Inorganica Chimica Acta, 13 (1975) L1 - L2

Titanium(III) and Chromium(III) Complexes of Tris(2-dimethylaminoethyl)amine

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(Received January 20, 1975)

Transition metal ion complexes with tris(2-dimethylaminoethyl)amine (Me$_6$tren) normally feature all four amine centres of the ligand in metal ← nitrogen σ-bonding.[1] Exceptionally, terdentate behaviour has recently been cited[2] in connection with the cadmium(II) complexes CdX$_2$·Me$_6$tren (X = Cl and Br). For the six coordinate complexes MCl$_3$·Me$_6$tren (M = Ti and Cr) described herein, reduced denticity for Me$_6$tren is again in evidence and a common bonding scheme involving only the central and two of the terminal tertiary amine sites in metal coordination is established from spectral data.

Experimental

The metal complexes were prepared on the vacuum line by slow addition of a benzene solution of Me$_6$tren to a similar solution of the appropriate metal complex MCl$_3$·2NMe$_3$ (M = Ti[3] and Cr[4]). The reaction mixture was stirred mechanically for several hours prior to the removal of excess ligand, solvent and released trimethylamine. The remaining solid product was thoroughly washed with n-pentane and then pumped *in vacuo* at room temperature for several hours.

Trichlorotris(2-dimethylaminoethyl)amine titanium(III)

(i) The product from the reaction using 1.23 g (5.35 mmol) of Me$_6$tren and 1.46 g (5.35 mmol) of TiCl$_3$·2NMe$_3$ was a blue air-sensitive solid insoluble in most of the common organic solvents but slightly soluble in dichloromethane. *Anal.* Calcd. for C$_{12}$H$_{30}$N$_4$TiCl$_3$: C, 37.5; H, 7.8; N, 14.5; Ti, 12.5; Cl, 27.6. Found: C, 37.3; H, 7.9; N, 14.1; Ti, 12.6; Cl, 27.4. μ_{eff}(293K) = 1.86 BM. Λ_M^{295K} = 0.003 ohm^{-1} cm^2 mol^{-1} at 10^{-3} *M* concentration in CH$_2$Cl$_2$. The infrared spectrum gave bands at 3030 (m), 2983 (sh), 2965 (s), 2918 (sh), 2892 (s), 2842 (m), 2825 (m), 2795 (m), 2765 (m), 1478 (sh), 1460 (s), 1440 (sh), 1401 (w), 1391 (w), 1349 (w), 1336 (w), 1320 (w), 1296 (sh), 1288 (w), 1276 (m), 1259 (m), 1232 (m), 1170 (w), 1161 (w), 1150 (m), 1100 (m), 1084 (sh), 1058 (m), 1040 (sh), 1030 (sh), 1016 (s), 1002 (s), 996 (sh), 988 (sh), 968 (m), 957 (m), 947 (m), 929 (m), 896 (sh), 881 (sh), 871 (w), 860 (w), 801 (s), 790 (sh), 776 (s), 742 (m), 723 (m), 672 (m), 616 (w), 600 (w), 581 (m), 492 (m), 460 (w), 445 (m), 410 (w), 390 (w), 355 (s), 317 (s), and 300 (m) cm^{-1} respectively.

(ii) A repeat experiment using a five-fold excess of ligand gave the same product as in (i).

Trichlorotris(2-dimethylaminoethyl)amine chromium(III)

(i) The product obtained from the reaction using 1.24 g (4.88 mmol) of Me$_6$tren and 1.35 g (4.88 mmol) of CrCl$_3$·2NMe$_3$ was a green air-sensitive solid; this material was found to be slightly soluble in dichloromethane and benzene. *Anal.* Calcd. for C$_{12}$H$_{30}$N$_4$CrCl$_3$: C, 37.1; H, 7.7; N, 14.4; Cr, 13.4; Cl, 27.4. Found: C, 37.3; H, 7.8; N, 14.0; Cr, 13.2; Cl, 27.3. μ_{eff}(293K) = 3.85 BM. Λ_M^{295K} = 0.002 ohm^{-1} cm^2 mol^{-1} at 10^{-3} *M* concentration in dichloromethane. The infrared spectrum gave bands at 3030 (m), 2985 (m), 2965 (s), 2920 (s), 2890 (sh), 2842 (sh), 2834 (m), 2795 (sh), 2770 (m), 1480 (sh), 1462 (s), 1431 (sh), 1400 (w), 1391 (w), 1383 (w), 1372 (w), 1340 (w), 1334 (sh), 1289 (m), 1273 (w), 1256 (m), 1231 (w), 1202 (w), 1183 (w), 1155 (w), 1100 (m), 1086 (sh), 1051 (m), 1038 (m), 1027 (m), 1012 (s), 996 (s), 977 (sh), 950 (s), 931 (s), 893 (w), 860 (m), 795 (m), 786 (w), 764 (s), 742 (m), 672 (w), 589 (m), 572 (m), 511 (m), 430 (m), 399 (sh), 383 (s), 335 (s) and 269 (m) cm^{-1} respectively.

(ii) A repeat experiment using a five-fold excess of ligand gave the same product as in (i).

Results and discussion

The blue (M = Ti) and green (M = Cr) MCl$_3$·Me$_6$tren complexes were obtained following treatment of the appropriate bis-trimethylamine adduct MCl$_3$·2NMe$_3$ with Me$_6$tren in benzene solution. Complex formation with release of trimethylamine is immediate and the product stoichiometry is independent of the ligand concentration. Magnetic susceptibility measurements confirm the presence of the respective tervalent metal and both complexes are neutral showing non-conducting behaviour in dichloromethane solution.

TABLE I. Electronic Spectra of $MCl_3 \cdot Me_6$tren Complexes.

Complex	Medium	Absorption Maxima (cm^{-1})
$TiCl_3 \cdot Me_6$tren	nujol mull	12,420 (sh) 13,000 38,610 (sh) 39,840 (sh) 46,510 (sh)
$CrCl_3 \cdot Me_6$tren	nujol mull	14,100 (sh) 15,430 21,645 36,900 41,150 45,870 (sh)
	benzene solution	14,060 (sh) 15,050 21,140

Identification of both as hexacoordinate M(III) species follows from the electronic spectra (Table I). For the chromium complex the bands observed at 15,430 cm^{-1} and 21,645 cm^{-1} are assigned to the expected '*d–d*' transitions $^4T_{2g} \leftarrow {}^4A_{2g}$ (10 Dq) and $^4T_{1g} \leftarrow {}^4A_{2g}$ respectively; the remainder, above 35,000 cm^{-1} are most likely chromium (*d*) ← chlorine (π) charge-transfer bands. The weak shoulder at ~ 14,000 cm^{-1} on the low energy side of the 10 Dq band can be assigned to the spin-forbidden $^2E_g \leftarrow {}^4A_{2g}$ transition and reflects some trigonal or lower distortion departure from octahedral symmetry.[5] The smaller 10Dq value, *c.f.* $CrCl_3 \cdot$tren [16,900 cm^{-1}],[6] is commensurate with increased methyl substitution of the ligand.[7] The broad asymmetric band observed at 13,000 cm^{-1} for the titanium complex is too low in value to be associated with the expected $^2E_g \leftarrow {}^2T_{2g}$ (10Dq) transition and is assigned to a $^2E \leftarrow {}^2A_1$ transition of an octahedral Ti(III) species with a strong trigonal distortion.[6,8]

The premise that coordination in both cases involves *fac*-octahedral geometry with Me_6tren acting as a terdentate ligand is based on the infrared spectral data. In the first place the presence of two strong bands in the 300 - 400 cm^{-1} region associated with metal–chlorine stretching frequencies, *viz.* ν(TiCl) 355 and 317 cm^{-1}; ν(CrCl) 349 and 335 cm^{-1}, signifies a mutual *cis*-grouping (C_{3v}) of chlorine atoms around the six coordinate metal centres.[9] Furthermore, the presence of several medium bands in the 2820 - 2760 cm^{-1} region associated with ν(CH) absorptions of uncoordinated $\rangle$NMe[10] groups and the splitting of the 1004 and 989 cm^{-1} $\nu(NMe_2)$ and 1291 cm^{-1} $\delta(NMe_2)$ ligand bands[11] into distinct doublet profiles on coordination, *e.g.* $TiCl_3 \cdot Me_6$tren [$\nu(NMe_2)$ 1016, 1002; 947, 929 cm^{-1}. $\delta(NMe_2)$ 1276, 1259 cm^{-1}]; $CrCl_3 \cdot Me_6$tren [$\nu(NMe_2)$ 1012, 996; 950, 931 cm^{-1}. $\delta(NMe_2)$ 1289, 1256 cm^{-1}] verifies the non-equivalence of the terminal $-NMe_2$ groups. One such site must be uncoordinated and the *cis*-arrangement of the two five-membered chelate rings implicit with such a situation is expected to give rise to two strong bands associated with CH_2 rocking modes.[12] Significantly, the intense 796 cm^{-1} (CH_2 rock) band of the ligand splits on coordination, *e.g.* $TiCl_3 \cdot Me_6$tren (801, 776 cm^{-1}); $CrCl_3 \cdot Me_6$tren (795, 764 cm^{-1}).

Since all the nitrogen donor sites in Me_6tren have essentially the same steric requirements, metal coordination solely through the terminal $-NMe_2$ groups, as found in the related M(III)–tren complexes,[6] would have no obvious advantage in the present instance. The arrangement envisaged with a terminal centre as a 'dangling arm' incorporates a fused five-membered chelate ring system and on energetic and steric groups is much preferred.[13]

We wish to thank the S.R.C. for a maintenance grant (to J. H.).

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