2,2′-Bipyridyl and 1,10-Phenanthroline Complexes of Oxochromium (v)

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Summary $[CrO(bipy)Cl_3]$ and $[CrO(phen)Cl_3]$ have been isolated from dehydrochlorination of the corresponding monodi-imine salts of hypothetical $H_2[CrOCl_5]$ in an inert atmosphere.

FEW five-valent chromium complexes have been reported and all are moisture sensitive. Among these, the only six-co-ordinate complex is the alkali metal salt of the ion, $[CrOCl_5]^{2-}$.[1] Here we report the preparation and characterization of two stable complexes of oxochromium-(v), $[CrO(bipy)Cl_3]$ (I) and $[CrO(phen)Cl_3]$ (II).

The complex $bipyH_2[CrOCl_5]$ was obtained as brown crystals, stable in dry air, from the reaction of CrO_3 with 2,2′-bipyridyl hydrochloride in concentrated HCl at 0°C. The compound was characterized by elemental analysis, bulk susceptibility measurement (1·69 B.M. at 24°), i.r. [ν(Cr=O) at 934 cm^{-1}], and reflectance spectrum (λ_{max} 13,800 and 23,000 cm^{-1}). The complex $[CrO(bipy)Cl_3]$ was obtained (brown crystals, stable in air, insoluble in water and common solvents but slightly soluble in acetone, readily soluble in aqueous alkalis to give a brown solution which slowly disproportionates) from the dehydrochlorination of the dipyridyl salt in dry CO_2 atmosphere at 80° according to reaction (1). The compound was characterized by

$$bipyH_2[CrOCl_5] \xrightarrow{80^\circ} [CrO(dipy)Cl_3] + 2HCl \qquad (1)$$

elemental analysis, inability to form any AgCl on trituration with $AgNO_3$ solution, nonconducting solution in acetone (18 ohm^{-1} cm^2), bulk susceptibility measurement (1·85 B.M. at 24°), i.r. [ν(Cr=O) at 954 cm^{-1}], and reflectance spectrum (λ_{max} at 14,920, 18,870, and 24,100cm^{-1}). Compound (II) was obtained by using phenanthroline instead of bipyridyl; it had similar properties to that of compound (I) and was characterized as for compound (I) (μ_{eff} = 1·87 at 24°, $\nu_{Cr=O}$ 957 cm^{-1}, λ_{max} 15,000, 18,570, and 24,350 cm^{-1}. Results are consistent with the studies for $[CrOCl_5]^{2-}$ (ref. 2) and similar to the corresponding molybdenum analogues.[3] Further studies are in progress.

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