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The Synthesis of Tetrahalogenodimolybdenum(II) Complexes from Molybdenum(III) Halides. A Re-investigation of the Reaction of Molybdenum(III) Bromide with Anhydrous Dimethylamine

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In 1969 Brencic and Cotton reported [1] that $K_4Mo_2Cl_8 \cdot 2H_2O$ contained the quadruply metal–metal bonded $Mo_2Cl_8^{4-}$ anion. Subsequently several related $Mo_2X_4L_4$ complexes (X = Cl, Br, and I; L = neutral donor) have been isolated [2–8]. These complexes have been prepared using the molybdenum (II) compounds $K_4Mo_2Cl_8$ [2], $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ [3–5], β-MoX_2 (X = Cl and Br) [2], $(picH)_2[Mo_2X_6(H_2O)_2]$ (pic = 4-methylpyridine; X = Br [6] or I [7]), or the molybdenum(III) compounds $Cs_3Mo_2X_8H$ (X = Cl and Br) [3] (originally thought to be $Cs_3Mo_2X_8$), as starting materials. These compounds are all in turn prepared from dimolybdenum(II) tetra-acetate.

We report here that some $Mo_2X_4L_4$ complexes may be prepared by a single-step reductive synthesis using the simple binary halides MoX_3 (X = Cl and Br) as convenient starting materials.

Fifteen years ago one of us reported [9] that $MoBr_3$ and anhydrous dimethylamine react at room temperature to afford a violet amine-insoluble product formulated as the molybdenum(III) solvolysed species $[MoBr_2(NMe_2) \cdot NHMe_2]_n$. This report appeared seven years before the structural characterization of $Mo_2Cl_8^{4-}$ [1] and ten years before the first report [4] of $Mo_2Cl_4L_4$ complexes. The acquisition of additional evidence has enabled us to now reformulate this product as $Mo_2Br_4(NHMe_2)_4$, a new example of the quadruply metal–metal bonded group of complexes, with two mutually *trans* amine ligands coordinated to each metal centre [3].

The complex is essentially diamagnetic at 20 °C ($\chi'_M = 70 \times 10^{-6}$ c.g.s.u.) and exhibits two absorption bands with maxima at 581 and 488 nm in its diffuse reflectance electronic spectrum, typical [3] of dinuclear molybdenum(II) complexes. A comparison of the infrared spectrum of the complex (4000–500 cm^{-1}) with those of dimethylamine [10], *fac* $Mo(CO)_3(NHMe_2)_3$, and several transition metal dimethylamides $M(NMe_2)_x$ [11] shows that all bands are assignable to coordinated amine modes, indicating the absence of $-NMe_2$ groups. [Major bands (cm^{-1}) at 3210, N–H stretch; 1470, N–H band; 1430, 1397, CH_3 deformations; 1260, 1210, 1120, 1050, CH_3 rock; 1030, 900, CN stretch]. Two strong infrared bands at 286 and 264 cm^{-1} are assignable to Mo–Br stretches, with the amine CNC band at 383 cm^{-1}. An X-ray photoelectron spectrum of the complex shows that the molybdenum 3d binding energies [$3d_{3/2}$ 232.1; $3d_{5/2}$ 228.9 e.V.] fall in the range previously determined [2, 12] for dinuclear molybdenum(II) compounds, the spin–orbit components having binding energies approximately 1 e.V. lower than those of molybdenum(III) halide species [12]. The bromine $3p_{1/2}$ and $3p_{3/2}$ binding energies of 188.7 and 182.0 e.V. respectively are consistent with the presence of terminal metal–bromine bonds.

$Mo_2Cl_4(NHMe_2)_4$ may be prepared in an analogous manner from $MoCl_3$. [$\chi'_M = 140 \times 10^{-6}$ c.g.s.u.; diffuse reflectance electronic spectrum, 555 and 472 nm; i.r. spectrum (4000–500 cm^{-1}) essentially identical to that of the bromo-analogue; ν(MoCl), 335 and 322 cm^{-1}].

These reactions are undoubtedly complex since the yields of the amine-insoluble $Mo_2X_4(NHMe_2)_4$ do not exceed 50% based on the weight of MoX_3 used. The remaining molybdenum is found as an amine-soluble product mixed with dimethylammonium halide. Disproportionation of the molybenum(III) to give the amine-insoluble binuclear molybdenum (II) complex and amine-soluble higher oxidation state solvolysis products may occur in these reactions.

The solid state structures of $MoCl_3$ [13] and $MoBr_3$ [14] are based on face-shared MoX_6 octahedra with adjacent metal atoms drawn together in pairs (Mo–Mo 2.76 Å in $MoCl_3$; 2.92 Å in $MoBr_3$). The formation of $Mo_2X_4(NHMe_2)_4$ must involve cleavage of the halide bridges but retention and enhancement of the metal–metal interactions of the trihalides.

Finally it is of interest to note that the reaction of $MoCl_3$ with $LiNMe_2$ [15] proceeds without reduction to molybdenum(II), the triply metal–metal bonded molybdenum(III) derivative $Mo_2(NMe_2)_6$ being formed.

Experimental

Tetrabromotetrakis(dimethylamine)dimolybdenum(II)

$MoBr_3$ was allowed to react with a large excess of anhydrous dimethylamine, (dried by vacuum line distillation from barium oxide), at room temperature for several days in a sealed ampoule. The violet amine-insoluble product was obtained by filtration of the contents of the ampoule in a vacuum line using solid CO_2–acetone slush baths. The product was washed at least six times with anhydrous dimethylamine before being pumped at room temperature for several hours. The amine-insoluble product (m.p. 208 °C dec.), was also insoluble in benzene, chloroform, cyclohexane, chlorobenzene and ethanol, and slowly decomposed in moist air. *Anal.* Calcd. for $Mo_2Br_4(NHMe_2)_4$: Mo, 27,7; Br, 46.2; N, 8.10. Found: Mo, 28.1; Br, 46.1; N, 8.11%.

$Mo_2Cl_4(NHMe_2)_4$ was obtained from $MoCl_3$ in an identical manner.

The heterogeneous dark brown amine-soluble products were obtained by distillation of the dimethylamine from the combined filtrates, followed by vacuum drying.

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