

SHORT COMMUNICATIONS

NEW COMPOUNDS OF MOLYBDENUM(III) WITH BIDENTATE LIGANDS*

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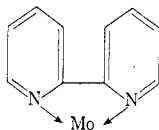
The coordination of bidentate ligands such as *o*-phenanthroline and 2,2'-dipyridyl with molybdenum(III) has not been reported previously.

Octahedral chelate complexes of the type $\text{Mo}(\text{phen})_3\text{X}_3$ and $\text{Mo}(\text{dipy})_3\text{X}_3$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) have been prepared. Magnetic susceptibilities consistent with the existence of three unpaired electrons are interpreted as arising from $4d^{25}5p^3$ binding.

Attempts to form perchlorates by replacement of bromine in the bromo complexes failed.

The described bidentates appear to be very stable, thus indicating that the lower *d* orbitals are used in the binding.

Because there is no electron pairing as evidenced by the effective μ value of 3.8, it is probable that only single bond structures exist such as :



Experimental

The halogen bidentates were prepared from hexahalides, R_3MoX_6 , with effective magnetic moments of 3.8 Bohr magnetons (B.M.).

(i) *Tris-o-phenanthroline Molybdenum(III) Chloride*.— $(\text{NH}_4)_3\text{MoCl}_6$ (0.5 g) was dissolved in water and ethanol and a few ml of HCl added. To this solution was added *o*-phenanthroline alcoholic solution (0.5 g). The resulting red solution was concentrated under reduced pressure at 60 °C. The dark red product was washed with water, then with ethanol, and dried (Found : Mo, 12.2 ; Cl, 13.5%. Calc. for $\text{Mo}(\text{phen})_3\text{Cl}_3$: Mo, 12.4 ; Cl, 13.6%).

Tris-o-phenanthroline molybdenum(III) chloride is a dark red powder, slightly soluble in ethanol and acetone, but insoluble in water or nitrobenzene. Mol. cond. in absolute ethanol at 25 °C for $M/8000=42.6$ r.o., $\mu_{\text{eff.}}=3.83$ B.M.

Each of the other preparations was carried out in a similar manner. The bromide preparations starting with K_3MoBr_6 gave at once orange coloured precipitates.

(ii) *Tris-o-phenanthroline Molybdenum(III) Iodide*.—This compound is a chocolate coloured powder, slightly soluble in ethanol and acetone but insoluble in water or nitrobenzene (Found : Mo, 9.0 ; I, 36.5%. Calc. for $\text{Mo}(\text{phen})_3\text{I}_3$: Mo, 9.1 ; I, 36.1%). Mol. cond. in absolute ethanol at 25 °C for $M/8000=43.2$ r.o., $\mu_{\text{eff.}}=3.84$ B.M.

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(iii) *Tris-o-phenanthroline Molybdenum(III) Bromide*.—This compound is an orange coloured powder, insoluble in water and ethanol but soluble in nitrobenzene (Found : Mo, 10.5 ; Br, 26.3%. Calc. for $\text{Mo}(\text{phen})_3\text{Br}_3$: Mo, 10.5 ; Br, 26.3%). Mol. cond. in nitrobenzene at 25 °C for $M/1000=43.6$ r.o., $\mu_{\text{eff.}}=3.84$ B.M.

(iv) *Tris-2,2'-dipyridyl Molybdenum(III) Chloride*.—This compound is a dark red powder, slightly soluble in ethanol and acetone, insoluble in water and nitrobenzene (Found : Mo, 14.4 ; Cl, 15.8%. Calc. for $\text{Mo}(\text{dipy})_3\text{Cl}_3$: Mo, 14.3 ; Cl, 15.9%). Mol. cond. in absolute ethanol at 25 °C for $M/8000=42.6$ r.o., $\mu_{\text{eff.}}=3.66$ B.M.

(v) *Tris-2,2'-dipyridyl Molybdenum(III) Iodide*.—This compound is a chocolate coloured powder, slightly soluble in ethanol and acetone, insoluble in water and nitrobenzene (Found : Mo, 10.0 ; I, 40.1%. Calc. for $\text{Mo}(\text{dipy})_3\text{I}_3$: Mo, 10.2 ; I, 40.2%). Mol. cond. in absolute ethanol for $M/8000=44.1$ r.o., $\mu_{\text{eff.}}=3.84$ B.M.

(vi) *Tris-2,2'-dipyridyl Molybdenum(III) Bromide*.—This compound is an orange-yellow powder, insoluble in water and ethanol but soluble in nitrobenzene (Found : Mo, 11.8 ; Br, 29.3%. Calc. for $\text{Mo}(\text{dipy})_3\text{Br}_3$: Mo, 11.8 ; Br, 29.2%). Mol. cond. in nitrobenzene at 25 °C for $M/1000=45.3$ r.o., $\mu_{\text{eff.}}=3.84$ B.M.