

Reaction of Oxomolybdenum(V) Complexes with Hydrogen Sulphide and Thiols

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As part of a general investigation of molybdenum-sulphur complexes, we have studied the reactions of the compounds $\text{Mo}_2\text{O}_3(\text{xan})_4$ (xan = ethylxanthate anion, EtOCS_2^-) and $\text{Mo}_2\text{O}_3(\text{dtp})_4$ [dtp = diethyldithiophosphate anion, $(\text{EtO})_2\text{PS}_2^-$] with hydrogen sulphide and thiols, RSH (R = Et, Ph, PhCH_2). The objects were to investigate the possibility of

preparing thio-analogues of oxomolybdenum complexes and to prepare complexes containing molybdenum fully co-ordinated with sulphur.

The complexes $\text{Mo}_2\text{O}_3(\text{xan})_4$ ¹ and $\text{Mo}_2\text{O}_3(\text{dtp})_4$ ² were prepared by published methods and by new methods which will be reported elsewhere.³ The molecular structure of the xanthate complex has

been determined by X-ray crystallography⁴ and we have evidence that the structure of the dithiophosphate complex is similar.³

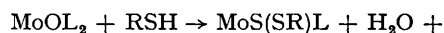
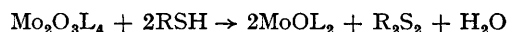
Hydrogen sulphide was passed into a solution of $\text{Mo}_2\text{O}_3(\text{xan})_4$ in a 1:1 mixture of benzene and ethanol at room temperature yielding a black precipitate of empirical formula $\text{MoS}_2(\text{xan})$. Molecular-weight determinations were frustrated by the general insolubility of the compound. The magnetic moment (0.5 B.M. at 20°) is much less than the spin-only value for molybdenum(v) indicating that the compound is a dimer (or polymer). The infrared spectrum shows the absence of terminal and bridging oxygen atoms and of SH groups. Hydrogen sulphide and $\text{Mo}_2\text{O}_3(\text{dtp})_4$ similarly give the corresponding black dithiophosphate complex. We are not able to suggest structures for these complexes at this stage although they are certainly polymeric. We note that other complexes of similar empirical formulae have been described: $\text{MoS}_2(\text{acetylacetonate})$,⁵ $\text{MoO}_2(\text{acetylacetonate})$.⁶

Reaction of the xanthate complex with thiols was carried out at room temperature by adding the complex to the pure liquid thiol under nitrogen. During 24 hr. the deep purple solutions darkened and deposited black crystals of empirical formulae $\text{MoS}(\text{RS})(\text{xan})$. Molecular-weight determinations were again frustrated by the low solubilities of the compounds. The magnetic moments (*ca.* 0.5 B.M. at 20°) were much below the spin-only value for molybdenum(iv) indicating polymerisation and/or spin-pairing in the distorted ligand field.

Reaction of the dithiophosphate complex with thiols is quite different from that of the xanthate complex. The product is a pale pink oxomolybdenum(iv) complex, $\text{MoO}(\text{dtp})_2$. This compound has been fully characterised by elemental analysis, molecular-weight determination, infrared, ultraviolet and visible, and proton magnetic resonance

spectroscopy. It is diamagnetic. We believe that this compound is the first authentic example of a square-pyramidal, low-spin, oxomolybdenum(iv) complex. It oxidises readily in air to $\text{Mo}_2\text{O}_3(\text{dtp})_4$. Livingstone *et al.*⁷ claim to have prepared a similar compound from the reaction in air of K_3MoCl_6 and di-isopropyl dithiophosphate but their description of the compound, the high reported molecular weight, and the method of preparation suggest to us that their material was a mixture of the molybdenum-(iv) and -(v) complexes.

The major organic products of the thiol reactions are disulphides, R_2S_2 . They were isolated from the reaction mixtures and characterised by their melting points and infrared spectra. We suggest that in these reactions the thiols initially reduce the oxomolybdenum(v) dithiophosphate and xanthate complexes to oxomolybdenum(iv) complexes. With the xanthate complex (which is less stable with respect to ligand dissociation than the dithiophosphate complex³) further reaction occurs involving dissociation and decomposition of a xanthate molecule (of which one sulphur atom is retained by the molybdenum) and co-ordination of a thiol anion:



decomposition products of L.

Reactions of the type described here have not previously been reported. Our preliminary results with other oxomolybdenum complexes indicate that the reactions are general.

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