Isopolymolybdenum Blue Complex as a Photoreduced Product: X-Ray Crystal Structure

By Toshihiro Yamase* and Tsuneo Ikawa
(Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan)

and Yuji Ohashi* and Yoshio Sasada
(Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan)

Summary X-Ray studies show that the blue crystalline isopropylammonium salt, isolated following the photoreduction of $(NH_3Pr^i)_6(Mo_7O_{24})$ in aqueous solution, contains $Mo_{13}O_{40}{}^{4-}$ (mixed-valence) and $H_4Mo_{12}O_{40}{}^{4-}$, both having the Keggin structure, randomly distributed over the anion sites in a 1 : 2 ratio.

An aqueous solution of various alkylammonium molybdates changes from colourless to blue upon irradiation with u.v. light. In an attempt to understand the mechanism of the photoreduction,[1] we have prepared a blue, crystalline complex from an aqueous solution of the photoreduced hexakis(isopropylammonium)heptamolybdate complex, $(NH_3Pr^i)_6(Mo_7O_{24})$. The structure has been analysed using X-ray diffraction.

The disordered crystals contain two anionic species, $Mo_{13}O_{40}{}^{4-}$ (**1**), and $H_4Mo_{12}O_{40}{}^{4-}$ (**2**) in a ratio of *ca.* 1 : 2. Both anions have configurations similar to that of the Keggin structure[2] with a central hetero atom. Although it is known that the 'heteropoly' complex with the Keggin structure can be reduced to a blue complex, 'heteropoly' blue, its structure has never been established. The anion of (**1**) shows that the Mo atoms have mixed-valencies, Mo^{5+} and Mo^{6+}, which explains the e.s.r. spectral data. We report here the salient structural results of this new reduced molybdate.

Crystal data: $(NH_3CHMe_2)^+{}_4(Mo_{13}O_{40})_{0\cdot33}{}^{4-}(H_4Mo_{12}O_{40})_{0\cdot67}{}^{4-}$,† M 2066·39, space group $I\bar{4}$, $a = 14{\cdot}908(2)$, $c = 10{\cdot}323(2)$ Å, $U = 2294{\cdot}3(6)$ Å^3, $D_m = 2{\cdot}97$ g cm^{-3}, $D_c = 2{\cdot}99$ g cm^{-3}, $Z = 2$. Intensity data were collected on a Rigaku four-circle diffractometer using Mo-K_α radiation; 1394 reflections were considered observed and used in the analysis. The structure was solved by the normal heavy atom method and refined by the block-diagonal least-squares with anisotropic temperature factors. The analysis reveals that the occupancy factor of the central Mo atom is 0·33 and the anisotropy of the temperature factors of the other Mo and O atoms is significantly large. This indicates that the crystal contains two anionic species, containing 13 and 12 molybdate ions, in the ratio of *ca.* 1 : 2. An

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† Found: C, 7·12; H, 1·92; N, 3·02%; calc, 6·97; H, 2·06; N, 2·71%.

attempt to resolve the two anionic structures was unsuccessful. The positions of the hydrogen atoms were obscure in the difference map owing to the disordered structure. The final R value is 0·037. The 13- and 12-molybdate anions were assigned the structures (**1**) and (**2**), respectively, from elemental analysis and the balancing of the charge in the crystal.‡

The average structure of the anions is shown in the Figure. It has S_4 symmetry. For the anion of (**2**) the central Mo atom, Mo(1), is lost. Mo(1) is tetrahedrally surrounded by four O(10) atoms; the Mo(1)–O(10) distance is 1·628(7) Å and O(10)–Mo(1)–O(10′) angle is 109·2(4)°. The other three Mo atoms, Mo(2), Mo(3), and Mo(4), are octahedrally co-ordinated by O atoms. The MoO_6 octahedra are joined together by sharing edges and corners to form a $Mo_{12}O_{40}$ group and connected to the central tetrahedron by sharing corners to form a $Mo_{13}O_{40}$ anion. The Mo atom in each octahedron is shifted from its centre towards the unshared O atom owing to repulsion between the neighbouring Mo atoms. The Mo–O distances and O–Mo–O angles in these octahedra are in fair agreement with the corresponding ones found in the octahedra of $(Mo_7O_{24})^{6-}$ [3] and $(H_2Mo_8O_{28})^{6-}$.[4]

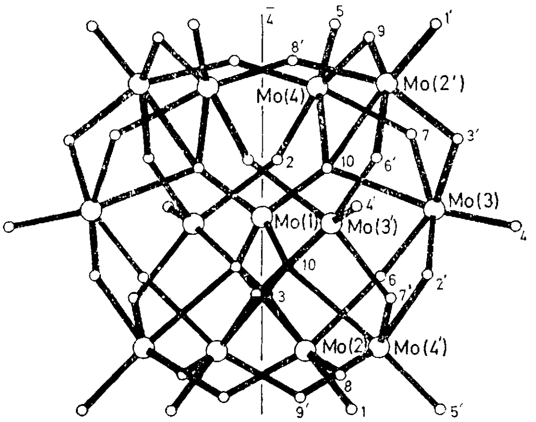

FIGURE. A perspective view of the mixed anions, $[Mo_{13}O_{40}]^{4-}$ and $[H_4Mo_{12}O_{40}]^{4-}$; in the latter the central Mo atom is lost. The oxygen atoms are indicated by the small circles with their numbering. The vertical line is the 4-fold rotatory–inversion axis.

E.s.r. study indicates that Mo^{5+} species are present in the crystal. The only signal detected at room temperature is a broad singlet (ΔH_{ms} *ca.* 150 G), with an isotropic g factor of 1·947. Neither hyperfine nor superhyperfine structures are observed in these spectra. These facts suggest that the paramagnetic electrons due to Mo^{5+} species may not be present in the 12-molybdate anion but only in the H-free 13-molybdate anion. Otherwise, the superhyperfine lines caused by H atoms would be seen in the spectra, as is observed in the spectrum of the irradiated single crystal of $(NH_3Pr^i)_6(H_2Mo_8O_{28})2H_2O$.[1] Also, both the paramagnetic electrons of (**1**) are not localized on the central Mo atom, one of them being delocalized on the surrounding Mo atoms in the octahedron network. This is supported by the e.s.r. studies of two-electron 'heteropoly' blue complexes.[5]

(*Received*, 12*th March* 1979; *Com.* 240.)

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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