

Communications

A Molybdenum System with One Active Site

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A system of the type $\text{MoO}_2(\text{tridentate})$ which can bind monodentate substrate (D) to produce hexacoordinated systems, $\text{MoO}_2(\text{tridentate})(\text{D})$, is described. These latter systems contain the *cis*- MoO_2 group, the stretching frequencies of which depend on the nature of D. The possible importance of these systems as models for molybdenum enzymes is indicated.

THE strategy used to generate the title system is to bind a tridentate ligand such as (I) (abbreviated as T^{2-}) to MoO_2^{2+} . The sixth coordination position is then available for binding a monodentate substrate.

The reaction of bis(acetylacetonato)dioxomolybdenum(VI) with TH_2 in the mole ratio 1:1 in boiling ethanol gives a brown solution which deposits yellow needles of $\text{MoO}_2\text{T}(\text{C}_2\text{H}_5\text{OH})$. On heating to 100° , the yellow compound is converted to brown MoO_2T^2 . This is reconverted to the ethanol adduct on recrystallization from ethanol. By reacting MoO_2T or the ethanol adduct with monodentate donor substrates (D) in ethanol, yellow to orange crystals of MoO_2TD are readily obtained where D can be, among many other things, nitrogen donors such as amines and oxygen donors, e.g. amides, sulphoxides and alcohols. Like the ethanol adduct, MoO_2TD loses D on heating. The temperature at which this happens depends on the nature of D (e.g. dimethylsulphoxide, 190° ; dimethylformamide, 120° ; pyridine, 170°).

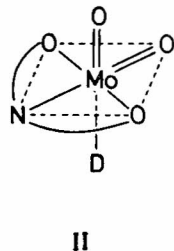
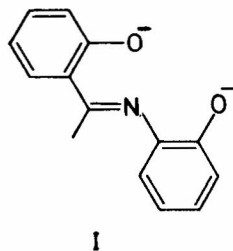


TABLE 1 — *cis*- MoO_2 STRETCHING FREQUENCIES^(a) IN MoO_2TD ^(b)

D	Frequencies (cm^{-1})
MoO_2T ^(c)	937, 909
Ethanol	931, 909
Dimethylsulphoxide ^(d)	924, 892
Dimethylformamide ^(d)	924, 900
Pyridine	918, 897
γ -Picoline	918, 893
Aniline	915, 890
Imidazole ^(e)	917, 901

(a) IR spectra were run in KBr pellets.

(b) Composition was established on the basis of elemental analysis (C, H, N, Mo).

(c) This may actually be dimeric with weak MoO_2Mo bridge where each T ligand provides one bridging oxygen.

(d) Binding through oxygen (IR data).

(e) Binding of imidazole is significant in relation to the possible reaction of MoO_2 (tridentate) with xanthine (see text).

It is reasonable to propose that MoO_2TD has the structure (II). Compounds of the type MoO_2TD show *cis*- MoO_2 stretches³ in the infrared (Table 1). The exact frequencies depend on the nature of D. In fact the MoO_2TD system provides a unique opportunity for a systematic study of ligand basicity based on *cis*- MoO_2 stretching frequencies. Such studies are in progress. For the present we only note that nitrogen donors tend to produce lower frequencies than oxygen donors (Table 1).

We are investigating the redox transformation of molybdenum and reactive D ligands such as aldehydes and xanthine using MoO_2T and a variety of MoO_2 -(tridentate) systems. Such studies are of considerable interest in relation to the role of molybdenum in enzymes⁴.

References

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