

MONO COMPLEXES OF 2,2'-BIPYRIDINE AND 1,10-PHENANTHROLINE WITH METAL HALIDES

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Summary

The mono complexes of 2,2'-bipyridine and 1,10-phenanthroline with the halides of Cr(III), Mn(II), and Ni(II) have been prepared in good yield by reaction of the base with excess of the anhydrous metal halide in boiling dimethylformamide solution. The Fe(II) complexes, which could not be prepared satisfactorily in this manner, were made in boiling normal hydrochloric acid, and salted out with solid calcium chloride. The magnetic moments showed that all were of the high-spin type. The high moments of $\text{Fe}(\text{bipy})\text{Cl}_2$ and $\text{Fe}(\text{phen})\text{Cl}_2$ (5.72 and 5.79 B.M.) suggest that the previous value for $\text{Fe}(\text{phen})\text{Cl}_2$ (1.8 B.M.) is in error, and that the change from high- to low-spin does not occur until the third molecule of the ligand has been attached.

I. INTRODUCTION

The ligands 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) are known to form tris, bis, and mono complexes with transition metal ions (Brandt, Dwyer, and Gyarfas 1954). Whereas the former two types are well known, few examples of the mono complexes have been isolated, though dissociation studies have suggested their presence in aqueous solution. Barbieri (1934) has described the preparation of potassium tetracyano(bipyridine)ferrate(II), and Wilkins and Williams (1957) obtained tetraquo(phenanthroline)nickel(II) nitrate from phenanthroline and nickel nitrate in large excess. The method has been extended to the nickel complexes of bipyridine, and various substituted phenanthrolines and bipyridines (Ellis, Hogg, and Wilkins 1959). Harris and Lockyer (1958) have described some monophenanthrolineiron(III) complexes. It is well known that whereas the hydrated iron(II) ion is paramagnetic, the tris(phenanthroline) and (bipyridine) complexes are diamagnetic, and it is of theoretical interest to determine where the change from high- to low-spin occurs. Basolo and Dwyer (1954) showed that the blue $\text{Fe}(\text{bipy})_2\text{Cl}_2$ and $\text{Fe}(\text{phen})_2\text{Cl}_2$ were of the high-spin type, but the red $\text{Fe}(\text{bipy})\text{Cl}_2$, obtained from the bis complex by pyrolysis, was found to have a moment of 1.8 B.M. The expected moment for low-spin planar Fe(II) is 2.5 B.M., and the low moment was ascribed to metal-metal interaction.

The mono complexes described in the present paper have been prepared either in dimethylformamide (dmf) solution using the anhydrous metal halide, or in normal hydrochloric acid solution. The latter method gave the better results with the iron mono compounds, but low yields of the manganous and nickel compounds. All substances were coloured, hygroscopic, crystalline solids. Those prepared in dimethylformamide separated originally with one molecule of the solvent, which could be removed only by heating at 100–150 °C in a vacuum. The chromium compound $\text{Cr}(\text{phen})\text{Cl}_3 \cdot \text{dmf}$ was stable at 150 °C/2 mm. With

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the exception of this substance all were easily soluble in water and methanol but underwent disproportionation rapidly, especially in aqueous solution. Under suitable conditions the mono complexes are useful for the preparation of complexes with "mixed" ligands, for example, $[\text{Ni}(\text{bipy})(\text{phen})_2]\text{Cl}_2$, to be described subsequently.

The magnetic moments of all substances showed that they were of the high-spin type. The iron(II) compounds, prepared in hydrochloric acid, were rose-red in colour, and gave the rather high values of 5.7 B.M. for the bipyridine complex, and 5.8 B.M. for the phenanthroline complex. These are slightly outside the normal range (5.0–5.5 B.M.) usually observed (Selwood 1956). Pyrolysis of $[\text{Fe}(\text{bipy})_3]\text{Cl}_2$ or $[\text{Fe}(\text{bipy})_2\text{Cl}_2]$ as described by Basolo and Dwyer (1954) gave a dark red solid ($\mu=4.8$ B.M.). Both the rose-red and dark red varieties disproportionated rapidly in methanol and water, but the difference in colour was still evident when both varieties were ground up to the same particle

TABLE 1
MAGNETIC MOMENTS OF MONO COMPLEXES

Substance	μ (B.M.)	$\mu_{\text{calc.}}$ (B.M.)
Cr bipy $\text{Cl}_3\cdot\text{dmf}$	3.77	3.88
Cr phen $\text{Cl}_3\cdot\text{dmf}$	3.72	3.88
Mn bipy Cl_2	5.87	5.92
Mn phen Cl_2	5.83	5.92
Ni bipy Cl_2	3.29	2.83
Ni bipy Br_2	3.52	2.83
Ni phen Cl_2	3.34	2.83
Ni phen Br_2	3.33	2.83
Fe bipy Cl_2	5.72	4.90
Fe phen Cl_2	5.79	4.90
Fe trpy Cl_2	4.60	4.90

size. The substance may well exhibit dimorphism. All attempts to prepare the variety with the low moment (1.8 B.M.) failed. It is also significant that 2,2',2''-terpyridinedichloroiron(II), $[\text{Fe}(\text{trpy})\text{Cl}_2]$, was found to have the normal high moment of 4.60 B.M. It is concluded that the previous value for the iron(II) mono compound is probably in error. It has usually been found that there is a stepwise decrease in the affinity of a metal ion for the progressive addition of ligands (Taube 1952), but this order is reversed for the iron(II) phenanthroline and bipyridine systems (Lee, Kolthoff, and Leussing 1948; Baxendale and George 1950), and presumably for the terpyridine system. The paramagnetism of both the mono and bis complexes confirm the presence of strong ligand field stabilization in the diamagnetic tris species, and is consistent with the reversed order of stepwise ligand affinity.

A 5-covalent distorted trigonal bipyramidal structure probably occurs in dichloroterpyridine iron(II), analogous to the cadmium, zinc, and copper(II) complexes (Corbridge and Cox 1956).

II. EXPERIMENTAL

(a) *Mono Complexes of Fe(III), Mn(II), Cr(III), Ni(II) Halides*.—The anhydrous halide of the metal (1 g) was dissolved completely in dry dimethylformamide (10 ml). A trace of zinc dust was added to effect dissolution of chromium(III) chloride (Burstall and Nyholm 1950), and the solution then filtered. Phenanthroline or bipyridine (1 mole) was added to the hot solution, which was kept agitated whilst being refluxed. After about a minute, solid commenced to separate, causing violent "bumping". After 10 min the mixture was cooled to room temperature, the solid collected and washed with cold dimethylformamide, and then dry ether. At this stage, the Fe(III) and Mn(II) complexes were pale yellow, the Cr(III) dark green, and the nickel compounds bright green, and contained a molecule of dimethylformamide. At 150 °C/10⁻² mm, the Mn(II), Fe(III), and Ni(II) but not the Cr(III) complex lost the solvent of crystallization. The nickel complex became yellow-green after removal of the dimethylformamide (Found: C, 36.0; H, 2.0%. Calc. for Ni(C₁₂H₈N₂)Br₂: C, 36.1; H, 2.0%); (Found: C, 46.1; H, 2.6; N, 9.0%. Calc. for Ni(C₁₂H₈N₂)Cl₂: C, 46.5; H, 2.6; N, 9.0%); (Found: C, 42.2; H, 3.0; Cl, 25.2%. Calc. for Mn(C₁₀H₈N₂)Cl₂: C, 42.6; H, 2.9; Cl, 25.2%); (Found: C, 46.7; H, 2.6; N, 9.1%. Calc. for Mn(C₁₂H₈N₂)Cl₂: C, 47.1; H, 2.6; N, 9.2%); (Found: C, 39.7; H, 4.1%. Calc. for Cr(C₁₀H₈N₂)Cl₂: C, 40.3; H, 3.9%); (Found: C, 43.2; H, 3.6; N, 10.1%. Calc. for Cr(C₁₂H₈N₂)Cl₂: C, 43.8; H, 3.7; N, 10.2%); (Found: C, 42.0; H, 2.8; Cl, 24.5%. Calc. for Ni(C₁₀H₈N₂)Cl₂: C, 42.0; H, 2.9; Cl, 24.9%); (Found: C, 32.3; H, 2.2; N, 7.4; Br, 42.5%. Calc. for Ni(C₁₀H₈N₂)Br₂: C, 32.1; H, 2.2; N, 7.5; Br, 42.7%).

(b) *Mono Complexes of Iron(II) Chloride*.—Iron(II) chloride 4-hydrate (6 g; 1 mole) in HCl (1N; 15 ml) was heated at 50–60 °C with finely divided iron metal (0.5 g) to reduce traces of iron(III) chloride. The mixture was filtered into a test tube filled with carbon dioxide and containing silver wool (0.2 g). After heating to boiling, the solution was decanted onto the base (0.1 mole; phenanthroline, bipyridine, or terpyridine) and carbon dioxide passed through the deeply coloured solution whilst it was boiled for 2 min. Calcium chloride 6-hydrate (13 g) was then added, and immediately rose-red crystals of [Fe(bipy)Cl₂] or [Fe(phen)Cl₂], or purple-red [Fe(trpy)Cl₂], commenced to deposit. After 2 min the product was collected and washed with absolute ethanol containing a drop of HCl, followed by absolute ethanol, and finally peroxide-free ether (yields: [Fe(bipy)Cl₂], 56%; [Fe(trpy)Cl₂], 75%; [Fe(phen)Cl₂], 95%) (Found: C, 42.4; H, 2.9; N, 9.8%. Calc. for Fe(C₁₀H₈N₂)Cl₂: C, 42.4; H, 2.9; N, 9.9%); (Found: C, 50.0; H, 3.2; N, 11.4%. Calc. for Fe(C₁₅H₁₁N₃)Cl₂: C, 50.0; H, 3.1; N, 11.7%); (Found: C, 46.9; H, 2.6; N, 9.1%. Calc. for Fe(C₁₂H₈N₂)Cl₂: C, 46.9; H, 2.6; N, 9.1%).

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