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Zinc(II), Iron(III), Molybdenum(II) Chloride and Molybdenum(V), Molybdenum(VI) Oxochloride Complexes of Trimethylamine: Synthesis, Spectra and X-ray Crystal Structure Characterisation

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Reactions of NMe_3 (L) with $ZnCl_2$, $FeCl_3$, $MoCl_3$, $MoCl_4$, $MoOCl_3$ and $MoOCl_4$ leading to possible reduction/adduct formation have been investigated. Complexes of the types MCl_2L_2 (M = Zn and Mo; the latter, obtained following reduction of Mo(III) chloride, is tentatively described as $Mo_2Cl_4L_4$ containing the quadruply bonded Mo_2^{4+} unit), $FeCl_3L_2$, MoOClL and $MoOCl_3L_2$ have been isolated and characterised spectroscopically. There is no reaction with Mo(IV) chloride.

X-ray crystal structure determinations have characterised '$ZnCl_2(NMe_3)_2$' as $[Me_3NH][ZnCl_3(NMe_3)]$ (I) following recrystallisation from benzene and confirmed that the iron complex $FeCl_3(NMe_3)_2$ (II) is monomeric. Crystals of (I) are orthorhombic, space group Pman, Z = 4, a = 9.785(8), b = 12.438(9), c = 11.497(11) Å. Crystals of (II) are orthorhombic, space group Pnma, Z = 4, a = 9.753(9), b = 10.150(11), c = 13.156(12) Å. 754, 1257 above background reflections have been collected on a diffractometer and refined to R 0.085, 0.052 respectively.

In (I) the zinc anion $[ZnCl_3(NMe_3)]^-$ is tetrahedral with Zn–Cl 2.232(3), 2.266(4) and Zn–N 2.074(11) Å. The cation is disordered. In (II) the iron atom is trigonal bipyramidal with chlorine atoms in equatorial positions (2.228(1), 2.207(2) Å) and nitrogens in axial positions (2.275(5), 2.270(5) Å).

Introduction

Trimethylamine is a powerful N-donor ligand which, by virtue of its reducing properties and comparatively large steric bulk, can form transition metal complexes combining both low oxidation state and low coordination number [1]. Herein we describe its reactions with several chlorides and oxochlorides of iron, molybdenum and zinc which illustrate these dual characteristics.

Experimental

NMe_3 (Aldrich Chemicals) was stored over KOH pellets and used as required. Anhydrous $FeCl_2$ was prepared from $FeCl_3$ following heating at reflux in chlorobenzene [2]. Other covalent metal halides were used directly as supplied commercially (Ventron).

The metal complexes were prepared by direct treatment of the anhydrous metal halide (oxohalide) (~2.0 g) with an excess (5–10 fold) of trimethylamine in a sealed double ampoule glass vessel. For those soluble in the parent amine, repeated filtration and subsequent back distillation across the sintered fritte provided pure (often crystalline) products directly. Those complexes that were insoluble in the parent amine were isolated and removed following pumping *in vacuo* at room temperature for several hours. Analytical data for the complexes are presented in Table I.

^{1}H nmr spectra were recorded on a Perkin Elmer R12 (60 MHz), Bruker WH90 (90 MHz) or a Perkin-Elmer R34 (220 MHz) spectrometer. Infrared spectra were recorded on a Perkin-Elmer 580B grating spectrophotometer. C, H, N analyses were carried out by Elemental Micro-Analysis Ltd, Beaworthy, Devon. Iron(III) and Zn(II) were determined by complexometric titration methods using EDTA following standard literature procedures [3]. Chloride was determined by the Volhard titration.

Structure Determination

Suitable crystals of (I) and (II) were selected from recrystallised samples obtained from methanol solutions and placed in Lindemann tubes. Precession photographs established preliminary cell constants and space groups. The crystals were then transferred to a Stoe STADI-2 diffractometer. Data were taken via ω scans of width (1.5 + $\sin\mu/\tan\theta$). The scan speed was 0.033° s^{-1} and the background was

0020-1693/84/$3.00

TABLE I. Microanalytical Data for Complexes.

Compound	Elemental (%), observed/calculated				
	C	H	N	Cl	Metal
$MoCl_2 \cdot 2NMe_3$	25.7/25.3	6.4/6.4	9.7/9.8	25.5/24.8	–
$MoOCl_3 \cdot 2NMe_3$ (green)	21.6/21.4	5.3/5.4	8.4/8.3	31.4/31.6	–
$MoOCl_3 \cdot 2NMe_3$ (brown)	21.8/21.4	5.6/5.4	8.5/8.3	29.9/31.6	–
$MoOCl \cdot NMe_3$	19.6/17.5	4.8/4.4	8.0/6.8	19.1/17.2	–
$[Me_3NH][ZnCl_3(NMe_3)]$	24.6/24.8	6.4/6.6	9.7/9.6	35.1/36.6	22.1/22.5
$FeCl_3 \cdot 2NMe_3$	25.2/25.7	6.5/6.5	9.8/10.0	19.7/19.9	38.2/37.9

TABLE II. Crystal Data and Refinement Details.

Compound	(I)	(II)
Formula	$[Me_3NH][ZnCl_3(NMe_3)]$ $C_6H_{19}N_2ZnCl_3$	$FeCl_3(NMe_3)_2$ $C_6H_{18}N_2FeCl_3$
M	290.9	280.3
Crystal Class	Orthorhombic	Orthorhombic
Space Group	Pman	Pnma
Absences	hk0, h + k = 2n + 1 h0l, l = 2n + 1	hk0, h = 2n + 1 0kl, k + l = 2n + 1
a(Å)	9.785(8)	9.753(9)
b(Å)	12.438(9)	10.150(11)
c(Å)	11.497(11)	13.156(12)
U(Å^3)	1399.2	1302.4
F(000)	596	580
Z	4	4
D_m	1.41	1.41
D_c	1.38	1.43
μ(cm^{-1})	23.2	17.5
λ(Å)	0.7107	0.7107
Crystal Size (mm)	0.4 × 0.5 × 0.5	0.5 × 0.8 × 0.9
Rotation Axis	a	a
2θ max (°)	45	50
No of Data Measured	1548	2056
No of Data Used in Refinement	754	1257
Criterion for Data Inclusion	$I > 3\sigma(I)$	$I > 3\sigma(I)$
Final R Value	0.085	0.052

measured at the ends of the ω scan for 20 s. Measurement of standard reflections showed no deterioration. Details of cell constants, data collection and refinement details are given in Table II.

In both structures, the Patterson function was used to determine the positions of the heaviest atoms. The positions of the remaining atoms were located from Fourier maps. In **(I)** both cation and anion had imposed m symmetry. The $[ZnCl_3(NMe_3)]^-$ anion was ordered with the metal Zn, a chlorine Cl(2), the nitrogen N(1) and a carbon atom C(13) on the mirror plane. The $[HNMe_3]^+$ cation was disordered with only the central nitrogen N(14) on the mirror plane. All three carbon atoms were located off the mirror plane and were given occupancy factors of 0.5. In **(II)** the molecule also had imposed m symmetry but there was no disorder.

Hydrogen atoms were included in **(I)** and **(II)** in calculated positions at 0.95 Å from the C or N atom to which they were bonded. Their thermal parameters were refined although those of H atoms bonded to the same atom were constrained to be the same. All non hydrogen atoms were refined anisotropically via full-matrix least squares. The scattering factors and dispersion corrections were taken from ref. 4. The final difference-Fourier maps showed no important features and in the final cycles of refinement no shift was greater than 0.1σ. Calculations were carried out using Shelx 76 [5] at the University of Manchester Computer Centre. The final R values for **(I)** and **(II)**

TABLE III. Atomic Co-ordinates ($\times 10^4$) for (I) with Estimated Standard Deviations in Parentheses.

Atom	X	Y	Z
Zn(1)	2500	17(1)	2381(1)
Cl(1)	600(4)	997(3)	2208(3)
Cl(2)	2500	−934(3)	4063(3)
N(1)	2500	−1156(9)	1102(9)
C(12)	3690(11)	−1809(11)	1182(13)
C(13)	2500	−595(19)	−48(14)
N(14)	2500	1073(10)	5742(11)
C(21)	2078(25)	871(21)	6953(20)
C(22)	3943(18)	1354(17)	5636(22)
C(23)	1826(24)	1949(19)	5073(22)

TABLE IV. Atomic Co-ordinates ($\times 10^4$) for (II) Estimated Standard Deviations in Parentheses.

Atom	X	Y	Z
Fe(1)	2970(1)	2500	232(1)
Cl(1)	2221(1)	4382(1)	905(1)
Cl(2)	4414(2)	2500	−1059(1)
N(1)	1186(5)	2500	−882(4)
N(2)	4768(5)	2500	1328(4)
C(1)	5626(5)	1302(5)	1155(4)
C(2)	4303(7)	2500	2380(5)
C(3)	1258(6)	1296(5)	−1547(4)
C(4)	−136(7)	2500	−349(5)

were 0.085 and 0.052 respectively. Atomic parameters are given in Tables III and IV, bond lengths and angles in Table V. The anisotropic thermal parameters, hydrogen positions and the structure factor Tables for both structures are deposited in the Supplementary Publication.

Results and Discussion

MoCl$_3$

Reaction of $MoCl_3$ with excess NMe_3 and a trace of Zn dust in a sealed double ampoule system provided a pale pink solution over a period of several months. Repeated filtration and back-distillation through the sintered disc gave purple micro-crystalline $MoCl_2 \cdot 2NMe_3$. This product proved to be exceptionally air-moisture sensitive with instantaneous decomposition to a green solid. The presence of a Zn catalyst is essential; when added directly $MoCl_3$ gave no sign of dissolution even after 6 months [6].

TABLE V. Molecular Dimensions, Distances, Å, Angles, Degrees.

IN (I)	
Zn(1)–Cl(1)	2.232(4)
Zn(1)–Cl(2)	2.266(4)
Zn(1)–N(1)	2.071(11)
N(1)–C(12)	1.423(13)
N(1)–C(13)	1.495(21)
N(14)–C(21)	1.474(24)
N(14)–C(22)	1.459(18)
N(14)–C(23)	1.488(25)
Cl(1)–Zn(1)–Cl(2)	111.18(12)
Cl(1)–Zn(1)–N(1)	108.74(18)
Cl(2)–Zn(1)–N(1)	103.8(3)
Cl(1)–Zn(1)–Cl(1*)	112.78(15)
Zn(1)–N(1)–C(12)	110.9(6)
Zn(1)–N(1)–C(13)	107.4(10)
C(12)–N(1)–C(13)	108.9(8)
C(12)–N(1)–C(12*)	109.8(10)
C(21)–N(14)–C(22)	113.0(15)
C(21)–N(14)–C(23)	119.3(14)
C(22)–N(14)–C(23)	102.2(16)
IN (II)	
Fe(1)–Cl(1)	2.228(1)
Fe(1)–Cl(2)	2.207(2)
Fe(1)–N(1)	2.275(5)
Fe(1)–N(2)	2.270(5)
N(1)–C(3)	1.505(6)
N(1)–C(4)	1.468(9)
N(2)–C(1)	1.494(5)
N(2)–C(2)	1.457(8)
Cl(1)–Fe(1)–Cl(2)	120.99(4)
Cl(1)–Fe(1)–N(1)	90.29(8)
Cl(2)–Fe(1)–N(1)	89.55(16)
Cl(1)–Fe(1)–N(2)	90.08(7)
Cl(2)–Fe(1)–N(2)	89.74(13)
N(1)–Fe(1)–N(2)	179.29(19)
Cl(1)–Fe(1)–Cl(1**)	118.0(5)
Fe(1)–N(1)–C(3)	109.82(29)
Fe(1)–N(1)–C(4)	111.4(3)
C(3)–N(1)–C(4)	108.6(3)
C(3)–N(1)–C(3**)	108.7(4)
Fe(1)–N(2)–C(1)	109.64(27)
Fe(1)–N(2)–C(2)	111.3(3)
C(1)–N(2)–C(2)	108.6(3)
C(1)–N(1**)–C(2)	109.0(4)

*Symmetry element 0.5 – X, Y, Z. **Symmetry element X, 0.5 – Y, Z.

The identity of this new Mo(II) species is not clear-cut. A previous complex isolated from the α-$MoCl_2/NMe_3$ system has been characterised as polynuclear $[Mo_6Cl_8]Cl_4 \cdot 2NMe_3$ [7]. This is but one of a general series *e.g.* $[Mo_6Cl_8]Cl_4 \cdot 2L$ where L = pyr, Et_3N, MeCN, Ph_3PO, NH_3, DMSO, DMF, which features retention of the α-form Mo_6 cluster unit found in the starting halide [7–10]. Accepting that simple room temperature reduction

$$\text{Mo(III)} \xrightarrow[\text{Zn}]{NMe_3} \text{Mo(II)}$$

is unlikely to lead to cluster formation [synthetic routes to octahedral Mo_6 units normally involve severe reaction conditions [11]], we favour a dinuclear formulation $Mo_2Cl_4(NMe_3)_4$ on the evidence of two strong IR bands ν(MoCl) at 332 and 280 cm^{-1}. Bands diagnostic for co-ordinated trimethylamine are present [1]. Tetrahalogenodimolybdenum(II) complexes of the types $Mo_2X_4L_4$ and $Mo_2X_4(L{-}L)_2$ where L = P, N, S, O donors, containing quadruply bonded pairs of molybdenum atoms are well documented [11]. These all show a distinctive twin-band profile in the far IR region [12], with one band at 337 ± 15 and the other at 285 ± 10 cm^{-1}, although spectral differentiation between the two idealised structures *trans–trans* eclipsed (D_{2h}) and *trans–trans* staggered (D_{2d}) for such $L_2X_2Mo\cdots MoX_2L_2$ species is virtually impossible. However, examples of both structures *e.g.* $Mo_2Br_4(pic)_4$ (D_{2h}) [13], $Mo_2Cl_4(SEt_2)_4$ (D_{2d}) [14], $Mo_2Cl_4(PMe_3)_4$ (D_{2d}) [15] have been identified by X-ray crystal structure studies.

As a comparison, dimethylamine and tertiary phosphines also form quadruply bonded complexes *e.g.* $Mo_2X_4(HNMe_2)_4$ and $Mo_2X_4(PR_3)_4$ R = Et, Pr^n for X = Cl, Br, following *reduction* of the Mo(III) halides [16, 17], but, as with our trimethylamine complex, only in very small yields. Adduct formation *without reduction* to give discrete mononuclear species *viz., fac*-MoX_3L_3 (L = pic, pyr, X = Cl, Br) [18] is yet another variant for these Mo(III) halides.

We were unable to obtain reliable solution spectra for the complex; deep purple solutions initially formed with a variety of donor and non-donor solvents decomposed to brown-black solids in a matter of seconds, *cf.* $Mo_2X_4L_4$ [12] (L = DMF, DMSO). Raman and X-ray crystal structure attempts also failed due to incipient decomposition of the complex under irradiation conditions.

MoCl₄

$MoCl_4$ proved to be totally unreactive towards trimethylamine over extended periods both with and without the use of a Zn catalyst. Equally, unchanged reactants were recovered from attempted ligand exchange reactions using $MoCl_4\cdot 2MeCN$ and an excess of amine.

MoOCl₃

Reaction of $MoOCl_3$ and excess trimethylamine in a double ampoule vessel gave a deep green solution and a pale brown solid. The green solution, following decantation *in situ*, invariably deposited a chocolate brown precipitate over a period of several hours. Total extraction of the amine-soluble products resulted in a mixture of green and brown solids which defied all attempts at separation. In a separate experiment, a single, rapid extraction, however, afforded a small sample of $MoOCl_3\cdot 2NMe_3$ as microcrystalline green crystals. These proved to be highly air-moisture sensitive and dissolved with decomposition in a range of donor solvents to give deep brown solutions with heavy sedimentation. The IR spectrum confirms the presence of co-ordinated trimethylamine [1] and shows one strong band at 955 cm^{-1} assigned as a ν(Mo=O) stretching mode, *cf.* $MoOCl_3\cdot 2PPh_3$, 950 cm^{-1}; $MoOCl_3\cdot 2Ph_3PO$, 967 cm^{-1} [19], and three intense broad bands at 345, 325 and 255 cm^{-1} assigned as ν(MoCl) modes. Again it is not possible to distinguish between the three idealised six co-ordinate structures, *viz., fac*(C_s), *mer*(C_s) and *mer*(C_{2v}) solely by infrared spectroscopy since all three are predicted to give the same number of bands; a single crystal X-ray determination of $MoOCl_3\cdot 2HMPA$ established the *mer*(C_s) structure [20]. A pure sample of the chocolate brown solid, obtained by careful re-extraction of the amine-soluble products, also analysed as $MoOCl_3\cdot 2NMe_3$. The IR spectrum confirms the presence of co-ordinated trimethylamine [1] and multiple bands in the 950–990 cm^{-1} region probably comprise $\rho(CH_3)$ ligand and ν(Mo=O) modes. Additional bands at 675 cm^{-1} and 656 cm^{-1}, which are absent in the spectrum of the parent green material, are assigned as ν_{as}(Mo–O–Mo) stretching vibrations implicit with a polymeric formulation [21].

MoOCl₄

Treatment of $MoOCl_4$ with excess trimethylamine provided a small amount (~3%) of the amine-soluble orange-brown solid (following 30 extractions *in situ*) approximating to $MoOCl\cdot NMe_3$. Reduction of Mo(VI) → Mo(III) under these conditions is perhaps not too surprising, bearing in mind the reducing properties of the amine and the oxidising power of $MoOCl_4$ towards organic substrates [22]. Multiple bands in the IR spectrum in the region 950–990 cm^{-1} and strong bands at 754, 655, and 450 cm^{-1} are again in line with an O-bridged polymeric formulation [21].

ZnCl₂

The adduct formed, following direct treatment of zinc(II) chloride with excess trimethylamine, is a flocculent white solid insoluble in the parent amine. Nöth *et al.* [23] have confirmed this, previously, as $ZnCl_2\cdot 2NMe_3$. The product is readily soluble in boiling benzene to give small white needles on cooling. Further recrystallisation gave small cubic crystals. Our preliminary single crystal X-ray diffraction studies indicated either an $[NMe_4][ZnCl_3(NMe_3)]$ or an $[Me_3NH][ZnCl_3(NMe_3)]$ formulation, the structure of the anion being unambiguous with a tetrahedral Zn(II) geometry. Microanalytical data supported the latter (see Table I). The room temperature ^1H nmr spectrum (60 MHz, $CDCl_3$ solution with tetramethylsilane (δ = 0 ppm) as internal reference) merely shows a singlet at δ_{CH} 2.67 and a small broad

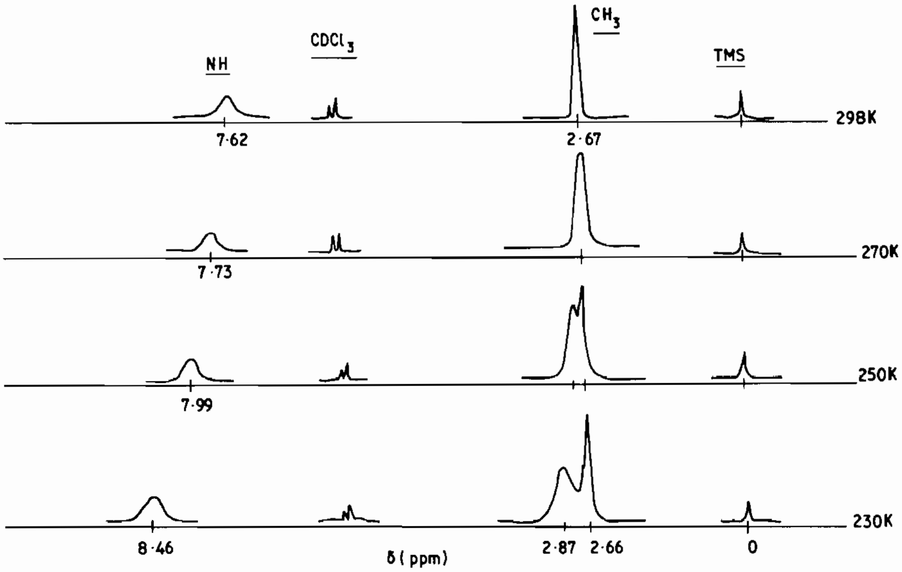

Fig. 1. Variable temperature ^1H nmr spectra of $[Me_3NH][ZnCl_3(NMe_3)]$.

singlet at δ_{NH^+} 7.62. On lowering the temperature (298 → 230 K), however there is broadening and then splitting of the methyl signal into two singlets, δ_{CH} 2.87 and 2.66, implicit with NMe_3 (cation ↔ anion) exchange in solution as expected. The amine proton signal moves steadily downfield, δ_{NH^+} 7.62 → 8.46, presumably as a reflection of increased hydrogen bonding at lower temperatures (Fig. 1). The IR spectrum shows a band at 2780 cm^{-1} assigned as $\nu(NH^+)$ (the corresponding band for $Me_3NH^+Cl^-$ occurs at 2735 cm^{-1}) and the characteristic bands due to co-ordinated trimethylamine [1]. The low IR region shows two intense $\nu(Zn-Cl)$ bands at 320 cm^{-1} and 297 cm^{-1}. Both $MX_2L_2(C_{2v})$ ($a_1 + b_1$) and $MX_3L(C_{3v})$ (a_1 + e) tetrahedral species are expected to show two $\nu(MX)$ normal modes as observed in $ZnCl_2 \cdot 2py$ (329, 296 cm^{-1}) [24, 25] and $ZnCl_2 \cdot 2DMF$ (332, 292 cm^{-1}) [26].

$FeCl_3$

In a very vigorous reaction which is complete after several minutes at room temperature iron(III) chloride and excess trimethylamine give a deep-red clear solution. Extraction *in situ* leads to large claret crystals of $FeCl_3 \cdot 2NMe_3$ (see Table I) suitable for X-ray crystallographic study. Leaving the reaction for periods over 24 hours results in a mixture of products namely claret crystals, yellow crystals and a white solid insoluble in the parent amine. The latter are presumed as Fe(II) reduction products and are under current investigation.

The claret bis-adduct $FeCl_3 \cdot 2NMe_3$ (**II**) has been isolated previously by Collis [27] and shown by low IR and Raman studies (unpublished) to have a trigonal bipyramidal structure. The present X-ray diffraction investigation now confirms this structure as having almost perfect D_{3h} symmetry and throws additional light onto the structural ramifications, electronic *versus* steric, for the 5 co-ordinate $MX_3 \cdot 2NMe_3$ series of the 1st row elements which presently includes M = Sc [27], Ti [1(b), 28], V [1(a), 29] and Cr [1(b), 30].

Discussion of the Structures

The X-ray structure determination of '$ZnCl_2(NMe_3)_2$' following recrystallisation from benzene has established an ionic structure consisting of disordered $[Me_3NH]^+$ cations and $[ZnCl_3(NMe_3)]^-$ anions. The anion has crystallographically imposed m symmetry and is illustrated together with the atomic numbering scheme in Fig. 2. Both the metal environment and that of the nitrogen atom are tetrahedral. The Zn–Cl bond lengths (2.232(4), 2.266(4) Å) lie within the range expected for tetrahedral $ZnCl_2L_2$ (L = monodentate N donor) species, *viz.* 2.20–2.30 Å [31, 32]. A search of the Cambridge Data Centre

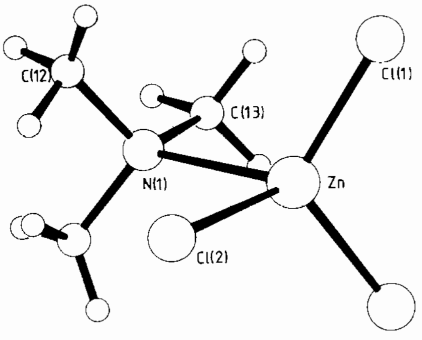

Fig. 2. Structure of (I).

files [33] gave seven tetrahedral $ZnCl_3N$ moieties but these are not directly comparable as all the donor nitrogen atoms were trigonal and part of unsaturated ring systems like adeninium, guaninium, pyridinium and purinium. The Zn–N distance in (I) is 2.071(11) Å and comparable with the Zn–N distances in the other tetrahedral compounds which average 2.069 Å. The geometry is slightly distorted from ideal symmetry with the Cl–Zn–Cl angles (111.18(12), 112.78(15)°) consistently larger than the Cl–Zn–N angles (108.74(18), 103.8(3)°).

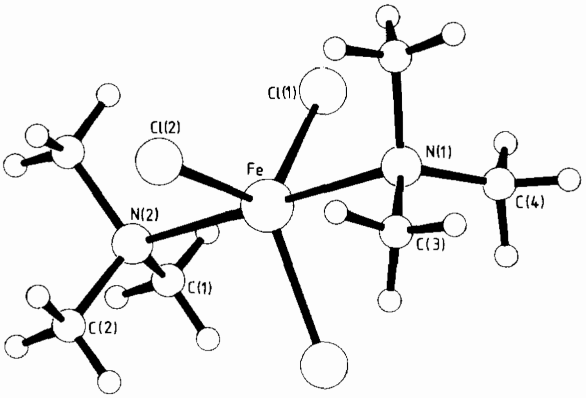

Fig. 3. Structure of (II).

The structure of (**II**) is quite different and contains monomeric discrete $FeCl_3(NMe_3)_2$ units. Again the metal atom has imposed crystallographic m symmetry (Fig. 3). This time the metal occupies a trigonal bipyramidal environment with the two nitrogen atoms occupying the axial positions. Hence (**II**) can be included in the isomorphous 5-co-ordinate $MX_3(NMe_3)_2$ series where M(III) = Sc [27], Ti [28], V [29], Cr [30], In [35]; X = Cl, Br which exhibit a common trigonal bipyramidal structure. The Fe–Cl bond lengths (2.228(1), 2.207(2) Å) compare favourably with those of $FeCl_3(4\text{-cpy})_2$ (4-cpy = 4-cyanopyridine) (2.204(1), 2.216(1), 2.229(1) Å) [34] which represents one of only a few such 5 co-ordinate MX_3L_2 (L = monodentate) complexes involving iron(III). Daran *et al.* [34] have already commented on the fact that the $MX_3(NMe_3)_2$ complexes all show obvious differences in the three equatorial M–X bond distances. Interestingly the axial Fe–N bond lengths in (**II**) (2.275(5), 2.270(5) Å) are identical (a situation unique for the $MX_3(NMe_3)_2$ series) and significantly longer than the Fe–N bond distances in $FeCl_3(4\text{-cpy})_2$ (2.232(3), 2.213(3) Å) [34] presumably as a result of the steric crowding (atom-atom repulsions) induced by the tetrahedral, as opposed to trigonal, axial nitrogen centres. There can be no π-component to the Fe–N bonds in (**II**). There is little distortion from D_{3h} symmetry: the Cl–Fe–Cl angle is 120.99(4), and the Cl–Fe–N angles 90.29(8), 90.08(7), 89.55(16), 89.74(13)° respectively.

Acknowledgements

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