Inorganica Chimica Acta, 24 (1977) L81–L83

Tri-μ-chloro-trichlorotris(trimethylamine)dimetallates (III) of Titanium, Vanadium and Chromium

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Received July 16, 1977

Trimethylamine adducts of the type $MX_3 \cdot 2NMe_3$ (M = Ti, V and Cr; X = Cl and Br) are now well established and recognised as five co-ordinate *trans*-trigonal bipyramidal (D_{3h}) species [1–3]. For $CrCl_3 \cdot 2NMe_3$ in benzene solution, however, we have observed [4] a spontaneous decomposition occurs with release of amine and formation of the binuclear chromium(III) complex $Cr_2Cl_6(NMe_3)_3$. Following similar studies using the vanadium(III) and titanium(III) analogues it is now evident that the decomposition is common to the series. Details of the respective binuclear complexes $M_2Cl_6(NMe_3)_3$ including kinetic data from controlled decomposition studies are herein presented and discussed.

Experimental

Details of spectral, magnetic and analytical measurements and general experimental conditions have been previously described [4].

Preparation of $M_2Cl_6(NMe_3)_3$ Complexes

In a typical reaction benzene (~ 50 cm^3) was distilled into a 500 cm^3 glass ampoule containing the appropriate bis-adduct $MCl_3 \cdot 2NMe_3$ (~ 2 g). After degassing at 93 K the vessel was sealed *in vacuo* and allowed to stand at room temperature when the *product* slowly deposited from solution. After removal of the released trimethylamine (confirmed by its IR spectrum) and the benzene solution by careful decantation, the solid product remaining was washed with benzene and n-hexane and then pumped *in vacuo* for several hours at room temperature before being sealed in glass tubes under nitrogen (Table I).

Discussion

The five co-ordinate metal complexes $MCl_3 \cdot 2NMe_3$ (M = Ti, V and Cr) evidently break down in benzene solution to give binuclear species $M_2Cl_6(NMe_3)_3$ with release of trimethylamine. The rate of decomposition varies markedly within the series and follows an increasing order Cr $\gg$ V $\gg$ Ti. For the chromium species the onset of decomposition is merely a matter of minutes; in contrast the yellow–brown $Ti_2Cl_6(NMe_3)_3$ only begins to separate out after a period of weeks and even after twelve months the product yield is low (~ 1%).

All three binuclear complexes are extremely air-moisture sensitive. The infrared spectra (4000–400) cm^{-1} contain bands characteristic of co-ordinated trimethylamine [1(d)] and apart from a few minor frequency shifts are virtually indistinguishable. In the 400–200 cm^{-1} region the titanium and vanadium complexes show four and three strong bands respectively assigned as metal–chlorine stretching vibrations. No immediate differentiation between $\nu(MCl)_{terminal}$ and $\nu(MCl)_{bridge}$ can be made (some mixing and in the latter, some contribution from bending modes and metal ligand $\nu(MN)$ vibrations is almost certainly present), but as with analogous dimetallate species, *e.g.* $(Et_4N)_3Ti_2Cl_9$, $\nu(TiCl)_{terminal}$ 416, 379; $\nu(TiCl)_{bridge}$ 268, 230 cm^{-1} and $[Et_2NH_2]_3V_2Cl_9$, $\nu(VCl)_{terminal}$ 350, 313; $\nu(VCl)_{bridge}$ 290, 260 cm^{-1}, only those bands in the energy region above 300 cm^{-1} are likely to be associated with $\nu(MCl)_{terminal}$ modes [5, 6].

The spectral and magnetic data for $Cr_2Cl_6(NMe_3)_3$ has been previously discussed [4].

The electronic spectrum of the vanadium complex is typical of octahedral vanadium(III) with the first two 'd–d' transitions, ${}^3T_{2g}(F) \leftarrow {}^3T_{1g}(F)$ and ${}^3T_{1g} \leftarrow {}^3T_{1g}(F)$, observed at 10,300 and 17,700 cm^{-1} respectively, the remainder being high intensity charge-transfer bands vanadium (d) $\leftarrow$ chlorine (π). Similar values are observed for the VCl_6^{3-} and $V_2Cl_9^{3-}$ ions [6]. The magnetic moment at room temperature (2.55 BM) is significantly reduced from the normal value expected for magnetically dilute vanadium(III) systems [7] and is strongly temperature dependent. This, and the marked deviations from Curie–Weiss behaviour gives evidence of some magnetic interaction in the solid and is curiously reminiscent of the magnetic (and spectral) character of the dimetallate salt $(Et_2NH_2)_3V_2Cl_9$ [6]. We have been unable to obtain reliable electronic and magnetic data for the titanium complex.

X-ray data for $Cs_3Cr_2Cl_9$ [8, 9] – which is isomorphous [10] with $Cs_3Ti_2Cl_9$ and $Cs_3V_2Cl_9$ – shows isolated dimetallate ions made up of two fused $CrCl_6$ octahedra sharing a common trigonal face. A similar type of confacial bioctahedral structure involving triple halogen bridging is proposed for the isoelectric $M_2Cl_6(NMe_3)$ series [11].

The kinetics of the decomposition of the chromium and vanadium bisadducts were investigated spectrophotometrically, using standard benzene solutions in sealed 1 cm silica cells thermostatted at 295 K. The rates of disappearance of the five co-ordinate metal species in $CrCl_3 \cdot 2NMe_3$ and $VCl_3 \cdot$

TABLE. Analytical, Spectral and Magnetic Data for $M_2Cl_6(NMe_3)_3$

Compound	Colour	Mp[a]		%C	%H	%N	%Cl	%Metal	Electronic[b]	Infrared[c]	
$Ti_2Cl_6(NMe_3)_3$	Yellow–Brown	410 K	Calcd	22.2	5.6	8.6	43.8	19.7		390(s), 353(s),	
			Found	21.6	5.0	8.1	43.2	19.0		260(m), 185(s)	
$V_2Cl_6(NMe_3)_3$	Brown	433 K	Calcd	22.0	5.5	8.5	43.3	20.7	10,300	335(s)	
			Found	21.4	5.4	8.2	43.1	20.6	17,700	315(s)	
									36,700(sh)	283(m)	
									40,000(sh)		
									47,600(sh)		
	Magnetic Data[d]	T(K)	292	259	240	225	209	195	182	166	156
		$10^6\chi'_M$ (cgsu)	2744	2885	2971	3046	3105	3207	3311	3442	3535
		μ_{eff} (BM)	2.55	2.40	2.32	2.26	2.17	2.10	2.03	1.94	1.88

[a] Melting with decomposition. [b] Nujol mull; absorption maxima (cm^{-1}). [c] (400–100) cm^{-1} region; absorption maxima (cm^{-1}). [d] χ'_M calculated per vanadium atom; diamagnetic correction $C_9H_{27}N_3Cl_6$ (270.42×10^6 cgsu); $\mu_{eff} = 2.84\ (\chi'_M T)^{1/2}$.

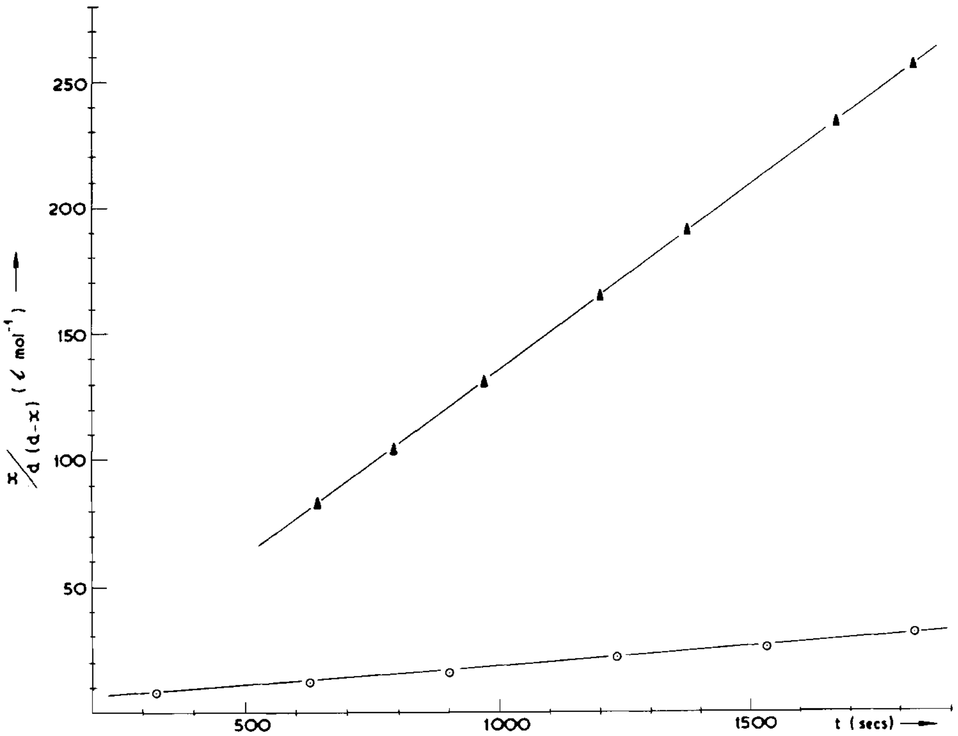

Figure 1. Integrated second order rate plots for $MCl_3 \cdot 2NMe_3$ decomposition: ▲ M = Cr; ○ M = V where a = initial concentration and x = amount reacted after time t.

$2NMe_3$ were followed by monitoring the characteristic peaks at 10,000 cm^{-1} [$^4E''(F) \leftarrow {}^4E'(F)$] and 20,000 cm^{-1} [$^3E'$, $^3A_2'(P) \leftarrow {}^3A_2'(F)$] respectively [3]. A similar approach for $TiCl_3 \cdot 2NMe_3$ using the characteristic [2] peak at 6,300 cm^{-1} [$^2E' \leftarrow {}^2E''$] proved abortive as a result of the extremely slow rate of decomposition. Provided that the initial concentrations of $CrCl_3 \cdot 2NMe_3$ were chosen such that the resulting concentrations of $Cr_2Cl_6(NMe_3)_2$ never exceeded 10^{-3} *M* at any instant no precipitation occurred in the chromium system. In such solutions $Cr_2Cl_6(NMe_3)_3$ shows no absorption in the 10,000 cm^{-1} region. For the vanadium system the complete insolubility of $V_2Cl_6(NMe_3)_3$ in benzene results in a very fine flocculent brown solid depositing continually. To avoid anomalous results the cell was centrifuged before each reading. Plots of Absorbance [A] against time (t) for each solution gave the following

($[A]_{t=0}$) values for ϵ_{max}: $CrCl_3 \cdot 2NMe_3[^4E''(F) \leftarrow {}^4E'(F)$ ϵ_{max}(obs) 46.5, ϵ_{max} (lit) [1(j)] 23; $VCl_3 \cdot 2NMe_3[^3E', {}^3A'_2(P) \leftarrow {}^3A'_2(F)]$ ϵ_{max} (obs) 26.5, ϵ_{max} (lit) [1(d)] 59. From comparisons with literature values it would appear that some decomposition had occurred when the original spectra were recorded with the precipitated $V_2Cl_6(NMe_3)_3$ markedly increasing the measured optical density in the vanadium case. From plots of *log initial rate* against *log concentration* the reactions were found to be second order with respect to the adduct concentration. Integrated second order rate plots (Fig. 1) give second order rate constants of 0.160 $l\ mol^{-1}\ s^{-1}$ for the $CrCl_3 \cdot 2NMe_3$ decomposition and 0.0166 $l\ mol^{-1}\ s^{-1}$ for the $VCl_3 \cdot 2NMe_3$ breakdown both at room temperature (295 °K).

Comment

From the relative d-orbital energy levels in ligand fields of $D_{3h}[d_{z^2}(a'_1) > d_{xy}, d_{x^2-y^2}(e') > d_{xz}, d_{yz}(e'')]$ and $O_h[d_{x^2-y^2}, d_{z^2}(e_g) > d_{xy}, d_{yz}, d_{xz}(t_{2g})]$ the stability of octahedral over trigonal-bipyramidal geometry, in terms of crystal field stabilisation energy, increases in the sequence $Cr(d^3) > V(d^2) > Ti(d^1)$. Any drive towards octahedral co-ordination will clearly be least favourable for titanium(III). The mechanism by which this decomposition occurs is open to question. Few kinetic investigations relate to five co-ordinate centres and these have been concerned mainly with the late transition metals where the reaction behaviour is not rigid. Dissociative [12–14] and associative [15] mechanisms have been observed and a situation where both occur simultaneously has been described [16]. For the early transition metals where four coordination under any circumstances is rare and where solvent participitation (metal ← benzene) in a mechanistic sense is most unlikely [17], a dissociative pathway would not intuitively be favoured. An associative mechanism involving the formation of an equilibrium dimer (halogen bridging) with subsequent loss of trimethylamine and closure of octahedra seems plausible. It is well known for various five coordinate titanium(III) [18, 19], vanadium(III) [1(d), 20, 21] and chromium(III) [20, 22] complexes to achieve octahedral co-ordination either by dimer formation (halogen bridging) or by solvation. All attempts to react the $M_2Cl_6(NMe_3)_3$ species with trimethylamine to form anew the parent five coordinate compounds have met with failure.

Acknowledgment

We thank the S.R.C. for a postgraduate award (J.H.).

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