

## A Binuclear Complex of Molybdenum(V) with Toluene-3,4-dithiol

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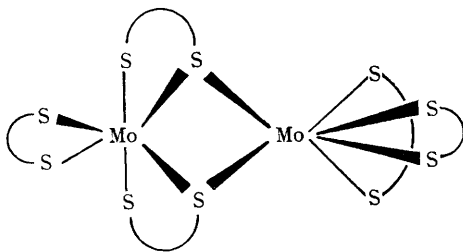
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TRIS-COMPLEXES of transition metals with toluene-3,4-dithiol ( $\text{H}_2\text{tdt}$ ) and related sulphur ligands have recently attracted much interest because of their ready electron-transfer reactions and trigonal prismatic stereochemistry.<sup>1</sup> A green molybdenum complex,  $\text{Mo}(\text{tdt})_3$ , was first prepared by Gilbert and Sandell<sup>2</sup> from toluene-3,4-dithiol and aqueous molybdenum(vi). With aqueous molybdenum(v) they obtained a mixture of the green complex and a red complex tentatively formulated with molybdenum(iv) as  $\text{Mo}(\text{Htdt})_2(\text{tdt})$  or  $\text{Mo}(\text{H}_2\text{tdt})(\text{tdt})_2$ . They considered that the mixture resulted from a valency disproportionation of molybdenum(v). Recent work<sup>1d</sup> on the green complex has indicated trigonal prismatic stereochemistry. We now report that the red complex is a binuclear molybdenum(v) complex,  $\text{Mo}_2(\text{tdt})_5$ .

We prepared the red complex by reacting ammonium oxopentachloromolybdate(v) and toluene-3,4-dithiolate anion in 2:5 molar ratio in 0.4 M-hydrochloric acid solution under nitrogen and also, together with  $\text{Mo}(\text{tdt})_3$ , from molybdenum(vi) and excess of toluene-3,4-dithiol. The complex was

purified by chromatography and reprecipitation from dichloromethane solution. In the reaction with molybdenum(v) there was no evidence of valency disproportionation since the product contained only two per cent  $\text{Mo}(\text{tdt})_3$ . The visible spectrum of our preparation is very similar to that of Gilbert and Sandell's red complex.<sup>2</sup>

We have obtained satisfactory elemental analyses for formulation of the red complex as  $\text{Mo}_2(\text{tdt})_5$ . The molecular weight in chloroform was consistent with a dimer. The absence of MoO and SH groups is shown by the infrared spectrum. The visible spectrum shows a charge-transfer peak at  $515 \text{ m}\mu$  ( $\epsilon$ , 9400) and a shoulder at *ca.*  $610 \text{ m}\mu$  [*cf.*,  $\text{Mo}(\text{tdt})_3$ , 684 and  $432 \text{ m}\mu$ ]. The magnetic moment of  $\text{Mo}_2(\text{tdt})_5$  (0.2 B.M. at  $17^\circ$ ) is much below the spin-only value for molybdenum(v); but the solution in dichloromethane shows a weak electron-spin resonance signal ( $\langle g \rangle = 1.999$ ,  $\langle A \rangle = 32$  gauss). The nuclear magnetic resonance spectrum of  $\text{Mo}_2(\text{tdt})_5$  in carbon disulphide shows four distinct signals due to methyl protons indicating four distinct ligand environments.



We consider that the red complex is binuclear with bridging thiol groups and that at least one

metal atom retains essentially trigonal prismatic coordination leading to an extensively delocalised ground state. Our present data are consistent with the structure shown in which two dithiol ligands bridge two molybdenum atoms. A binuclear complex of molybdenum with bridging sulphur atoms has recently been reported<sup>3</sup> and we have prepared similar complexes with a wide range of sulphur ligands.<sup>4</sup> It appears that sulphur bridges in higher-valent molybdenum complexes may be as important as oxygen bridges.

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<sup>2</sup> T. W. Gilbert and E. B. Sandell, *J. Amer. Chem. Soc.*, **1960**, **82**, 1087.

<sup>3</sup> G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *J. Amer. Chem. Soc.*, **1966**, **88**, 5174.

<sup>4</sup> R. N. Jowitt and P. C. H. Mitchell, *Chem. Comm.*, **1966**, 605; A. Butcher, R. N. Jowitt, and P. C. H. Mitchell, to be published.