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A Study of Some Solvolysis Reactions of Bis(trimethylamine)chromium(III) Chloride

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Two competing reactions are present when benzene solutions of the five co-ordinate complex $CrCl_3 \cdot 2NMe_3$ are treated with donor molecules viz., a) ligand substitution via solvolysis of metal–nitrogen bonds and b) the independent decomposition of the bis-trimethylamine adduct into tri-μ-chloro-trichlorotris(trimethylamine) dichromium(III), $Cr_2Cl_6(NMe_3)_3$, and trimethylamine. For all but very feeble donors reaction a) predominates and in the ensuing adduct formation the chromium(III) ions assume hexacoordination, e.g. pyridine and tetrahydrofuran react immediately to give the corresponding $CrCl_3 \cdot 3L$ complexes. Reaction b) shows second order kinetics with a rate constant $k = 0.160$ l mole^{-1} sec^{-1}. The spectral and magnetic properties of the binuclear compound $Cr_2Cl_6(NMe_3)_3$ have been interpreted in terms of adjacent six co-ordinate metal atoms and a proposed structure is based on two fused octahedra sharing a common trigonal face. The product obtained on treatment of $CrCl_3 \cdot 2NMe_3$ with $AgClO_4$ involves only bidentate (C_{2v}) perchlorate ions as co-ordinated ligand and is formulated as $Cr(ClO_4)_3$.

Introduction

Where direct reaction of chromium(III) chloride with donor molecules proves obdurate, ligand substitution reactions featuring the tris-adducts $CrCl_3 \cdot 3C_4H_8O$ and $CrCl_3 \cdot 3C_5H_5N$ offer a practical alternative[1]. Apart from the obvious stereochemical implication the bis-adduct $CrCl_3 \cdot 2NMe_3$ should behave in similar fashion; indeed with tris(2-aminoethyl)amine (tren) as ligand, the six co-ordinate compounds $CrCl_3 \cdot$(tren) and [Cr (tren)$_2$]Cl$_3$ have been prepared by this approach.[2] From corresponding studies with hexamethylcyclotrisilazane[3] and tetrakisdimethylaminodiboron[4] however, it appears that ligand replacement is not a consistent theme and adverse kinetic factors alone cannot be held responsible.

We now find that this apparent disparate behaviour between ligands is caused by the presence of the halogen-bridged chromium(III) compound $Cr_2Cl_6(NMe_3)_3$ which results from decomposition of the parent bis-trimethylamine adduct. In this report we describe the formation and characterisation of this binuclear species and comment on the general pattern of solvolysis reactions of $CrCl_3 \cdot 2NMe_3$.

Experimental

Materials

Chromium(III) chloride (Pfaltz and Bauer Inc., Flushing N.Y.) was obtained as the anhydrous material and its bis-trimethylamine adduct was prepared following the method of Fowles *et al.*[5]. Hydrogen chloride and carbon dioxide were used directly from their storage cylinders (BDH Chemicals Ltd., Poole). The liquid ligands and benzene were stored over calcium hydride and phosphoric oxide and distilled in vacuo when required.

Physical Measurements and Analyses

Infra red spectra were recorded on Perkin Elmer 621 (4000–200) cm^{-1} and Fourier FS 720 (400–50) cm^{-1} spectrometers as nujol and fluorolube mulls. Absorption spectra were recorded on a Cary 14 instrument with samples either as solutions in 1 cm sealed silica cells or as thin nujol mulls between silica plates and KBr discs. A Wayne Kerr Universal B221 conductance bridge was used for conductivity measurements the particular conductivity cell being calibrated with standard aqueous KCl solutions. Readings were taken at 298.0 ± 0.1 K on samples approximately $1 \times 10^{-3} M$ in dichloromethane. For molecular weight measurements a Mechrolab 301 A vapour pressure osmometer was used with benzil as calibrant. Magnetic susceptibility measurements were obtained by the standard Gouy procedure. Carbon, hydrogen, oxygen and nitrogen analyses were performed by the A. Bernhardt Microanalytical Laboratory, Mullheim, Germany. Chloride was determined by the Volhard titration method and chromium was estimated spectrophotometrically following oxidation to chromate.

Reactions

All manipulations were carried out in a glove-box under a dry oxygen-free nitrogen atmosphere and, where appropriate, in sections of a standard glass high-vacuum system. In a typical reaction the bis(trimethylamine)chromium(III) chloride adduct (~2 g) was sealed in a glass ampoule with a twenty-fold excess of the particular ligand and benzene (~20 ml) as solvent. The vessel was then placed on a mechanical shaker until reaction was adjudged complete. After removal of trimethylamine, solvent and unused ligand by thorough washing with n-hexane on the vacuum system, the solid product remaining was pumped *in vacuo* at room temperature for several hours prior to being sealed into ampoules under a nitrogen atmosphere.

Formation of $Cr_2Cl_6(NMe_3)_3$

Bis(trimethylamine)chromium(III) chloride slowly decomposes in benzene solution, over a period of ~2 weeks, to yield a lilac precipitate. Following removal of trimethylamine and undecomposed starting material (by extraction with benzene) the lilac complex tri-μ-chloro-trichlorotris(trimethylamine) dichromium (III) was isolated. *Anal.* Calcd. for $C_9H_{27}Cl_6N_3Cr_2$: C, 21.9; H, 5.4; Cl, 43.1; N, 8.5; Cr, 21.1. Found. C, 21.8; H, 5.3; Cl, 43.2; N, 8.4; Cr, 20.9. *Mol. Wt.* Calcd. 494, Observed (osmometric) 520. $\Lambda_M = 2.1$ ohm^{-1} cm mole^{-1} for a $10^{-3} M$ solution in CH_2Cl_2. The infra-red spectrum contained bands at 3100 (vs), 3025 (m), 2995 (w), 2930 (w), 2910 (m), 2858 (w), 2830 (w), 2795 (w), 1480 (vs), 1465 (vs), 1405 (m), 1370 (w), 1260 (w), 1230 (m), 1108 (m), 1035 (m), 1018 (w), 980 (vs), 818 (w), 720 (m), 680 (m), 530 (m), 445 (w), 425 (w), 364 (s), 354 (vs), 297 (m), 255 (m), 202 (w), 176 (w) and 151 (w) cm^{-1} respectively.

Attempted reactions of $CrCl_3 \cdot 2NMe_3$ with carbon dioxide, carbon disulphide and di-iso-propylether

In each case no immediate reaction occurred but a common lilac precipitate was obtained over a period of several weeks with accompanying release of trimethylamine. This precipitate was extracted with benzene and found to be identical to the $Cr_2Cl_6(NMe_3)_3$ complex described above.

Reaction of $CrCl_3 \cdot 2NMe_3$ with pyridine

Bis(trimethylamine)chromium(III) chloride reacted immediately with pyridine to give release of trimethylamine and a dark green solution. After removal of solvent and extraction with $CHCl_3$ the dark green tris (pyridine)trichlorochromium(III) was obtained in 100% yield. The infra red spectrum was identical to that of an authentic sample.[6]

Reaction of $CrCl_3 \cdot 2NMe_3$ with tetrahydrofuran

The reaction between the chromium(III) adduct and tetrahydrofuran was immediate and provided release of trimethylamine, a pale purple solution and a purple precipitate. Removal of solvent yielded the purple solid tris(tetrahydrofuran)trichlorochromium(III) in 100% yield. The infra red spectrum was identical to that of an authentic sample.[7]

Reaction of $CrCl_3 \cdot 2NMe_3$ with hydrogen chloride

The reaction with dry HCl gas, co-condensed with benzene into the reaction vessel, yielded a clear benzene solution and a purple precipitate. After removal of solvent a white crystalline solid was obtained from the purple residue, either by vacuum sublimation at T = 450 K, or soxhlet extraction with chloroform, which was identified as $Me_3NH^+Cl^-$ (yield: expected, 0.98 g; obtained, 0.93 g). The purple residue was chromic chloride. *Anal.* Calcd. for $CrCl_3$: Cr, 32.9; Cl, 67.1. Found. Cr, 32.1; Cl, 66.7.

Reaction of $CrCl_3 \cdot 2NMe_3$ with silver perchlorate

A benzene solution of $CrCl_3 \cdot 2NMe_3$ was added in a 1:3 molar ratio to a stirred benzene solution of $AgClO_4$. The reaction was immediate and the red colour initially imparted to the solution rapidly dispersed to give a dark green solution and a white precipitate with release of trimethylamine. The white precipitate of silver chloride was filtered and washed with benzene (yield: expected 2.01 g; obtained 1.95 g). Removal of solvent from the filtrate yielded a dark green solid. The infra red spectrum contained bands at: 1261 (m), 1180 (m), 1122 (s), 1079 (s), 1018 (s), 981 (m), 895 (m), 850 (m), 818 (m), 722 (w), 681 (w), 655 (m), 619 (s), 602 (s), 489 (w), 390 (m) and 348 (w) cm^{-1} respectively.

Reaction of $Cr_2Cl_6(NMe_3)_3$ with pyridine

The binuclear chromium(III) adduct reacted immediately with excess pyridine to give a green solution. After removal of solvent and trimethylamine, extraction with $CHCl_3$ provided the dark green tris(pyridine) trichlorochromium(III) adduct in 100% yield. The infra red spectrum was identical to that of an authentic sample.[6]

Discussion

All the reactions in this study were carried out with freshly prepared benzene solutions of $CrCl_3 \cdot 2NMe_3$ and, unless stated otherwise, an excess of ligand; the results are summarised in Figure 1.

Direct addition either by bubbling or co-condensation of anhydrous hydrogen chloride gives quantitative formation of trimethylamine hydrochloride (2 mol) and chromium(III) chloride (1 mol). By analogy with the behaviour of pyridinium hydrochloride, further reaction to give the hexametallate ion $CrCl_6^{3-}$ might have been expected[8], but did not, in fact occur even

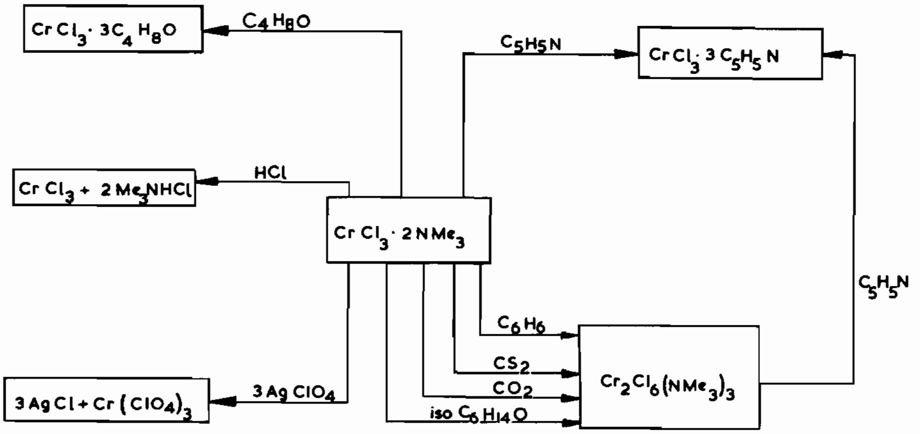

Figure 1. Summary of reactions based on $CrCl_3 \cdot 2NMe_3$ + L (excess) $\xrightarrow{\text{benzene}} \boxed{\text{Products}}$

under forcing conditions. The reaction with pyridine goes very smoothly and provides the green adduct $CrCl_3 \cdot 3C_5H_5N$; similarly tetrahydrofuran gives the purple adduct $CrCl_3 \cdot 3C_4H_8O$. Of particular interest was the outcome of the attempted preparation of adducts of the potential ligands carbon dioxide, carbon disulphide and di-iso-propylether. The lilac solid obtained as a common product proved to be untainted with ligand and was identified as tri-μ-chloro-trichloro-tris(trimethylamine)dichromium(III) $Cr_2Cl_6(NMe_3)_3$. Quite by accident, we happened upon the same product following a recrystallization of a batch of $CrCl_3 \cdot 2NMe_3$ by washing it *in vacuo* with a continuous stream of warm benzene. By inspection the semi-crystalline solid left on the sinter, although partially soluble in benzene, was obviously of a different nature than the purple-blue starting material. The inference was obvious: what we were in fact observing in all four cases was decomposition of the bis-trimethylamine adduct in benzene solution. Clearly only donor systems of strong basicity and/or low steric impedance will effect ligand substitution and some caution is advised in the indiscriminant use of the bis-trimethylamine adduct as a precursor for other chromium species via solvolysis.

The lilac solid, of empirical formula $Cr_2Cl_6(NMe_3)_3$ by analysis, is extremely sensitive to air-moisture hydrolysis, non-conducting in dichloromethane solution ($\Lambda_M^{298} = 2.1$ ohm^{-1} cm mole^{-1} at $10^{-3}M$) and monomeric in benzene solution. The electronic spectrum obtained by diffuse reflectance and in benzene solution resembles that of both the hexahalometallate $CrCl_6^{3-}$ [8] and the enneahalodimetallate $Cr_2Cl_9^{3-}$ [9] ions and can be interpreted likewise, *e.g.* transitions are essentially localised on adjacent chromium(III) ions set in pseudo-octahedral environments. The two peaks at 13,330 cm^{-1} and 18,520 cm^{-1} are assigned to the $^4T_{2g}(F) \leftarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \leftarrow {}^4A_{2g}(F)$ 'd–d' transitions respectively; the remainder at 31,750 (sh), 38,460 (sh), 45,870 (sh) and 51,280 cm^{-1} respectively are associated with metal (t_{2g} or e_g) ← halogen (π) charge-transfer and effectively obscure the third allowed d–d transition $^4T_{1g}(P) \leftarrow {}^4A_{2g}(F)$. The magnetic susceptibility data for the compound is listed in Table I.

The room temperature magnetic moment μ_{eff} (297 K) = 3.68 BM and the excellent Curie–Weiss law behaviour over the temperature range 297–103 K ($\Theta = 14°$) shows the material to be a 'normal' chromium(III) species[11] and a direct comparison with similar values of $Cr_2Cl_9^{3-}$ salts[9,12] further belies the presence of any significant metal–metal interaction. This close similarity of magnetic and spectral behaviour between $Cr_2Cl_9^{3-}$ and $Cr_2Cl_6(NMe_3)_3$ presages some degree of structural compatibility and the structure proposed for the latter is based on two fused octahedra sharing a common trigonal face as determined by X-ray analysis for $Cs_3Cr_2Cl_9$.[13] The alternative situation with a trimethylamine group rather than a chlorine atom occupying the common apex position, although favoured on symmetry grounds is much less likely from a stereochemical and bonding viewpoint involving as it does a bridging (Cr $\cdots$ NMe_3 $\cdots$ Cr) linkage. Other possible structure arising from apex–apex or edge–edge sharing

TABLE I. Magnetic Data for $Cr_2Cl_6(NMe_3)_3$[a].

Temp (K)	297	273	243	213	183	153	123	103
$\chi_M' \times 10^6$ cgsu	5665	6180	6900	7775	8985	10490	12985	15010

[a] χ_M' is calculated per chromium atom, diamagnetic corrections were estimated from Pascal's constants[10] and the room temperature magnetic moment was calculated using the expression $\mu_{eff} = 2.83\,(\chi_M' T)^{1/2}$.

of octahedra are at variance with the $M_2X_6L_3$ molecular stoichiometry and can be discarded. The infra red spectrum (4000–400 cm^{-1}) confirms the presence of co-ordinated trimethylamine with characteristic bands at $1230\nu_{as}(CN)$, $818\nu_s(CN)$, $980\varrho(CH_3)$, $530\delta_{as}(CN)$ and $445\delta_s(CN)$ cm^{-1} respectively[5]. The far infra red (400–200 cm^{-1}) profile is very similar to that for thc $A_3Cr_2Cl_9$ series where A = K, Rb, Cs, Et_4N and the two strong bands at 364 cm^{-1} and 354 cm^{-1} and the two medium bands at 297 cm^{-1} and 255 cm^{-1} are correspondingly assigned to $\nu(CrCl)_{terminal}$ and $\nu(CrCl)_{bridging}$ vibrations respectively.[14] Some contribution from metal–ligand $\nu(CrN)$ vibrations[15] may well be incorporated in the latter. Judged by the value of 83 cm^{-1} for the wave-number difference between the average of the two $\nu(CrCl)_{terminal}$ and the two $\nu(CrCl)_{bridging}$ bands, a fair degree of coupling between the terminal and bridging stretching modes is present.[14]

The formation of $Cr_2Cl_6(NMe_3)_3$ as represented by equation (1) can be conveniently monitored by following the rate of disappearance of the 10,100 cm^{-1} band ($^4E' \rightarrow {}^4E''$ (ν_1))[16] in the electronic spectrum of the bis-trimethylamine adduct:

$$2\,CrCl_3 \cdot 2NMe_3 \xrightarrow[\text{room temperature}]{\text{benzene}} Cr_2Cl_6(NMe_3)_3 + NMe_3 \quad (1)$$

Decomposition studies at 295K at various concentrations were carried out and from the results obtained the reaction is shown to be of second order kinetics with a rate constant $k = 0.160$ l $mole^{-1}$ sec^{-1}. Although the actual mechanism has not been established we are tempted to suggest a dimerisation process involving halogen-bridging with synchronous trimethylamine expulsion and ligand re-orientation rather than a dissociative mechanism featuring $[CrCl_3 \cdot NMe_3]$ species[17]. The reaction is irreversible in the presence of excess trimethylamine but degradation of the binuclear species into mononuclear chromium(III) units can be effected, *e.g.* direct treatment with hot pyridine gives complete conversion to $CrCl_3 \cdot 3C_5H_5N$.

Lastly we make brief mention of the reaction of the bis-trimethylamine adduct with perchlorate ion. Addition with silver perchlorate in 1:3 molar ratio gave immediate formation of silver chloride (3 mol) and a clear green solution with release of trimethylamine. Characterisation of the green solution proved hazardous – CAUTION: *the liquid is extremely air-moisture sensitive and the solid remaining on evaporation is temperature- and shock-sensitive and can explode with tremendous violence* – but spectral evidence establishes the presence of an octahedral chromium(III) species involving only bidentate (C_{2v}) perchlorate ions as co-ordinated ligand, *e.g.* $Cr(ClO_4)_3$. All three expected 'd–d' transitions were observed in the electronic spectrum (nujol and benzene solution), *i.e.*

$^4T_{2g}(F) \leftarrow {}^4A_{2g}(F)$ 16,100 cm^{-1} [10Dq], $^4T_{1g}(F) \leftarrow {}^4A_{2g}(F)$ 22,500 cm^{-1} and $^4T_{1g}(F) \leftarrow {}^4A_{2g}(F)$ 37,000 cm^{-1} and characteristic bands at 1018 (ν_6), 981 (ν_1), 1180 and 1122 (ν_8), 850 and 895 (ν_2), 681 and 655 (ν_3), 619 and 602 (ν_7) and 489 (ν_9) cm^{-1} respectively in the infra red spectrum confirm bidentate ligand attachment.[18] Provided great care is exercised this perchlorate species should prove a useful intermediate in the synthesis of non-halogen chromium(III) compounds and exploration in this area is under way.[4]

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17 From work in progress we have established that both $TiCl_3 \cdot 2NMe_3$ and $VCl_3 \cdot 2NMe_3$ decompose in benzene solution to give binuclear formation and a detailed study of the series $M_2Cl_6(NMe_3)_3$ and the relationships with their $M_2Cl_9{}^{3-}$ counterparts (M = Ti, V and Cr) will be presented for publication shortly.

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