

## SOME STUDIES IN INORGANIC COMPLEXES

### XIII. CHROMIUM(III) AND MOLYBDENUM(III) WITH 2-AMINOMETHYLPYRIDINE (2-PICOLYLAMINE)

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#### Summary

A study has been made of complexes of chromium(III) and molybdenum(III) with the chelating ligand 2-aminomethylpyridine (2-picolylamine). They are of the type  $\text{Crpic}_3^{3+}$ ,  $\text{Crpic}_2(\text{H}_2\text{O})_2^{3+}$ , and  $\text{Mopic}_3^{3+}$ , in which pic is the ligand 2-picolylamine. Conductance measurements in methanol and nitromethane are in agreement with their structures as six-coordinate complexes. The magnetic moments were found to be in the vicinity of 3.7 B.M. in all cases, showing that the chromium(III) and manganese(III) atoms are spin-free. The following salts were prepared and studied:  $[\text{Crpic}_3]_2[\text{SO}_4]_3 \cdot 3\text{H}_2\text{O}$ ,  $[\text{Crpic}_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ ,  $[\text{Crpic}_2(\text{H}_2\text{O})_2]\text{Br}_3$ ,  $[\text{Crpic}_2(\text{H}_2\text{O})_2][\text{ClO}_4]_3$ , and  $[\text{Mopic}_3][\text{ClO}_4]_3 \cdot 3\text{H}_2\text{O}$ .

#### I. INTRODUCTION

Although Balthis and Bailar (1936) have stated that the ethylenediamine complex  $[\text{Cren}_3]\text{Cl}_3$  may be formed in aqueous solution, it is generally conceded that chromium(III) complexes of bases having nitrogen as the donor atom are only obtained under anhydrous conditions or when the base concentration is greater than that of the water molecules present. The preparation of the ethylenediamine complex  $\text{Cren}_3^{3+}$  by direct combination from anhydrous chromic salts has been described by Rollinson and Bailar (1943) and Fowles and McGregor (1958). Complexes of chromium(III) and 1,10-phenanthroline or 2,2'-bipyridyl have been described by various workers, and a summary of these investigations has been given by Brandt, Dwyer, and Gyarfás (1954). By use of the unsymmetrical chelating ligand 2-picolylamine (2-aminomethylpyridine), it was thought that complexes having 2 or 3 molecules of ligand per chromium atom might be obtained. It was also thought feasible that the chromium congener molybdenum might be coordinated by the ligand in the trivalent state, since Steele (1957) has described the preparation of the phenanthroline and bipyridyl complexes  $[\text{Mophen}_3]\text{X}_3$  and  $[\text{Modipy}_3]\text{X}_3$ .

#### II. RESULTS AND DISCUSSION

When added to aqueous chromic salts, 2-picolylamine precipitates chromic hydroxide. However, under comparatively anhydrous conditions, replacement of aquo molecules by the base takes place with the formation of the yellow complex  $\text{Crpic}_3^{3+}$ . The halides of the latter complex failed to yield pure samples

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of the type  $\text{Crpic}_2\text{X}_2^+$  by careful pyrolysis, due to decomposition of the ligand at the required temperature for the formation of the diacido complexes. In boiling aqueous solution the complex  $\text{Crpic}_3^{3+}$  loses 1 molecule of ligand, which is replaced by two aquo molecules, forming the orange complex  $\text{Crpic}_2(\text{H}_2\text{O})_2^{3+}$ . The corresponding dull yellow molybdenum(III) complex  $\text{Mopic}_3^{3+}$  may also be obtained by allowing the ligand to react with hexachloromolybdate(III) anion in aqueous ethanol. It was found that some of the complexes investigated crystallized as hydrates. The complexes were found to have the expected conductances in methanol and nitromethane of about thrice that of a uni-univalent electrolyte,

TABLE 1

CONDUCTANCES OF COMPLEXES IN  $10^{-3}\text{M}$  CONCENTRATION IN METHANOL AND NITROMETHANE AT  $25^\circ\text{C}$ 

Substance	Con- ductance ( $\Omega^{-1}$ ) in Methanol	Con- ductance ( $\Omega^{-1}$ ) in Nitro- methane	Substance	Con- ductance ( $\Omega^{-1}$ ) in Methanol	Con- ductance ( $\Omega^{-1}$ ) in Nitro- methane
$[\text{Crpic}_3]_2[\text{SO}_4]_3 \cdot 3\text{H}_2\text{O}$	625	419	$[\text{Crpic}_2(\text{H}_2\text{O})_2][\text{ClO}_4]_3$	342	234
$[\text{Crpic}_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ ..	322	213	$[\text{Mopic}_3][\text{ClO}_4]_3 \cdot 3\text{H}_2\text{O}$	355	238
$[\text{Crpic}_2(\text{H}_2\text{O})_2]\text{Br}_3$ ..	336	231			

indicating appreciable stability in these solvents. For comparison, the conductances for uni-univalent electrolytes in nitromethane and methanol are in the vicinity of 65 and  $100 \Omega^{-1}$  respectively. Measurements of magnetic susceptibility gave moments of about 3.7 B.M. for the metal atom in the complexes and showed that with three unpaired electrons in the respective  $3d$  and  $4d$  levels of the chromium and molybdenum atoms no electron-pairing had taken place. The results are non-diagnostic of bond type, but since the complexes are labile in aqueous solution it is likely that outer  $d$  orbitals are used in bond formation. The conductance measurements are summarized in Table 1 and the magnetic measurements are given in Table 2.

TABLE 2

MAGNETIC MEASUREMENTS CORRECTED TO  $20^\circ\text{C}$ 

Substance	$\chi_g \times 10^{-6}$	$\chi_M \times 10^{-6}$	$\chi_{M_1} \times 10^{-6}$	$\mu$ (B.M.)
$[\text{Crpic}_3]_2[\text{SO}_4]_3 \cdot 3\text{H}_2\text{O}$ ..	11.0	12034	12438	3.83*
$[\text{Crpic}_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ .. ..	10.3	5521	5753	3.69
$[\text{Crpic}_2(\text{H}_2\text{O})_2]\text{Br}_3$ .. ..	10.2	5549	5760	3.69
$[\text{Crpic}_2(\text{H}_2\text{O})_2][\text{ClO}_4]_3$ ..	9.1	5478	5722	3.68
$[\text{Mopic}_3][\text{ClO}_4]_3 \cdot 3\text{H}_2\text{O}$ ..	7.1	5481	5779	3.70

\* Per metal atom.

## III. EXPERIMENTAL

The conductance measurements were made with a Philscope model GM4249/01 and cell GM4221. The nitromethane was purified by drying over anhydrous  $\text{CaSO}_4$  and retaining the distillate boiling at  $101\text{--}101.5^\circ\text{C}$ . The methanol (500 ml) was purified by treating with furfural (25 ml) and 10%  $\text{NaOH}$  soln. (60 ml) and refluxing for 8 hr. After distilling, it was dried by heating with magnesium activated with iodine, refluxed and redistilled. Slight corrections were made for low conductances of both solvents. Magnetic measurements were carried out by the Gouy method.

(a) *Tris(2-picolyamine)chromium(III) Sulphate Trihydrate*.—Chromium(III) sulphate hexahydrate was heated at  $110^\circ\text{C}$  for 4 days with intermittent grinding. Portion of the purple powder which resulted (4 g) was treated with excess 2-picolyamine (8 g) until the reaction had subsided and then heated to  $190^\circ\text{C}$ . The residue was then dissolved in 50% ethanol, filtered, and set aside in a refrigerator. The yellow crystals which settled out after 2 days were washed with ethanol and dried in an oven at  $105^\circ\text{C}$  (yield 8.4 g) (Found: C, 39.5, 39.3; H, 5.3, 5.4;  $\text{SO}_4$ , 26.7%. Calc. for  $\text{C}_{36}\text{H}_{54}\text{N}_{12}\text{S}_3\text{O}_{15}\text{Cr}_2$ : C, 39.5; H, 5.1;  $\text{SO}_4$ , 26.3%).

(b) *Tris(2-picolyamine)chromium(III) Chloride Trihydrate*.—Hexaquo chromium(III) chloride was treated with excess thionyl chloride and after the reaction had subsided the mass was heated to  $120^\circ\text{C}$  for 3 hr, crushed, and reheated. Portion of the purplish brown residue (3 g) was treated with 2-picolyamine (6.5 g) and when the reaction had subsided, heated to  $190^\circ\text{C}$ . On cooling, the residue was dissolved in 50% cold ethanol, filtered, and allowed to stand for 2 days in a refrigerator after the addition of 5N  $\text{HCl}$  (5 ml). The golden-yellow crystals which resulted were washed with ethanol and dried at  $105^\circ\text{C}$  (yield 7.7 g) (Found: C, 39.8; H, 5.4; Cl, 20.1%. Calc. for  $\text{C}_{18}\text{H}_{30}\text{N}_6\text{Cl}_3\text{O}_3\text{Cr}$ : C, 40.2; H, 5.6; Cl, 19.9%).

(c) *Bis(2-picolyamine)diaquo chromium(III) Bromide*.—The complex  $[\text{Crpic}_2]_2[\text{SO}_4]_3 \cdot 3\text{H}_2\text{O}$  (3 g) was dissolved in water (12 ml) and boiled for 20 min in the presence of a few drops of  $\text{HBr}$ . On cooling, the solution was treated with conc.  $\text{HBr}$  (5 ml) and the orange coloured soln. set aside for crystallization in a refrigerator for 2 days. Orange crystals resulted which were washed with ethanol and dried at  $105^\circ\text{C}$  (yield 1.4 g) (Found: C, 26.7; H, 3.6; Br, 43.6%. Calc. for  $\text{C}_{12}\text{H}_{20}\text{N}_4\text{Br}_3\text{O}_2\text{Cr}$ : C, 26.5; H, 3.7; Br, 44.2%).

(d) *Bis(2-picolyamine)diaquo chromium(III) Perchlorate*.—Procedure (c) was repeated using 70% perchloric acid (5 ml) in lieu of  $\text{HBr}$ , when orange crystals resulted (yield 1.9 g) (Found: C, 23.9, 23.6; H, 3.3, 3.1%. Calc. for  $\text{C}_{12}\text{H}_{20}\text{N}_4\text{Cl}_3\text{O}_{14}\text{Cr}$ : C, 23.9; H, 3.3%).

(e) *Tris(2-picolyamine)molybdenum(III) Perchlorate Trihydrate*.—A solution of ammonium molybdate in 5N  $\text{HCl}$  was reduced by cathodic reduction in a 250 ml beaker, using a porous pot diaphragm and current from a 6 V accumulator. The red-brown soln. which resulted in the cathodic compartment was treated with conc.  $\text{NH}_4\text{Cl}$  soln. and evaporated to dryness under reduced pressure. The brown solid (2 g) was dissolved in 95% ethanol (15 ml) and treated with excess of 2-picolyamine (2 g), when a brownish colour developed, and after the addition of lithium perchlorate (3 g) in ethanol (10 ml) dull yellow plates settled out. These were washed with ethanol and then with ether and dried at  $105^\circ\text{C}$  (yield 3.6 g) (Found: C, 27.9; H, 4.0; Mo, 12.4%. Calc. for  $\text{C}_{18}\text{H}_{30}\text{N}_6\text{Cl}_3\text{O}_{15}\text{Mo}$ : C, 28.0; H, 3.9; Mo, 12.4%).

## IV. ACKNOWLEDGMENT

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