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The Chemistry of Oxohalochromates(V)

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Although oxopentachlorochromates(V) and oxotetrachlorochromates(V) have been known for almost eighty years [1–4], there are still only a few examples of these complexes which have been authentically characterised. There have been a number of investigations made upon these complexes (principally e.s.r. spectral studies) [5–16], but much of the work appears to have been carried out with either impure or uncharacterised compounds [12]. Ziebarth and Selbin have reported [12] the only detailed study, upon species of the type $M_2[CrOCl_5]$ (M = Cs, Rb) and $(R_4N)[CrOCl_4]$ (R = alkyl groups). As part of an extensive study of the chemistry of chromium(V), we present here a preliminary account of some related complexes, principally of the type $LH_2[CrOCl_5]$ { L = 2,2′-dipyridyl (2,2′-dipy), 4,4′-dipyridyl (4,4′-dipy)} and $LH[CrOCl_4]$ { L = pyridine (py), quinoline (quin), iso-quinoline (isoquin)}, comment upon a number of anomalies in the literature, and report the preparation of a new series of complexes containing the anion $[CrCl_4(CH_3COOH)_2]^-$, and related bromo- analogues.

All the chromium(V) complexes (listed in the Table) were prepared (using a method based on that developed by Weinland and Fiederer [4]) by dissolving chromium(VI) oxide in glacial ethanoic acid saturated with hydrogen chloride, adding the appropriate base (or the chloride salt of the appropriate cation) dissolved in a second solution of glacial ethanoic acid (usually containing dissolved hydrogen chloride), and finally resaturating the mixture with hydrogen chloride. The elemental analyses of these complexes were in good agreement with theory, and the magnetic moments (see Table) confirmed that they were indeed chromium(V) complexes. The literature contains a number of contradictions with respect to the assignment of the infrared spectra of some of these complexes. For $(Ph_4As)[CrOCl_4]$, we agree with the assignments of Ziebarth and Selbin [12], and differ from those of Majumdar and Mitra [16]: for $Cs_2[CrOCl_5]$, we agree with the data of Brown [8], and differ from those of Ziebarth and Selbin [12] and Wendling [10]. The infrared spectrum of $(pyH)[CrOCl_4]$ has been depicted [6] (but no assignments were made), but no analysis figures for the complex were reported: our spectrum differs from the spectrum shown.

TABLE. Magnetic and I.r. Data.

	Colour	μ_{eff}/BM	μ_{eff}/BM (lit.)	ν(Cr=O)/cm^{-1}	ν(Cr=O)/cm^{-1} (lit.)	ν(Cr–Cl)	ν(Cr–Cl) (lit.)
$(pyH)[CrOCl_4]$	Dark Red	1.78	–	1019	–	398, 382 (s, d), 343 (sh)	–
$(quinH)[CrOCl_4]$	Dark Red	1.75	–	1016	–	397 (s), 347 (sh)	–
$(isoquinH)[CrOCl_4]$	Dark Red	1.84	–	1016	–	398 (s), 348 (sh)	–
$(Et_4N)[CrOCl_4]$	Dark Red	1.78	1.78 [12]	1022	1035 [12]	395 (s), 348 (sh)	395 [12]
$(Ph_4As)[CrOCl_4]$	Yellow–Brown	1.62	1.65 [12]	1019	948 [16], 1020 [12]	398 (s)	405 [12]
$(2,2'\text{-dipy}H_2)[CrOCl_5]$	Brown	1.77	–	$*^a$	–	366 (s)	–
$(4,4'\text{-dipy}H_2)[CrOCl_5]$	Dark Brown	1.78	–	$*^a$	–	354 (s)	–
$Cs_2[CrOCl_5]$	Dark Red		1.85 [12]	927	945 [12], 925 [8], 930 [10]	334 (s), 312 (sh)	340 [12], 336 [8], 343 [10]

^{a}$*$ = Obscured by ligand bands; s = strong; d = doublet; sh = shoulder.

The complex $K_2[CrOCl_5]$ has been reported in three different publications in the past twenty years [6, 7, 9]. None of these report either elemental analysis or infrared data below 600 cm^{-1}, and only one of these [7] reports a magnetic moment (1.93 BM). We have attempted to repeat the preparations described [2, 4, 6, 7, 9] for this complex, but on no occasion has a pure sample of $K_2[CrOCl_5]$ been obtained. The sample was always contaminated with varying amounts of $K_2[CrCl_5(H_2O)]$, resulting in high magnetic moments, and a band below 600 cm^{-1} in the infrared spectrum due to ν(Cr–O). The nature of the sample varied from dark-red crystals (the purest samples [2]) to an orange–brown powder, depending upon the method of preparation employed. By slightly increasing the amount of water used in the preparations, a pure sample of $K_2[CrCl_5(H_2O)]$, an orange–brown powder, was prepared. It should be noted that the theoretical elemental analysis figures for $K_2[CrOCl_5]$ and $K_2[CrCl_5(H_2O)]$ are closely similar.

When the reaction mixture from which (quinH)$[CrOCl_4]$ could be isolated was allowed to stand at *ca.* 5 °C for several weeks, the dark-red chromium(V) complex was slowly reduced, giving a bright purple chromium(III) complex. Analysis of this product showed it to be (quinH)$[CrCl_4(CH_3COOH)_2]$. Similarly, when the reaction mixture from which (quinH)$[CrOCl_4]$ could be isolated was heated under reflux for several hours, cooled, and resaturated with hydrogen chloride, the product was again (quinH)$[CrCl_4(CH_3COOH)_2]$. $(Et_4N)[CrCl_4(CH_3COOH)_2]$ and $(pyH)_2[CrCl_5(CH_3COOH)]$ were prepared in a similar manner. Attempts to prepare (pyH)$[CrOBr_4]$ and (quinH)$[CrOBr_4]$ by an analogous method to that used for the chloro- complexes, using hydrogen bromide instead of hydrogen chloride, resulted in the preparation of the green crystalline $(pyH)_2[CrBr_5(CH_3COOH)]$ and the dark red–brown crystalline (quinH)$[CrBr_4(CH_3COOH)_2]$, respectively. Complexes containing the anion $[CrX_4(CH_3COOH)_2]^-$ show infrared absorptions similar to those observed for complexes containing $[MX_4(CH_3COOH)_2]^-$ (M = Ti, V; X = Cl, Br) [17, 18], have reflectance spectra showing bands consistent with a ligand field of four halide ions and two ethanoic acid molecules around chromium(III), and possess magnetic moments characteristic of six-coordinate chromium(III) complexes.

Finally, attempts to prepare the recently reported complex, $(2,2'\text{-dipyH}_2)[CrOBr_5]$ [19], under the conditions described, yielded a material (with properties similar to those described) which has been shown to be a mixture with a high perbromide content. Perbromide formation has been observed in previous attempts to prepare oxobromochromates(V) [12].

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