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## Molybdenum in Oxidation State 2.5+ in Aqueous Solution

*Sir:*

We wish to report the existence of a stable molybdenum species in the 2.5+ oxidation state in aqueous solution.

Cotton, Frenz, and Webb[1] observed that when $K_4Mo_2(SO_4)_4 \cdot 2H_2O$ (compound I) was recrystallized by allowing its solution to mix by diffusion, through a glass frit, with a saturated solution of $K_2SO_4$, a mixture of two different crystals was obtained: pink crystals of the parent compound I and red-blue crystals of a new compound II, which was shown by X-ray structure analysis to be $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ and to have a bond of order 3.5 between the Mo atoms. A similar compound derived from an ethylene diammine complex of Mo(II) was recently prepared by Bowen and Taube.[2] The oxidation state of molybdenum in these compounds is 2.5+.

In the course of this study it became necessary to prepare compound II in a pure state, i.e., free from admixture with I. The mode of preparation is given at the end of this communication.

When the pure compound II was dissolved in oxygen free $H_2SO_4$ (2 *N*) a blue solution was obtained. The solid II may be recovered from the solution by the addition of a saturated $K_2SO_4$ solution. This solution could be oxidized by air to Mo(IV)[3] but was stable in oxygen-free solutions of this acid. The spectrum of this blue solution had maxima at 412 nm ($\epsilon = 16.9$) and 573 nm ($\epsilon = 17.5$) (Figure 1) and was similar to the reflectance spectrum of II (with maxima at 410 and at 573 nm).

The oxidation state of molybdenum in this solution was derived from the ratio of the permanganate titer of an aliquot (after discharging into excess Fe(III)) to the permanganate titer of the total molybdenum analysis (carried out on an air-oxidized aliquot after it was reduced to Mo(III) by a Jones Reductor and discharged into excess Fe(III)).[4] The ratio found was $1.17 \pm 0.01$ and corresponded to an oxidation number of 2.5+. The same result was obtained when a weighed sample of solid II was dissolved directly in a ferric salt solution and its permanganate titer compared to that of its total Mo analysis.

The identity of the oxidation state and the similarity of the spectra of solid II and the blue solution support the conclusion that the solution contains a molybdenum species of oxidation number 2.5+ in which the fundamental unit $Mo_2^{5+}$ of II, with its Mo-to-Mo bond of order 3.5 is preserved.

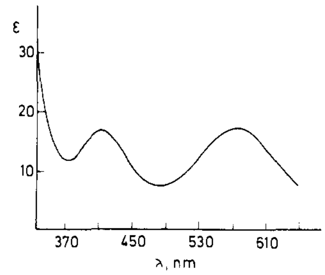

**Figure 1.** Absorption spectrum of $Mo_2^{5+}$ in $H_2SO_4$ (2 *N*).

The blue solution of Mo 2.5+ was reduced to a red solution of $Mo_2^{4+}$ [2,6] by a Jones reductor. Reduction of $Mo_2^{5+}$ to $Mo_2^{4+}$ would involve the transfer of one electron from the reducing agent to the half-filled $\delta$ molecular orbital of the 3.5 order bond.[1]

The stability of Mo 2.5+ in sulfuric acid solutions is in marked contrast to its instability in other strong acids. When II was dissolved in aqueous HCl or *p*-toluenesulfonic acid (HPTS) the pale blue color observed initially turned into a deep red color. This red solution passed unchanged through a Jones reductor, thereby ruling out the possibility that the color was due to Mo(IV)[3] or any other species of higher oxidation number (all of which would be reduced to the green binuclear Mo(III) ion[5]).

A typical absorption band of $Mo_2^{4+}$ at 514 nm[2,6] appeared within minutes in a freshly prepared solution of II in HPTS and its intensity increased with time. The conclusion that $Mo_2^{4+}$ was formed spontaneously in these solutions was confirmed by the chromatographic behavior of the red species on both cation and anion exchange columns, which was characteristic[6] for $Mo_2^{4+}$. A typical deep blue color which appears immediately upon addition of KCNS to $Mo_2^{4+}$ was also observed upon addition of this reagent to the red solution.

The average oxidation number of Mo in the solution of II in HPTS did not change after it had turned red, and remained 2.5+; therefore it was evident that the blue molybdenum 2.5+ species underwent disproportionation in this solution. The disproportionation reaction may be reversed by the addition of a saturated solution of $K_2SO_4$; the red color disappears and solid II is precipitated.

While Mo(II) was established as the reduced product of the disproportionation reaction, the nature of the oxidized product could not be determined unequivocally. The decomposed solution of II in HPTS was absorbed on a cation exchange column, after removal of Mo(II). A band of a 3+ ion similar to $Mo(H_2O)_6^{3+}$ [2,6] was observed, but could not be eluted in sufficient purity to allow positive spectral identification.[2,7] A Mo(IV) band[3] was observed on the column and identified after elution, but one may not conclude that it was necessarily a primary product of the disproportionation reaction. Mo(IV) might have been formed by a secondary reaction such as the oxidation of $Mo(H_2O)_6^{3+}$ by water.[3]

The fact that Mo 2.5+ is stable only in the presence of sulfate supports the conclusion that it exists in solution as a sulfato complex related to II, such as the $Mo_2(SO_4)_4^{3-}$ ion or a partly aquated sulfato complex. The reversal of the disproportionation reaction by $K_2SO_4$ indicates that this stabilization of Mo 2.5+ by sulfate is of thermodynamic rather than of kinetic origin.

Work is in progress in this laboratory on the kinetics of the disproportionation reaction and the identification of the oxidation products.

In the preparation of $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$, a saturated solution of $K_4Mo_2(SO_4)_4 \cdot 2H_2O$ in $H_2SO_4$ (2 *N*) was oxistantially longer than normal covalent bonds by 0.32 and 0.24 Å in **1** and **2a**, respectively. The observed lengthening dized with an air stream for a few minutes, until the red color of Mo(II) disappeared and was replaced by a pale blue color. Addition of a saturated solution of $K_2SO_4$ to this partly oxidized solution precipitated the crystalline blue-gray compound II which was filtered, washed with ethanol, and dried in vacuo over KOH.

Anal. Calcd for $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$: Mo, 25.4; K, 15.5; $SO_4$, 50.8. Found: Mo, 24.8; K, 15.4; $SO_4$, 50.0.

The magnetic susceptibility of II was measured by the Faraday method. The magnetic moment of 1.69 BM obtained from this measurement indicated one unpaired electron per $Mo_2(SO_4)_4{}^{3-}$ ion as expected.[1] Raman and ir spectra will be reported separately.

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## Synthesis, Characterization, and Bonding of Tetrameric Triphenylphosphine Silver Halide Cluster Systems. Evidence of Dictation of Stereochemistries by van der Waals Interactions

*Sir:*

As part of a continuing effort to elucidate the observed geometrical characteristics of tetrameric cubane-like transition metal cluster systems,[1-6] we report here preliminary results on the solid-state geometries of three tetrameric triphenylphosphine silver halide clusters. This work has unexpectedly revealed a new type of isomerism: the occurrence of $(Ph_3P)_4Ag_4I_4$ in the solid state in both a cubane and chair-like form. Furthermore, this research is of interest in enabling an assessment of the relative importance of the effects of metal-ligand bonding and van der Waals interactions on the stereochemistries of $(Ph_3P)_4Ag_4X_4$ (X = Cl, Br, and I).[6]

Addition of a stoichiometric amount of triphenylphosphine in ether to AgX in a saturated solution of aqueous KX gave $(Ph_3P)_4Ag_4X_4$ (X = Cl, Br, I) as a white precipitate. Slow crystallization of $(Ph_3P)_4Ag_4Cl_4$ (**1**) from $CHCl_3$-ether afforded rectangular crystals which were shown by a complete structural analysis to possess a cubane-like structure defined by two interpenetrating silver and chlorine tetrahedra situated on alternate corners of a highly distorted cube, with each silver atom being further coordinated to a triphenylphosphine ligand (Figure 1a).[7a] A similar crystallization of $(Ph_3P)_4Ag_4I_4$ from $CHCl_3$-ether gave rise to rod-shaped crystals of monoclinic symmetry (**2a**), while crystallization from $CH_2Cl_2$-ether produced parallelepipeds of triclinic symmetry (**2b**). X-Ray diffraction studies have shown that **2a** possesses a cubane-like structure (Figure 1b)[7b] whereas **2b** adopts a centrosymmetric chair-like configuration (Figure 1c).[7c]

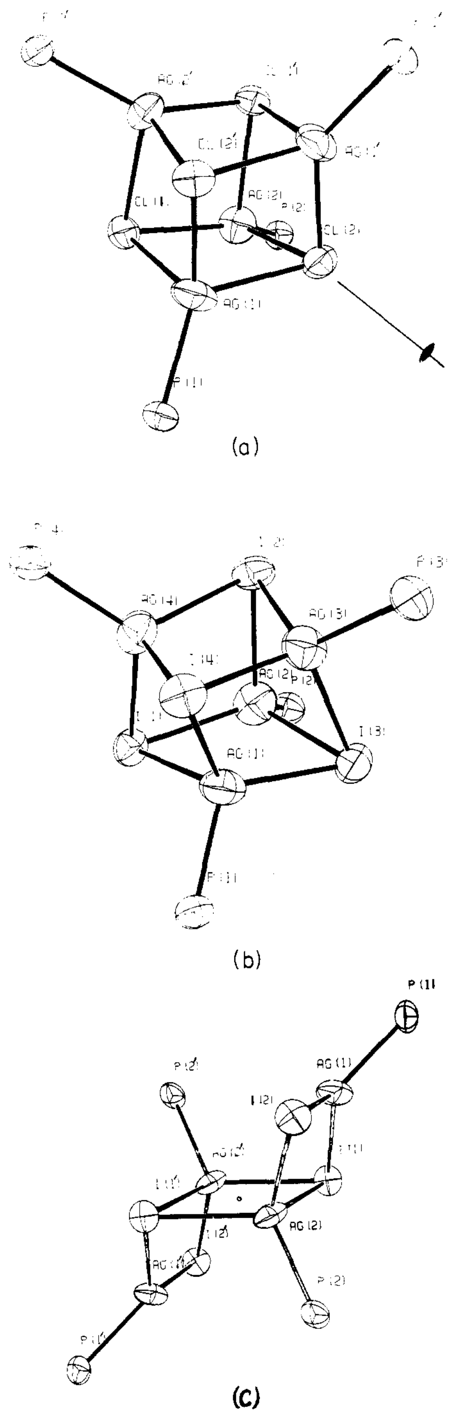

**Figure 1.** The highly distorted $P_4Ag_4X_4$ core (ORTEP diagram, 50% probability ellipsoids) of the $(Ph_3P)_4Ag_4X_4$ molecules: (a) X = Cl, cubane-like structure with crystallographic $C_2$-2 site symmetry; (b) X = I cubane-like configuration with no crystallographic constraint; and (c) X = I, chair-like configuration with crystallographic $C_i$-$\bar{1}$ site symmetry.

The most striking structural feature of the two cubane-like silver tetramers $(Ph_3P)_4Ag_4Cl_4$ (**1**) and $(Ph_3P)_4Ag_4I_4$ (**2a**) is the great deviation of the $M_4X_4$ core from the idealized $T_d$ geometry. The unusual degree of the *nonsystematic* distortions[9] manifest themselves in the intracluster parameters listed in Table I. Other noteworthy structural characteristics are: (1) the average Ag···Ag distances are 0.74 Å (**1**) and 0.59 Å (**2a**) longer than that in the metal (however, the shortest one in **2a** is only 0.23 Å greater); (2) all X···X contacts are close to or greater than the sum of van der Waals radii; and (3) the average Ag–X distances are sub-