

Syntheses of oxochlorochromates(V)

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Abstract. Syntheses of three stable complexes of Cr(V) have been described which were characterised by elemental analysis, IR, electronic spectral, ESR and magnetic studies. The size and charge of the counter ion determines the overall composition of the Wienland salts. Apparently the isolation of oxotetra-, penta- and hexachlorochromates(V) of benzimidazolium, biquinolinium and terpyridinium cations respectively were achieved. These oxochlorochromates possibly contained the same oxotetrachlorochromate(V) species.

Keywords. Cr(V); oxochlorochromates(V); Wienland salts.

1. Introduction

Our earlier work (Majumder and Mitra 1975; Mitra 1979; Majumder and Saha 1976) on the syntheses of chromium(V) compounds, together with others from the literature, corroborates the general impression of preparative chemists, which has been described as 'inorganic symbiosis' by Jorgenson (1964) and elaborated by Basolo (1968) that ions of similar size, charge and shape usually tend to associate with like ions to produce crystals of good stability. Often this is a useful guide for chemical syntheses. If the counter ions are large and univalent, oxotetrachlorochromates(V) like $M[\text{CrOCl}_4]$ (where $M = R_4N$, $R = \text{alkyl group, PyH, Ph}_4\text{As, Ph}_4\text{P}$ etc) are isolated from a solution of $\text{Cr}^{\text{V}}\text{OCl}_3$ containing HCl. On the other hand, if the cations are large and bivalent $\text{RH}_2[\text{CrOCl}_5]$ are isolated (where $R = \text{phenanthroline, bipyridine, phenazine}$ etc). With these cues it was decided to study the effects of uni-, bi- and trivalent cations on the overall composition and properties of the oxochlorochromates(V) and hence the following experiments were undertaken.

2. Materials and methods

2.1 Materials

The preparation and/or purification of chromylchloride, acetic acid, benzene, etc. have been described earlier (Majumder and Mukhopadhyay 1973). Benzimidazole was prepared by the condensation of *o*-phenylenediamine with formic acid in alkaline solution. The crude benzimidazole was purified from water and the m.p. found to be 171°C, 2,2'-biquinoline (GR, E. Merck) and 2,2',6',2'' terpyridine (Fluka AG) were used as such.

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2.2 Synthetic outlines

The preparative method used here was a slight modification of the classical method of Meyer and Best (1899) and of Wienland and Friederger (1907). We have used pure chromyl chloride in anhydrous acetic acid through which dry HCl gas was passed under cold conditions (0°C). To this reduced chromyl chloride (presumably containing CrOCl₃ plus HCl) the base (also dissolved in acetic acid) was added (actually pumped into the solution in a specially designed all glass apparatus fitted with a filter stick). Filtration was done in the same assembly by tilting the flask out of contact with the atmosphere. The compound was washed with cold purified acetic acid and finally with benzene and left overnight in a vacuum desiccator over conc. H₂SO₄. The yields were excellent. The methods of analysis have been described earlier (Majumder and Mitra 1975).

2.3 The infrared spectra

The IR spectra were recorded in the KBr phase. The electronic spectra were recorded on a Beckmann DU 2 spectrophotometer at room temperature. Magnetic susceptibilities were measured in a Guoy balance at room temperature (25°C). HgCo(SCN)₄ was used as the calibrant. Calculations and corrections of the magnetic moment values were made according to Figgis and Lewis. The ESR instrument was an X-band spectrometer (at the Saha Institute of Nuclear Physics, Calcutta, through the courtesy of Dr. Asis Roy) operating near 9.44 GHz, using a 100 kHz field modulation. The first derivative ESR spectra were recorded.

3. Results and discussions

Analytical and spectral data are presented in tables 1 and 2, the ESR spectra in figure 1. Conductances of II and III could not be measured due to the non-availability of a suitable solvent. II and III on dissolution in some solvents (e.g. acetonitrile, nitromethane) yielded white precipitates of the hydrochlorides of biquinoline and terpyridine. Molar conductance of I in acetone was found to be 125 ohm⁻¹ cm² mol⁻¹ indicating a 1:1 type of electrolyte.

The substances were apparently magnetically dilute and the IR spectra showed no evidence for either Cr=O . . . Cr or Cr-Cl . . . Cr interactions. The Cr(V) was in a 2D ground state term. Contributions due to Van Vleck paramagnetism (TIP) were also not expected. Although in the present case susceptibilities could not be measured at different temperatures, the values obtained for the magnetic moments which were close to the spin only value point clearly to the pentavalency of chromium, corroborating the chemical evidences like the oxidation state determined and the other chemical tests. The ESR spectra (figure 1) of the solid powders also pointed to a *d*¹ state.

The IR spectra reveal the presence of Cr-O and a C_{4v} point group is indicated. For the oxotetrachlorochromate(V) in I, the peaks (in cm⁻¹) at 1005 *m* and 950 *m* are due to ν(Cr=O) stretching vibrations (Kon and Sharpless 1965a, b; Ziebarth and Selbin 1970; Seddon and Thomas 1977). The strong and sharp band at 950 cm⁻¹ for II and at 928 cm⁻¹ for III appears to be due to ν(Cr=O) stretching vibrations. In the absence of more detailed and careful spectral studies, definitive and detailed interpretations of IR data cannot be made.

Table 1. Analytical and magnetic data of the oxochlorochromates(V).

Compound	Colour	Elemental analysis			Oxidation state	μ_{eff} (B.M.) at 298°C
		Cr	Cl	N		
I $\text{C}_7\text{H}_6\text{N}_2[\text{CrOCl}_4]\text{H}_2\text{O}$ Benzimidazolium oxotetra-chlorochromate(V) monohydrate	Shiny red	15.00 (14.98)	41.00 (40.92)	8.16 (8.10)	5.02 5.00	1.81
II $\text{C}_{18}\text{H}_{12}\text{N}_2\text{H}_2[\text{CrOCl}_5]2\text{H}_2\text{O}$ Biquinolinium oxopentachlorochromate(V) dihydrate	Yellow	9.62 (9.64)	33.14 (32.90)	4.99 (5.13)	4.99 5.00	1.83
III $\text{C}_{15}\text{H}_{11}\text{N}_3\text{H}_3[\text{CrOCl}_6]$ Terpyridinium oxohexachlorochromate(V)	Yellow	10.04 (10.06)	41.00 (41.19)	8.10 (8.12)	5.02 5.00	1.78

Along with the scantiness of literature in electronic spectral studies, doubts exist not only in the assignment of bands but even in the number and positions of peaks. Results of electronic spectral measurements in nujol mull along with the IR peak due to Cr=O stretch are presented in table 2. The peak around 18 kK has been noted by Kon and Sharpless (1965a,b), Ziebarth and Selbin (1970), and also by Seddon and Thomas (1977). This is a narrower band which is unsplit and of higher intensity than the band

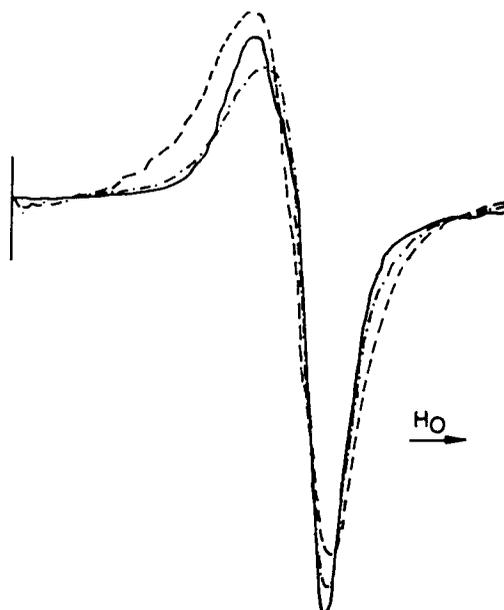


Figure 1. ESR spectra of compounds I (—), II (-----) and III (- · - · -). Central field = 3300 Gauss; sweep = 250.

Table 2. IR bands and electronic spectral data of oxochlorochromates(V).

Compound	(Cr=O)cm ⁻¹	Electronic spectral peaks in kK (ϵ_M)
I	1005 m, 950 s	23.81, 22.22, 16.39, 15.62, 14.29, 13.0, 12.2 (nujol) 24.39 (1127.8), 22.22 (815.5), 17.25 (98.9), 12.5 (15.2) (acetone)
II	950 s	24.39, 22.72, 18.5, 13.85, 13.0 (nujol) 25.63 (1292.3), 22.72 (357.5), 16.96 (108.7), 11.9 (25.3) (acetone)
III	928 s	25.00, 23.25, 18.08, 14.08, 13.3, 12.3 (nujol)

around 13 kK which appears to be the measure of 10 Dq. The spectra cannot possibly be interpreted in terms of a simple crystal field theory because of the existence of considerable π -bonding between Cr and O. The broad similarities of the mull spectra of the three types of oxochlorochromates(V) appears to indicate the presence of the same point group C_{4v} (viz CrOCl_4).

4. Concluding remarks

From the principle of inorganic symbiosis and from the above considerations, it appears that the nature, particularly the charge, of the counterion dictates the composition of the precipitating solid but discrete ions like $[\text{CrOCl}_5]^{2-}$ or $[\text{CrOCl}_6]^{3-}$ are probably not present. Large univalent cations (Van der Waals radii $> 3.4\text{Å}$) naturally would give crystals like $M[\text{CrOCl}_4]$. But smaller cations $M^1 \leq 1.67\text{Å}$ (Cs^+) would give $M\frac{1}{2}[\text{CrOCl}_5]$ due to packing requirements. II and III of the present work are probably $(\text{BiquH}_2)\text{Cl}[\text{CrOCl}_4]$ and $(\text{Terpy H}_3)\text{Cl}_2[\text{CrOCl}_4]$. Without further work particularly x-ray studies, it is hardly possible to say anything definite about the stereo-chemistry of oxochlorochromate(V) anions. The tendency of assigning a definite coordination number and a given stereochemistry from chemical analysis alone may often be misleading as the following example (Zaslow and Ferguson 1967) will show. CuCl_3^- and CuCl_4^{2-} are known in solids and also in solutions but CuCl_5^{3-} is known mainly in the solid state e.g. $(\text{dien H}_3)-[\text{CuCl}_5]$ (dien = diethylene triamine) X-ray studies show that the crystals of the latter actually contain $[\text{dien H}_3]\text{Cl}[\text{CuCl}_4]$ and not $[\text{CuCl}_5]^{3-}$.

The packing in a crystal possibly determines part of the stability and some physical features as well. $M\frac{1}{2}[\text{CrOCl}_5]$ ($M^1 = \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+$) type is somewhat hygroscopic, slowly turns pasty and decomposes easily, almost constantly losing chlorine like the $\text{RH}[\text{CrOCl}_4]$ ($R = \text{pyridine, picolines, quinoline etc}$). But some compounds of Cr(V) like the tetraphenyl arsonium, tetraphenyl phosphonium, biquinolinium and terpyridinium compounds are of much better stability and of much less hygroscopicity. It may be that the flexible chains of relatively heavier biquinoline and terpyridine molecules favour more compact packing, thereby increasing the lattice energy and making attack by atmospheric moisture more difficult. Similarly, the much better spherical nature of tetraphenyl arsonium with the similar oxotetrachlorochromate(V) give decent crystals and it is not surprising that the only single crystal study (Gahan *et al* 1977) on a oxochlorochromate(V) compound was that on $\text{Ph}_4\text{As}[\text{CrOCl}_4]$.

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