distorted clusters	regular clusters	distorted clusters
Mo1-Mo2	2.697 (2)	2.837 (2)	2.616 (1)	2.847 (1)
Mo1-Mo2′	2.596 (2)	2.565 (2)	2.578 (1)	2.546 (1)
Mo2-Mo2′	2.551 (3)	2.527 (3)	2.578 (1)	2.560 (1)
Mo1-O1	2.066 (11)	2.086 (11)	2.079 (6)	2.082 (6)
Mo1-O2	2.043 (10)	2.037 (10)	2.034 (6)	2.046 (6)
Mo1-O2′	2.121 (11)	2.078 (11)	2.095 (6)	2.104 (6)
Mo1-O3	1.935 (11)	1.939 (10)	1.936 (6)	1.931 (6)
Mo1-O4	2.135 (10)	2.090 (11)	2.143 (6)	2.079 (6)
Mo1-O8	1.974 (10)	1.914 (10)	2.022 (6)	1.894 (6)
Mo2-O1	2.047 (10)	2.042 (10)	2.053 (6)	2.051 (6)
Mo2-O1′	2.062 (11)	2.044 (10)	2.053 (6)	2.038 (6)
Mo2-O2	2.032 (11)	2.093 (11)	2.055 (6)	2.062 (6)
Mo2-O3	2.020 (11)	1.988 (10)	2.023 (6)	2.003 (6)
Mo2-O4	2.130 (11)	2.150 (11)	2.128 (6)	2.119 (6)
Mo2-O7	2.055 (10)	2.037 (10)	2.043 (6)	2.030 (6)

[a] From ref 8 and 19. [b] Atomic labels refer to Figure 3.

cell with dimensions $a = 10.232$ (3) Å, $b = 10.286$ (4) Å, $c = 5.758$ (1) Å, and $\gamma = 90.14$ (3)°. For $Z = 2$, the calculated density is 6.04 g/cm³.

A total of 1651 reflections were collected at ambient temperature by the ω mode from $2 \leq \theta \leq 27.5°$ and merged to yield 1194 independent data with $I \geq 2\sigma(I)$ in $2/m$ symmetry. The data were treated in the usual fashion for Lorentz and polarization effects. An absorption correction ($\mu = 86.0$ cm^{-1}) was not necessary because the fluctuation in a ψ scan for the crystal varied less than 1% (calculated transmission factors ranged from 0.87 to 0.89). There was no evidence of radiation damage during the data collection.

An examination of the data revealed systematic absences compatible with the space group *P*2/*n* (*c* unique). The structure was determined by using the heavy-atom Patterson method. Molybdenum and potassium atoms were refined with anisotropic thermal parameters, and oxygen atoms were refined isotropically. Full-matrix least-squares refinement on all positional and thermal parameters including terms for anomalous dispersion for Mo and K, anisotropic extinction, and potassium occupation converged with $R = 0.057$ and $R_w = 0.060$ where $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ with w proportional to $1/[\sigma^2(I) + (0.02I)^2]$. The potassium ion occupation factor refined to a value of 0.48 (1) (i.e., $K_{1.92(4)}Mo_8O_{16}$). No superlattice layer lines were observed from Weissenberg oscillation photographs of the *c* axis.

Structure Description

Final positional parameters are given in Table I, and important interatomic distances are listed in Table II.

The structure of $K_2Mo_8O_{16}$ consists of double strings of edge-sharing MoO_6 octahedra (each octahedron sharing four edges with four other octahedra), with the double strings being interconnected via corner sharing of oxygen atoms (Figures 1 and 2). Molybdenum atoms within the strings are shifted from their octahedral centers so as to form planar tetranuclear clusters. An alternative description views the structure as consisting of molybdenum oxide cluster chains extended parallel to the *c* axis. The chains are built from Mo_4O_{16} clusters that share oxygen atoms on opposite edges of the planar tetrameric molybdenum atom cluster (Figure 3). The potassium ions occupy sites along the *c* axis in channels formed by four metal oxide cluster chains crosslinked by molybdenum–oxygen bonds (Figure 4).

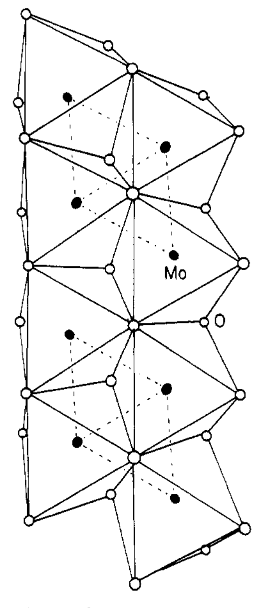

Figure 1. Double strings of edge-sharing MoO_6 octahedra in $K_2Mo_8O_{16}$. Tetrameric molybdenum atom clusters are shown.

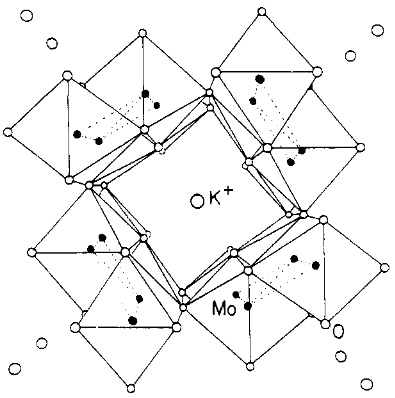

Figure 2. Corner sharing of the double strings in $K_2Mo_8O_{16}$ creating channels where potassium ions are located.

A section of a molybdenum oxide cluster chain is given in Figure 3. The Mo atom clusters and connectivity within and between chains via the sharing of oxygen atoms are shown. The tetranuclear units contain two types of molybdenum atoms: (i) the apical atoms, Mo1, that are each bonded to two other molybdenum atoms and six oxygen atoms; (ii) the atoms labeled Mo2 that are each bonded to three molybdenum atoms and six oxygen atoms. The cluster chains contain four types of oxygen atoms, each bonded to three molybdenum atoms. Intrachain atom types O1 and O2 are triply bridging to Mo atoms within and between Mo_4O_{16} clusters, respectively, and are also coordinated to potassium ions. These oxygen atoms may be considered sp³ hybridized. Interchain atom types (O3, O7) and (O4, O8) connect the individual cluster chains and are in trigonal-planar-like coordination with molybdenum. Atoms O3 and O7 are each shared between two separate Mo_4O_{16} clusters while atoms O4 and O8 are each shared by three cluster units. These oxygen atoms may be considered sp² hybridized since the sum of the Mo–O–Mo bond angles around each oxygen atom is 359.8–360.0°. The inter- and

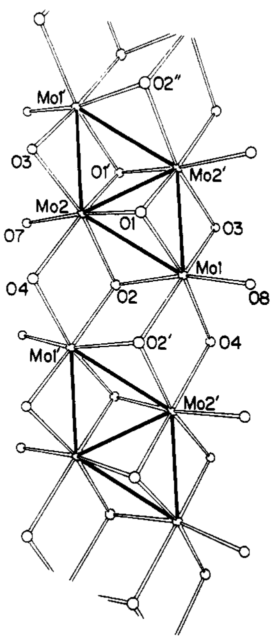

Figure 3. Section of one type of molybdenum oxide cluster chain in $K_2Mo_8O_{16}$. The other type differs mainly in the Mo1–Mo2 and Mo1'–Mo2' bond distances. Mo–Mo bonds are represented as solid black lines.

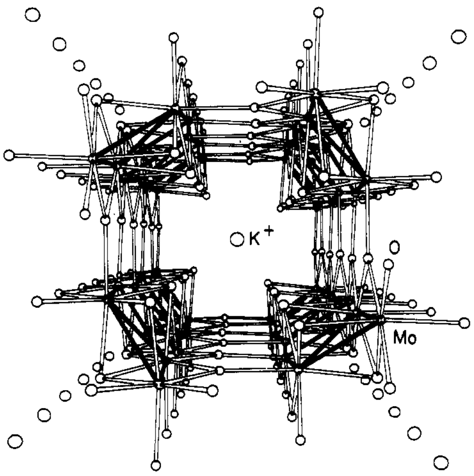

Figure 4. Three-dimensional view down the *c* axis of $K_2Mo_8O_{16}$. The sp^3- and sp^2-hybridized oxygen atoms are shown.

intrachain linking of the cluster units may be represented by the formula $Mo_4O_2{}^{intra}O_{4/2}{}^{intra}O_{4/2}{}^{inter}O_{6/3}{}^{inter}$.

The structure displays two slightly different types of cluster chains. Both types possess inversion symmetry within and between the planar Mo_4 units, but the five Mo–Mo bonds in the clusters of one chain are closer to being equivalent than in the clusters of the other chain. A comparison of bond lengths in the two types of clusters is given in Table II with reference to Figure 3. Also included in the table are the related bond distances in $Ba_{1.14}Mo_8O_{16}$.[8,19] In this compound, the two Mo_4 clusters are more regular and more distorted, respectively, than in $K_2Mo_8O_{16}$. Figure 3 is an ORTEP drawing of the more distorted cluster chain in $K_2Mo_8O_{16}$. For convenience, the atomic labeling in this figure is used in Table II to represent all the cluster types in $K_2Mo_8O_{16}$ and $Ba_{1.14}Mo_8O_{16}$. The 2.697-Å sides of the more regular cluster units in the potassium compound (represented as Mo1–Mo2 and Mo1'–Mo2' in Figure 3) are elongated to 2.837 Å in the more distorted units, whereas the dimensions of the other bonds of the two cluster types remain comparable. A similar situation exists in the barium compound. In both compounds, a cluster chain of one type is linked to four cluster chains of the other type.

Table III. Calculated Valence[a] for the Molybdenum Atoms in $K_2Mo_8O_{16}$ and $Ba_{1.14}Mo_8O_{16}$

	$K_2Mo_8O_{16}$		$Ba_{1.14}Mo_8O_{16}$ [b]	
	regular clusters	distorted clusters	regular clusters	distorted clusters
Mo1	3.74	3.99	3.66	4.03
Mo2	3.53	3.54	3.51	3.61
cluster av	3.64	3.77	3.59	3.82
no. of cluster electrons	9.4	8.9	9.6	8.7

[a] Reference 22. [b] Reference 8.

A three-dimensional view down the *c* axis of $K_2Mo_8O_{16}$ is given in Figure 4. The molybdenum oxide cluster chains are connected via the sp^2-type oxygen atoms to form tunnels in which the K^+ ions are located. Potassium is coordinated to eight oxygen atoms in a distorted square-prismatic arrangement. The spacings between potassium ions along a channel are 2.79 and 2.96 Å. Also discernible from Figure 4 are the smaller sized channels running parallel with the *c* axis and composed of trans edge-sharing oxygen atom octahedra as found in rutile-related structures.

Discussion

Within an Mo_4 cluster, the Mo–Mo bonding results from 8 to 10 electrons in cluster bonding orbitals directed along the five edges of the cluster. Both types of Mo_4O_{16} clusters in $K_2Mo_8O_{16}$ and $Ba_{1.14}Mo_8O_{16}$ possess only $\bar{1}$ (C_i) symmetry but may be approximated by $2/m$ (C_{2h}) symmetry.[20] A 10-electron cluster (2 electrons/bond) would be expected to give five essentially equivalent bonds in $2/m$ symmetry. After two d orbitals are assigned per Mo atom for bonding with oxygen (i.e., the e_g set in an octahedral environment), the 12 remaining Mo orbitals combine in $2/m$ symmetry to give five bonding ($2a_g + b_g + a_u + b_u$), two approximately nonbonding ($a_g + b_u$), and five antibonding molecular orbitals ($a_g + b_g + 2a_u + b_u$).[21] Because there are 18 electrons per formula unit available for Mo–Mo bonding in $K_2Mo_8O_{16}$, it appears the "regular" clusters possess more than 9 electrons and the distorted clusters contain less than 9 electrons in their bonding orbitals. Equivalent Mo_4 clusters would be expected if the electron count in all clusters were the same.

This difference in the electron count for the two rhomboidal clusters is seen in the calculated valence (i.e., oxidation state) of the Mo atoms. The valence of each crystallographically different Mo atom was estimated by a summation of the Mo–O bond strengths for that atom. Bond strengths were calculated from

$$s = (d/1.882)^{-6.0}$$

where s = bond strength of an Mo–O bond, d = crystallographic Mo–O bond length, and the values 1.882 (Mo–O bond of unit strength) and −6.0 are fitted parameters.[22] The results for $K_2Mo_8O_{16}$ and $Ba_{1.14}Mo_8O_{16}$ are shown in Table III. As the Mo1–Mo2 and Mo1'–Mo2' edges become longer, the remaining three Mo–Mo bonds become shorter (Table II). For this reason, the calculated valence for Mo2, which is the atom that forms the unique central bond Mo2–Mo2', changes only slightly as the number of cluster electrons is varied. The apical

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(19) Torardi, C. C.; McCarley, R. E., to be submitted for publication.

(20) It should be noted that the Mo_4O_{16} clusters in these hollandite phases *can never have ideal* $2/m$ (C_{2h}) *symmetry*.

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atoms, Mo1, are most affected by changes in the number of cluster electrons.

Reasons for the elongation of only two opposite bonds are not immediately apparent. Recently, molecular orbital calculations were made on similar *molecular* tetrameric Mo atom clusters containing 10-electron (C_{2h}—all five bonds of equal length) and 8-electron (C_i—two opposite bonds elongated) environments.[21] These show that such a unique distortion can arise from a second-order Jahn–Teller effect. Another explanation for the observed distortion could be the affects of Mo d–O p π bonding, which would involve the sp^2-like interchain oxygen atoms. For these atoms in the clusters of $K_2Mo_8O_{16}$ and $Ba_{1.14}Mo_8O_{16}$, three criteria were examined: the length of the Mo–O bonds; the alignment of the oxygen lone pair with molybdenum atom d orbitals; and the sum of the bond strengths[22] around each oxygen atom. Even though the Mo1–O8 bond lengths are the shortest, O8 does not appear to have good positioning for π bonding. Also, the valence sums of 1.85 ($K_2Mo_8O_{16}$) and 1.90 ($Ba_{1.14}Mo_8O_{16}$) for O8 imply an overall weaker bonding to molybdenum than expected (i.e., a valence sum of 2.0). The only interactions that optimize the three criteria are Mo1–O3 and Mo2–O3. These have relatively short bond lengths, good π alignment, and bond strength sums greater than 2.1. Note that O3 is doubly bridging along an outside edge of the Mo_4O_{16} cluster. The lone pair on O3 may effectively overlap with a "nonbonding" d orbital on Mo1 as well as with a d orbital on Mo2. The latter is an orbital that participates in the pair of Mo–Mo bonds in question. As the number of metal cluster electrons decreases, the Mo2–O3 π interactions may increase, thereby raising the energy of the orbitals involved in the Mo1–Mo2 and Mo1′–Mo2′ bonds and stabilizing the observed distorted Mo atom configuration. Atom O4 appears to be well positioned for π overlap with the d orbital on Mo1 that forms the elongated Mo–Mo bonds. However, the Mo1–O4 distances are not unusually short, and the valence sums for O4 are low with values of approximately 1.7.

Only a very simple description of the Mo–O bonding has been given here. Molecular orbital or band calculations would give insight into the role of molybdenum–oxygen π bonding on the deformation process within these Mo_4O_{16} clusters.

Registry No. $K_2Mo_8O_{16}$, 92014-66-9.

Supplementary Material Available: Listings of atomic thermal parameters and structure structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Chemistry and Structure of Hexakis(thiourea-*S*)technetium(III) Trichloride Tetrahydrate, $[Tc(SC(NH_2)_2)_6]Cl_3.4H_2O$

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The preparation and characterization of hexakis(thiourea-*S*)technetium(III) trichloride tetrahydrate, $[Tc(SC(NH_2)_2)_6]Cl_3.4H_2O$ (A), is described. Crystals of A are monoclinic, *C*2/*c*, with a = 11.876 (2) Å, b = 12.048 (2) Å, c = 19.662 (3) Å, and β = 95.32 (1)°, and have four formula units in the unit cell. The structure was determined by standard methods and refined to $R_1 = 0.0391$, $R_2 = 0.0452$ on the basis of 1753 independent reflections. Data were measured with use of Mo Kα radiation and a Syntex P2$_1$ diffractometer. The cation is roughly octahedrally coordinated by the six sulfur atoms of the thiourea groups. The Tc–S bonds (2.431 (1), 2.412 (1), 2.440 (1) Å) are significantly longer than Tc(V)–S lengths reported previously, but bond lengths within the thiourea groups are normal. The structure is held together by an extensive hydrogen-bonding network. Chemical reactions of A are described, as well as the preparation and characterization of $[Tc(SC(NH_2)_2)_6](BF_4)_3$, $[TcCl_2(diphos)_2]Cl\cdot 2H_2O$, $[Tc(CNC(CH_3)_3)_6]PF_6$, and $[Tc(P(OCH_3)_3)_6]PF_6$ from A.

Introduction

The red-orange species formed by the reaction of the pertechnetate ion and thiourea in dilute mineral acids has been known since 1959.[2] The oxidation state of the technetium in this complex has been proposed by various workers to be Tc(VII), Tc(V), Tc(IV), or Tc(III).[3-5] No thorough study of the isolated complexes has, as yet, appeared. In this paper, we report the identification of these species as salts of the technetium(III) cation $[Tc^{III}(tu\text{-}S)_6]^{3+}$ (tu = thiourea). The crystal structure of $[Tc^{III}(tu\text{-}S)_6]Cl_3\cdot 4H_2O$ and the reactions of the cation with various ligands are described.

Experimental Section

Technetium as $NH_4{}^{99}TcO_4$ was obtained as a gift from New England Nuclear (NEN), Billerica, MA. All manipulations were carried out in laboratories approved for low-level radioactivity (^{99}Tc is a weak β-emitter with a half-life of 2.12 × 10^5 years and particle energy of 0.292 MeV). All precautions followed have been detailed elsewhere.[6-8]

Infrared spectra were recorded in the range 4000–300 cm^{-1} on a Perkin-Elmer PE180 grating infrared spectrophotometer as KBr pellets. Optical spectra, in solution, were measured with a Cary 17 spectrophotometer. Conductivity measurements were performed in methanol and acetonitrile by using a Yellow Springs Model 3403 conductivity cell and a Beckman RC-16C conductivity bridge. Magnetic susceptibility measurements were made on methanol solutions via the Evans NMR method[9] using a Varian T-60 spectrometer. The ^{1}H NMR measurements were also made on the T-60 with Me_4Si as the internal calibrant. ^{31}P NMR measurements were made on a JEOL 90Q 90-MHz spectrometer with H_3PO_4 as an external reference. Melting points were obtained with a Mel-Temp apparatus

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