SHORT COMMUNICATIONS

NEW COMPOUNDS OF MOLYBDENUM(III) WITH BIDENTATE LIGANDS*

By M. C. STEELE†

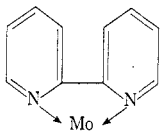
The coordination of bidentate ligands such as *o*-phenanthroline and 2,2′-dipyridyl with molybdenum(III) has not been reported previously.

Octahedral chelate complexes of the type $Mo(phen)_3X_3$ and $Mo(dipy)_3X_3$ (X=Cl, Br, I) have been prepared. Magnetic susceptibilities consistent with the existence of three unpaired electrons are interpreted as arising from $4d^25s5p^3$ 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.*—$(NH_4)_3MoCl_6$ (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 $Mo(phen)_3Cl_3$: 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., $\mu_{eff.}$=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 $Mo(phen)_3I_3$: Mo, 9·1 ; I, 36·1%). Mol. cond. in absolute ethanol at 25 °C for M/8000=43·2 r.o., $\mu_{eff.}$=3·84 B.M.

* Manuscript received May 13, 1957.

† School of Applied Chemistry, N.S.W. University of Technology, Sydney ; present address : Metal Manufactures Ltd., Port Kembla, N.S.W.

(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 $Mo(phen)_3Br_3$: Mo, 10·5 ; Br, 26·3%). Mol. cond. in nitrobenzene at 25 °C for M/1000=43·6 r.o., $\mu_{eff.}=3·84$ 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 $Mo(dipy)_3Cl_3$: Mo, 14·3 ; Cl, 15·9%). Mol. cond. in absolute ethanol at 25 °C for M/8000=42·6 r.o., $\mu_{eff.}=3·66$ 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 $Mo(dipy)_3I_3$: Mo, 10·2 ; I, 40·2%). Mol. cond. in absolute ethanol for M/8000=44·1 r.o., $\mu_{eff.}=3·84$ 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 $Mo(dipy)_3Br_3$: Mo, 11·8 ; Br, 29·2%). Mol. cond. in nitrobenzene at 25 °C for M/1000=45·3 r.o., $\mu_{eff.}=3·84$ B.M.