Molybdenum(IV) and Tungsten(IV) Oxocyanide Complexes

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AQUEOUS solutions of $K_4[Mo(CN)_8],2H_2O$ and $K_4[W(CN)_8],2H_2O$ change colour when irradiated with near-ultraviolet light and the changes have been shown to correspond to the loss of four cyanide ligands from the complex.[1–3] The addition of KOH to the resultant blue (molybdenum) and violet (tungsten) solutions precipitates red and yellow–brown crystals respectively which dissolve in water giving solutions having the original colours.[4,5] In the molybdenum case, a blue solid may be obtained by adding ethanol to the blue solution.[3] Compounds of similar colours also have been prepared from quinquevalent molybdenum and tungsten hydroxides[4–6] which appear to be identical to the compounds obtained photochemically. The red molybdenum and yellow–brown tungsten compounds have usually been formulated as $K_4[M(CN)_4(OH)_4],4H_2O$, where M is eight-co-ordinate Mo^{IV} or W^{IV}, and the blue molybdenum compound as $K_3[Mo(CN)_4(OH)_3(H_2O)],2H_2O$. We now present evidence which suggests that these compounds are six-co-ordinate Mo^{IV} and W^{IV} oxocyanide complexes, $K_4[MO_2(CN)_4],6H_2O$ and $K_3[MO(OH)(CN)_4],nH_2O$ and that the red–blue equilibrium should be written (*e g.*, for molybdenum) as:

$$\underset{\text{red}}{[MoO_2(CN)_4]^{4-}} + H_2O \rightleftharpoons \underset{\text{blue}}{[MoO(OH)(CN)_4]^{3-}} + OH^-$$

Single-crystal *X*-ray-diffraction studies of the red molybdenum compound, prepared by the photolytic method, shew the space group to be $P2_1/c$ with $a = 7{\cdot}23$, $b = 13{\cdot}48$, $c = 9{\cdot}35$ Å, $\beta = 113° 45'$, $V = 835$ Å^3, and $Z = 2$. The measured density, 1·95 g./cc., agrees well with that calculated from the crystallographic data, 1·97 g./cc. Space-group symmetry therefore necessitates that both molybdenum atoms in the unit cell occupy centres of inversion.[7] This result is important because the formulation of the red crystals as $K_4[Mo(CN)_4(OH)_4],4H_2O$ would require the molybdenum atom to be situated at the centre of a cube, the only eight-co-ordination polyhedron which can accommodate a centre of symmetry. Since this is unlikely for several reasons,[8] we conclude that the correct centrosymmetric formulation of the anion is *trans*-dioxotetracyanomolybdate(IV). The yellow–brown tungsten analogue was found by X-ray diffraction to be isomorphous with the molybdenum complex (both grow as needles developed along 101) and therefore is probably isostructural. In view of these findings, we are currently investigating the reported $[Re(CN)_4(OH)_4]^{3-}$, $[Os(CN)_4(OH)_4]^{2-}$, and $[U(CN)_4(OH)_4]^{2-}$ complex anions[9] which may possibly also be $[MO_2(CN)_4]^{n-}$ species.

In order to obtain information about the composition of the blue molybdenum and purple tungsten compounds, we have measured their infrared spectra in Nujol mulls. Of major interest is an intense band at ~920 cm.$^{-1}$ in the molybdenum complex which occurs at ~875 cm.$^{-1}$ in the tungsten analogue. We assign these bands tentatively to M=O stretching frequencies and suggest that the complexes are best formulated as *trans*-$[MO(OH)(CN)_4]^{3-}$ ions by analogy with the red species. Consistent with this assumption is the observed diamagnetism (-100×10^{-6} c.g.s. mole^{-1} as against the value calculated from Pascal's constants, -150×10^{-6} c.g.s. mole^{-1}) of $K_3[MoO(OH)(CN)_4],2H_2O$, a result which might be expected since under C_{4v} symmetry both electrons would occupy a low-lying d_{xy}-orbital.

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