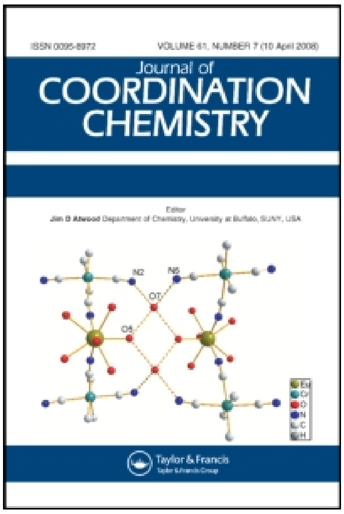

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TRIS (2-AMINOETHYL)AMINE COMPLEXES OF TERVALENT TITANIUM AND CHROMIUM

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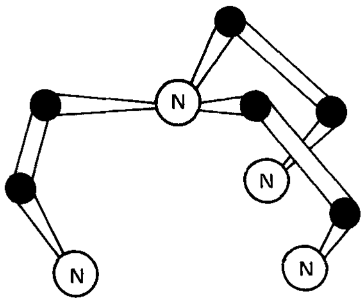
Tris(2-aminoethyl)amine(tren) reacts with the bis(trimethylamine) adducts of titanium(III) chloride and chromium(III) chloride to give complexes of the type $MCl_3 \cdot x$(tren) where $x = 1$ or 2 depending on the stoichiometry used. On the evidence of magnetic, conductometric, spectral, and conductivity measurements the structures of these complexes are discussed in terms of six-coordinate metal atoms with tren adopting a terdentate role in both series in marked contrast to its normal tetradentate behaviour. Coordination via (metal←nitrogen) σ-bonding is seen to involve the primary amine centres of the ligand to the complete exclusion of the tertiary site(s). Whereas the $MCl_3 \cdot$(tren)compounds are non-ionic, the bis-adducts contain ionic chlorine atoms and a formulation based on $[M(tren)_2]^{3+}3Cl^-$ is proposed for the latter.

INTRODUCTION

With a common 'tripod' framework (I) involving primary and tertiary nitrogen centres, tris(2-aminoethyl)amine (tren)† and its methyl analogue tris(2-dimethylaminoethyl)amine (Me_6tren) clearly have the potential to act as powerful chelating ligands.



(I)

Of continuing interest in this respect is (a) their ability to give five-coordinate high-spin complexes[1] and (b) the ability, apparently exclusive to tren, to give six-coordinate complexes[2] with various divalent and trivalent metal ions of the 1st Transition Series. Tren complexes involving metal ions of the Lanthanide Series have also been recently investigated[3]. A notable feature of all these studies is the seemingly inviolable total involvement of ligand nitrogen atoms in coordination[4] and subsequent X-ray structural investigations on many of these Me_6tren- and tren-metal complexes not only confirm a consistent tetradentate role for both ligands, but also give clear evidence on the influence that the metal plays in determining the geometry of the resulting coordination polyhedron. This is most discernible in tren derivatives e.g., $Ni(tren)(NCS)_2$[5] has a distorted octahedral geometry whereas [Zn(tren)NCS] SCN[6] and [Cu(tren)NCS] SCN,[7] albeit trigonal bipyramidal, still show quite marked differences in molecular structure; similarly, the Me_6tren series $[M^{II}(Me_6tren)Br]Br$ where M = Co[8] Ni[9] Cu[9] Mn[10] Fe[10] and Zn[10] although based on a trigonal bipyramidal skeleton, nevertheless exhibits significant structural variations. Bearing in mind this enhanced 'metal sensitivity'[11] of tren and its less bulky and more flexible nature as compared with Me_6tren, it seemed likely that with a suitable choice of metal substrate the tetradentate behaviour of this ligand might well be subjugated. The tervalent halides of titanium and chromium which are well known to provide stable complexes of various coordination geometries with nitrogen donors[15] – six-coordinate species based on $MX_3 \cdot 3L$ or $MX_3 \cdot D_3$ being especially favoured – presented an obvious choice, and in this paper we report the synthesis and characterisation of tren derivatives of titanium(III) chloride and chromium(III) chloride and discuss their most likely stereo-chemistry.

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†Other abbreviations used in the text include
en=$H_2N-(CH_2)_2-NH_2$;
dien=$H_2N-(CH_2)_2-NH-(CH_2)_2-NH_2$;
trien =$H_2N-(CH_2)_2-NH-(CH_2)_2-NH-(CH_2)_2-NH_2$;
tetren=$H_2N-(CH_2)_2-NH-(CH_2)_2-NH-(CH_2)_2-NH-(CH_2)_2-NH_2$.

EXPERIMENTAL

Materials

All solvents were stored over calcium hydride and/or phosphoric oxide and distilled in vacuo prior to use. Chromium(III) chloride (Pfaltz and Bauer Inc., Flushing, NY), titanium(III) chloride (K and K Laboratories, Plainview, NY) and trimethylamine (Hopkins and Williams, Essex) were obtained as anhydrous materials, the latter being stored over potassium hydroxide and distilled in vacuo when required. Tren(Strem Chemicals Inc., Danvers, Mass) was repeatedly vacuum distilled over potassium hydroxide and obtained as a clear colourless liquid b.p. 338-339K/0.2 mm Hg whose purity was established by nmr and infrared analyses. Sodium tetraphenylborate (B.D.H. Ltd., Poole, Dorset) was oven dried at 383 K and used directly. Bis(trimethylamine-)titanium(III) chloride and the chromium(III) analogue were prepared from the anhydrous metal halide and trimethylamine using the double ampoule method as described by Fowles et al.[16] Trichloroacetic acid (Fisons Ltd, Loughborough) was used as obtained.

Apparatus and Analyses

Infrared spectra (4000-200)cm^{-1} were recorded on a PERKIN–ELMER 621 spectrometer with samples held as nujo and fluorolube mulls between caesium iodide plates. Conductivity measurements were carried out with a WAYNE–KERR Universal B221 conductance bridge and a cell of standard design previously calibrated with aqueous potassium chloride solutions: unless otherwise stated all solutions were thermostatted at 298.0 ± 0.1K.

Room temperature magnetic susceptibility measurements were made using a Faraday balance. Electronic absorption spectra were recorded on a CARY 14 spectrophotometer with samples either as solutions in 1 cm silica cells, or as nujol mulls held between silica plates or as thin transparent potassium bromide discs. Proton nmr spectra were recorded (60MHz) on a PERKIN–ELMER R12 spectrometer.

Elemental carbon, hydrogen and nitrogen analyses were performed by the A. Bernhardt Microanalytical Laboratory, Mullheim, Germany. Titanium was determined gravimetrically following ignition to the oxide and chromium was evaluated spectrophotometrically as chromate. Chloride was determined by the Volhard method.

Preparation of Complexes

Due to the air-moisture sensitivity of reactants and products, all manipulations were carried out in a glove box flushed with dry, oxygen-free nitrogen and, where appropriate, in sections of a standard all-glass high vacuum system. Metal-tren derivatives were prepared on the vacuumline by slow addition of a benzene solution of the ligand to a similar solution of the appropriate bis(trimethylamine) adduct of the metal halide. Although immediate precipitation ensued, the flask was sealed under vacuo and placed on a mechanical shaker for 24 hrs. to ensure complete equilibration. On returning the vessel to the vacuumline and opening at 273K, the side-product trimethylamine was trapped at 93K in a special tube fitted with an infrared gas cell. As a result of the small volume of gas involved e.g., approximately 250 mls in a typical reaction, no attempt at quantitative evaluation was made, but identification as trimethylamine was obtained through its infrared spectrum[17]. The solid product remaining was then thoroughly washed with benzene to remove any excess starting material, pumped in vacuo at room temperature for 48 hours and finally sealed into ampoules under a nitrogen atmosphere.

(a) Trichlorotris (2-aminoethyl)aminetitanium(III) The product from the reaction using 0.94 g (6.4 mmol) of tren and 1.89 g (6.9 mmol) of $TiCl_3 \cdot 2NMe_3$ was a sage green air-sensitive solid. m.p., decomposes at T > 443K to a grey solid. Anal. Calcd for $C_6H_{18}N_4TiCl_3$: C, 24.0; H, 6.0; N, 18.7; Ti, 16.0; Cl, 35.4, Found: C, 23.8; H, 6.2; N, 18.6; Ti, 15.8; Cl, 35.2

$$\mu\text{eff}\,(296\text{K}) = 1.45\ \text{BM}.$$

$\Lambda_M = 0.011$ ohm^{-1} cm^{2}mole^{-1} at 1×10^{-3} M concentration. The infrared spectrum gave bands at 3198(s), 3130(s), 2945(m), 2898(m), 2720(w), 1580(m), 1475(m), 1320(w), 1290(m), 1144(m), 1070(m), 1060(m), 1030(m), 1010(m), 990(w), 885(m), 795(m), 725(m), 682(m), 672(m), 575(w), 543(w), 372(m) and 310(m) cm^{-1} respectively.

(b) Trichlorobis[tris(2-aminoethyl)amine]titanium(III) The product obtained from the reaction using 1.53 g (10.5 mmol) of tren and 1.33 g (4.9 mmol) of $TiCl_3 \cdot 2NMe_3$ was a cream yellow air-sensitive solid. m.p., decomposes at T > 403K to a grey solid. Anal. Calcd for $C_{12}H_{36}N_8TiCl_3$, C, 32.3; H, 8.1; N, 25.1; Ti, 10.7; Cl, 23.8. Found C, 31.9; H, 7.8; N, 24.8; Ti, 10.5; Cl, 23.6.

μeff (295K) = 1.52 BM.

The infrared spectrum contained bands at 3180(s), 3120(s), 2942(m), 2880(m), 2640(w), 1595(m), 1472(m), 1330(m), 1294(m), 1150(m), 1080(m), 1060(m), 1035(m), 1010(m), 980(w), 880(m), 795(m), 720(m), 680(m), 670(m), 580(w), and 540(m) cm^{-1} respectively.

(c) Trichlorotris(2-aminoethyl)aminechromium(III)

The product from the reaction of 0.54 g (3.7 mmol) of tren and 1.04 g (3.8 mmol) of $CrCl_3 \cdot 2NMe_3$ was a blueish-grey air-sensitive solid. m.p., decomposes at $T > 420K$ to a dark grey solid. Anal. Calcd for $C_6H_{18}N_4CrCl_3$: C, 23.7; H, 5.9; N, 18.4; Cr, 17.1; Cl, 34.9. Found: C, 23.2; H, 6.2; N, 18.1; Cr, 16.9; Cl, 34.6

μeff (295K) = 3.83BM. $\Lambda_M = 0.086$

ohm^{-1} cm^2 $mole^{-1}$ at 1×10^{-3} M concentration in dichloromethane. The infrared spectrum contained bands at 3195(s), 3110(s), 2950(m), 2890(w), 2850(w), 1578(m), 1465(m), 1358(w), 1262(m), 1151(m), 1075(m), 1043(m), 1030(m), 990(w), 885(w), 800(m), 720(m), 685(m), 675(m), 545(w), 338(s) and 300(m) cm^{-1} respectively.

(d) Trichlorobis[tris(2-aminoethyl)amine] chromium(III) The product from the reaction of 2.12 g (14.6 mmol) of tren and 1.7 g (6.2 mmol) of $CrCl_3 \cdot 2NMe_3$ was a pink hygroscopic solid. m.p., decomposes at $T > 395K$ to a dark red-brown solid. Anal. Calcd for $C_{12}H_{36}N_8CrCl_3$ C, 32.0; H, 8.0; N, 24.9; Cr, 11.5; Cl, 23.6. Found = C, 31.8; H, 8.0; N, 24.6; Cr, 11.4; Cl, 23.6.

μeff (294K) = 3.86 BM $\Lambda_M = 201$

ohm^{-1} cm^2 $mole^{-1}$ at 1×10^{-3} M concentration in aqueous solution at 273K. The infrared spectrum gave bands at 3140(s), 3090(s), 2940(s), 2865(m), 2820(w), 1588(m), 1462(m), 1360(m), 1260(m), 1164(m), 1080(w), 1045(m), 1035(m), 992(w), 888(m), 800(m), 720(m), 690(w), 670(w), 550(w) and 508(w) cm^{-1} respectively.

RESULTS AND DISCUSSION

Treatment of $MCl_3 \cdot 2NMe_3$ (M = Ti and Cr) with the chelating ligand tren in benzene solution gives two types of metal-tren derivative depending on the stoichiometry used. With an equi-molar ratio – in reality a very slight excess of metal species was used –, the mono-adducts $MCl_3 \cdot (tren)$ were obtained as the green (M = Ti) and blue-purple (M = Cr) solids respectively; with an excess of ligand the yellowish-green (M = Ti) and pink (M = Cr) bis-adducts $MCl_3 \cdot (tren)_2$ were isolated. In each reaction the ligand substitution proceeded quite smoothly with release of trimethylamine and precipitation of the appropriate adduct. The complexes are hygroscopic powders which decompose rapidly on exposure to the atmosphere. Room temperature magnetic susceptibility data e.g., $TiCl_3 \cdot (tren)$, μeff = 1.45 BM; $CrCl_3 \cdot (tren)$, μeff = 3.83 BM; $TiCl_3 \cdot (tren)_2$, μeff = 1.52 BM; $CrCl_3 \cdot (tren)_2 \cdot \mu$eff = 3.86 BM confirms that they are genuine tervalent titanium (d^1) and chromium (d^3) species with magnetic moments close to the appropriate spin-only value.[18]

The mono-adducts decompose immediately (solvolysis) in polar solvents such as acetonitrile, methanol, acetone and tetrahydrofuran, even at 273K, but show limited solubility ($\sim 10^{-4}$M) in dichloromethane. At this concentration level molecular weight measurements proved to be unreliable, but electrical conductivity studies indicated non-conducting behaviour[19] e.g., $TiCl_3(tren)$, $\Lambda_M = 0.011$ ohm^{-1} cm^2 $mole^{-1}$; $CrCl_3 \cdot (tren)$, $\Lambda_M = 0.086$ ohm^{-1} cm^2 $mole^{-1}$ thus discrediting any ionic formulation for the series.

The bis-adducts were found to be insoluble in hydrocarbon and halogenated hydrocarbon solvents and to generally decompose in polar solvents at room temperature. At 273K, however, the chromium complex gave methanol and aqueous solutions stable over periods of time sufficient to allow spectral and electrical conductivity studies and in the latter case we obtained a value of $\Lambda_M = 201$ ohm^{-1} cm^2 $mole^{-1}$ at 1×10^{-3} M concentration in aqueous solution. Conductivity values quoted at this temperature are scarce and for means of comparison we prepared[29] and measured the conductivity of $[Cr(en)_3]^{3+}3Cl^-$ at 1×10^{-3}M concentration in aqueous solution over the temperature range 273–298 K. From the value of 207 ohm^{-1} cm^2 $mole^{-1}$ obtained at 273 K, we conclude that our chromium bis-adduct shows ionic dissociation typical of a 3:1 electrolyte. Further evidence in support of a $[Cr(tren)_2]^{3+}3Cl^-$ formulation was obtained from a controlled metathetical reaction with sodium tetraphenylborate. The reaction of this chromium complex and sodium tetraphenylborate in standard aqueous solution at 273 K was found to occur according to equation (a)

$$[Cr(tren)_2]Cl_3 + 3NaBPh_4 \rightarrow 3NaCl + [Cr(tren)_2](BPh_4)_3 \qquad (a)$$

The chromium cation species was quantitatively precipitated as the tetraphenylborate salt and titration of the remaining solution (Volhard) indicated the presence of three equivalents of ionised chloride ion. The titanium complex was not amenable to similar solution studies, but corroborative evidence for a common ionic formulation $[M(tren)_2]Cl_3$, for the series was obtained from the far infrared spectra (500–200) cm^{-1} – see ·Table I. Metal-chloride stretching frequencies ν (MCl) for a variety of titanium(III) and chromium(III) chloro-complexes are located in the 300–400 cm^{-1} region and their number and position(s) may be correlated with the coordination character of the particular species. With the $[M(tren)_2]Cl_3$ series no such bands were observed, and in fact the spectra showed a complete lack of absorption below 500 cm^{-1}. For the non-ionic $MCl_3 \cdot$(tren) series, however, the spectra contained two well-defined intense broad bands viz., ν (TiCl) 372 and 310 cm^{-1}, ν (CrCl) 338 and 300 cm^{-1} respectively, which is consistent with a *fac*-arrangement of the ligands and C_{3v} molecular symmetry.[20]

The electronic spectra of the complexes are summarised in Table I. The spectrum of $[Cr(tren)_2]Cl_3$ obtained in aqueous solution at 273 K is essentially identical with that obtained by diffuse reflectance e.g., the stereochemistry of the complex is the same both in the solid state and in solution, and can be interpreted in terms of the chromium(III) ion experiencing a pseudo-octahedral ligand field environment.[21] The bands at 20,060 cm^{-1} and 26,300 cm^{-1} are assigned (O_h) to the $^4T_{2g} \leftarrow {}^4A_{2g}$ (F) and $^4T_{1g}$ (F) $\leftarrow {}^4A_{2g}$ (F) transitions respectively, with the former representing the ligand field splitting parameter 10 Dq of tren. As might be expected, the value obtained is commensurate with other CrN_6 chromophores e.g., $[Cr(en)_3]^{3+}$ 21,850 cm^{-1} [24] $[Cr(dien)_2]^{3+}$ 21,830 cm^{-1} [28] $[Cr(NH_3)_6]^{3+}$ 21,650 cm^{-1} [28]. From calculations[22] based on the authenticity of these assignments, the allowed third band $^4T_{1g}$ (P) $\leftarrow {}^4A_{2g}$ (F) is predicted at 48,800 cm^{-1} but could not be observed experimentally. A similar analysis of the spectrum of $CrCl_3 \cdot$(tren) leads to the assignments $^4T_{2g} \leftarrow {}^4A_{2g}$ (F) 16,900 cm^{-1} and $^4T_{1g}$ (F) $\leftarrow {}^4A_{2g}$ (F) 24,500 cm^{-1} the latter being only resolved as a shoulder however. Adopting the Dq values of 2006 cm^{-1} and 1345 cm^{-1} for tren (this work) and Cl^- [23] respectively, the first ligand field band of $CrCl_3 \cdot$(tren) is computed at 16,755 cm^{-1} under Jørgensens rule of average environment.

For an octahedral Ti(III) species the d-d spectrum will be modified to differing degrees according to whether a tetragonal or trigonal field component is present. Both $TiCl_3 \cdot$(tren) and $[Ti(tren)_2]Cl_3$ show a broad asymmetric band at ~ 13,000 cm^{-1} which, in view of the 10 Dq value (20,060 cm^{-1}) for tren obtained from the Cr(III)- derivatives above, is unlikely to be associated with a $^2E_g \leftarrow {}^2T_{2g}$ (10 Dq) transition. By analogy with the spectral analysis of $[Cr(en)_3]^{3+}$ and $[Ti(en)_3]^{3+}$ complexes[24], we assign this broad band to a $^2E \leftarrow {}^2A_1$ transition expected

TABLE I
Spectral data for the Ti(III)- and Cr(III)-tren complexes

		Electronic	*Infrared*^{e}					
Complex	Medium	Absorption Maxima†	ν_{as}(NH)	ν_s(NH)	ν_s(NH)^f	NH_2 bend	CH_2 rock	ν(MCl)
tren	a	rising to 40,000	3358 (s)	3282 (s)	3283	1590 (s)	904 (m)	
$TiCl_3 \cdot$(tren	b	~ 12,300 vw (sh); 12,900 asym. broad; 39,200 vw (sh).	3198 (s)	3130 (s)	3142	1580 (m)	885 (m)	310 (m) 372 (m)
$[Ti(tren)_2]Cl_3$	b	~ 12,150 vw (sh); 12,800 asym. broad; 24,690 w (sh); 39,680 vw (sh).	3180 (s)	3120 (s)	3126	1595 (m)	880 (m)	
$CrCl_3 \cdot$(tren)	b	16,900; 24,500 (sh); 45,800 vw (sh)	3195 (s)	3110 (s)	3140	1578 (m)	883 (w)	300 (m) 338 (s)
$[Cr(tren)_2]Cl_3$	c	19,600; 25,780; 39,000 vw (sh); ~ 45,500 vw (sh)	3140 (s)	3090 (s)	3089	1588 (m)	888 (m)	
	d	20,060; 26,300; 39,200 (sh)						

† λ_{max} given as cm^{-1}; ^{a}methanol solution ^{b}nujol mull ^{c}KBr disc ^{d}aqueous solution at 273 K

^{e}only major absorption bands of diagnostic use are included with assignments following (i) L. J. Bellamy, 'The Infrared Spectra of Complex Molecules', Methuen, London, 1964, ch. 14; (ii) J. R. Ferraro 'Low Frequency Vibrations of Inorganic and Coordination Compounds' Plenum, N.Y. 1971; ^{f} calculated from the equation $\nu_s = 345.53 + 0.875\ \nu_{as}$ see (i) above and reference.[25]

for a Ti(III) species experiencing a strong trigonal field distortion.[21]

The infrared spectra of the complexes were obtained in the range (4000–200) cm^{-1} and the major absorption bands useful in a diagnostic sense are collected in Table I. Several important observations concerning the mode of coordination in these metal-tren derivatives are possible from this data and these include:

(a) the absence of bands characteristic of coordinated trimethylamine[16a] verifies the chemical evidence that tren has effectively replaced this tertiary amine from the metal chloride adducts,

(b) the two absorption bands in the 3500–3300 cm^{-1} region for tren originate from the asymmetric ν_{as}(NH) 3358 cm^{-1} and symmetric ν_s(NH) 3282 cm^{-1} stretching frequencies, and conveniently identify the primary amine centres. These are retained in all the complexes but the frequencies are lowered by some 100–200 cm^{-1}. This result is typical for amine coordination and suggests that all the primary nitrogens of the ligand are in identical environments vis-a-vis metal-nitrogen bonding; any situation to the contrary e.g. *cis* – (tren)Co(III) complexes,[2g] gives rise to a complex band profile in this region. Confirmation of this point is obtained by application of the equation $\nu_s = 345.53 + 0.875\nu_{as}$ which represents the interdependence of ν_{as}(NH) and ν_s(NH) for primary amines, whether free or coordinated, *only* when there is nitrogen site-equivalence;[25] – see Table I –

(c) the band at ~ 1590 cm^{-1}, assigned to an antisymmetric NH_2 bending vibration, is common to all the spectra and its constancy is taken to infer a basic ligand structure throughout the two series,

(d) the implications of the ν(MCl) assignments have already been discussed

(e) perhaps the most important region in complexes of this type is that between 850–900 cm^{-1} which contains the CH_2 rocking mode of the metal-chelate ring. One of the most consistent variations between the spectra of the octahedral series $[Co(en)_2Cl_2]X$ where X = Cl, Br, I, SCN, ClO_4, $\frac{1}{2}S_2O_6$, is that the cis-isomers always show two bands in this region whereas the trans-isomers show just one, irregardless of the choice of counter-ion.[26] In similar vein, cis-isomers of $[Co(trien)X_2]X^1$ where X = Cl,Br,N_3,NO_2,H_2O and X^1 = Cl,Br,I show two infrared active bands in this region while trans-isomers only contain the one.[27] Again, the two bands observed for the $[Co(tren)X_2]X^1$ series, where X and X^1 = Cl,Br, provide strong evidence for a cis-configuration for these octahedral Co(III) complexes[1c] and in the series $Zn(tren)X_2$ and Zn(tren)XY where X = Cl,Br,I and Y = BPh_4, ClO_4 the presence of only one strong band at ~ 882 cm^{-1} was seen to refute any possible cis-octahedral geometry; a five coordinate assignment was made[1e] and later confirmed by an X-ray study (X = Cl, Y = BPh_4)[12]. The question of trans-isomers in all such octahedral $[M(tren)XY]X^1$ species is clearly outlawed on steric grounds.

All our metal-tren derivatives show only one band at ~ 884 cm^{-1} which, although consistent with a common basic structure, seriously impugns the presence of tren as a tetradentate ligand. For example, the $MCl_3 \cdot (tren)$ complexes with an octahedral M(III) centre would be forced into a cis-configuration (2 bands) should tren be tetradentate in the normal fashion; this is clearly untenable since the concomitant $[M(tren)Cl_2]Cl$ formulation has been disproved. Similar considerations for the $[M(tren)_2]Cl_3$ series provide the same denial.

Summarising the accumulated spectral and chemical evidence, we conclude that for the two series in question viz., $MCl_3 \cdot (tren)$ and $MCl_3 \cdot (tren)_2$ where M = Ti and Cr, tren has assumed a terdentate donor role with three primary amine nitrogen atoms, in conjunction with chlorine atoms where appropriate, making up the six-coordinate environment of the tervalent metal species. In this event the only uncommitted nitrogen has to be the apical tertiary amine which, although fairly weak in terms of donor strength, nevertheless should impart its basic character in aqueous solution. For $[Cr(tren)_2]Cl_3$ a conductometric titration with aqueous trichloroacetic acid at 273 K convincingly gave a titration curve typical of a strong acid ~ weak base system with the break corresponding to an equivalent point of 1:1.9.

Perhaps the one irregularity of the molecular geometry proposed for these metal-tren derivatives concerns the formation of 8-membered chelate rings implicit with the presence of 'free' tertiary amine site(s). Molecular models show that whereas this is stereochemically feasible the most obvious arrangement would favour a primary amine site as a 'dangling end' of the ligand with the preservation of 5-membered chelate rings. Compliance with this steric preferment is simply not possible, however, without serious contravention of the spectral and chemical evidence. This type of situation where the ligand is 'partially unwrapped' to show a lessened donor capacity is already known for tetren,[30] trien,[31] dien,[32] and en[33] and mitigating factors for the proposed terdentate behaviour in the present instance might include (a) the strong preference of the tervalent metal ions for an octahedral or pseudo-octahedral environment and (b) the weakness of the metal-nitrogen bond with a tertiary as compared with a primary source.[2d, 34] The general instability of the complexes in solution and the anomalous sequence en > dien > NH_3 > tren obtained from the observed 10 Dq value of tren are contrary to expected behaviour – the ligand field strength of tren is believed to be between that of en and NH_3 and to be less than that of trien[2g] – and possibly reflects some steric strain imposition. An X-ray structural analysis would clearly be most useful, and efforts in this direction are in progress.

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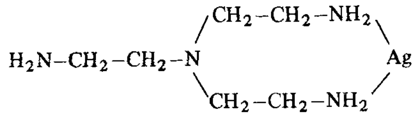

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