

Reactions of trimethylamine with Mn(II) and Cd(II) chlorides: crystal and molecular structure of $[\text{Me}_3\text{NH}][\text{MnCl}_3]$

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(Received January 18, 1990; revised March 22, 1990)

Abstract

Trimethylamine reacts with MCl_2 ($\text{M} = \text{Mn}, \text{Cd}$) to give the mono-adducts $\text{MnCl}_2(\text{NMe}_3)$ (I) and $\text{CdCl}_2(\text{NMe}_3)$ (II), respectively. Attempted crystallisation of I from MeCN provides the anionic complexes $[\text{Me}_3\text{NH}][\text{MnCl}_3]$ (III) and $[\text{Me}_3\text{NH}]_2[\text{MnCl}_4]$ (IV) both from the same solution. Compound III has been fully characterised via an X-ray crystal structure determination; crystals are orthorhombic, space group *Pcmm* (non-standard setting of *Pnma*, No. 62) with cell constants $a = 8.938(7)$, $b = 6.474(8)$, $c = 14.396(14)$ Å, $V = 833.0$ Å³, $M_r = 221.4$, $Z = 4$, $D_c = 1.76$ g cm⁻³. The final *R* value for 603 unique reflections [$I > 2\sigma(I)$] is 0.077. The structure consists of polymeric linear chains of six coordinate Mn atoms linked by triple halogen bridges together with discrete $[\text{Me}_3\text{NH}]^+$ cations. Similar treatment of II with MeCN results in the formation of $[\text{Me}_3\text{NH}][\text{CdCl}_3]$. Single crystal diffraction data confirm that $[\text{Me}_3\text{NH}][\text{MnCl}_3]$ (III) and $[\text{Me}_3\text{NH}][\text{CdCl}_3]$ are isomorphous.

Introduction

As part of a systematic investigation of the structural chemistry of trimethylamine complexes of bivalent transition metal halides, we have described the anionic zinc(II) complex $[\text{Me}_3\text{NH}][\text{ZnCl}_3(\text{NMe}_3)]$ [1]. This complex was obtained, along with other unidentified Zn(II) residues, via an attempted crystallisation from benzene of the neutral adduct $\text{ZnCl}_2(\text{NMe}_3)_2$ initially isolated from the $\text{ZnCl}_2\text{-NMe}_3$ system. The anion belongs to the tetrahedral Zn(II) series $[\text{ZnCl}_3\text{Y}]^-$ which includes $\text{Y} = \text{Cl}$ [2], H_2O [3], THF [4], acetone [5] and tBu_3P [6a]**; they can be viewed as precursors to $[\text{Zn}_2\text{Cl}_6]^{2-}$ following dimerisation with loss of 2Y [4]. This present study is concerned with the $\text{MCl}_2\text{-NMe}_3$ systems where $\text{M} = \text{Mn}, \text{Cd}$.

Experimental

All manipulations of reactants and products were carried out either under an atmosphere of dry ni-

trogen using a standard 'dry-box' or *in vacuo* using a conventional all-glass high vacuum line. Trimethylamine was stored over P_2O_5 and used as required. Acetonitrile was heated at reflux over KMnO_4 for 6 h and distilled on to CaH_2 . After further treatment by heating at reflux (6 h) under a N_2 atmosphere, the product was fractionally distilled as required. Benzene was distilled from benzophenone ketyl prior to use. Anhydrous CdCl_2 and MnCl_2 were used as supplied commercially.

Microanalyses were performed by Medac Ltd., Department of Chemistry, Brunel University, Uxbridge, Middlesex, U.K. Chloride was determined by the Volhard titration. ^1H NMR spectra were recorded on a Perkin-Elmer R34 (220 MHz) spectrometer. IR spectra were obtained using a Perkin-Elmer 580B spectrophotometer with samples as nujol mulls placed between CsI plates.

Preparation of complexes

The metal complexes were prepared by direct treatment of the anhydrous metal chloride (2 g) with an excess (30 cm³) of trimethylamine in a double-ampoule vessel following the procedures described previously [1].

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**Though not discrete anions the complex $\text{V}(\text{THF})_2[(\mu\text{-Cl})_2\text{ZnCl}_3\text{PPh}_3]_2$ contains two tetrahedral $\text{ZnCl}_3\text{PPh}_3$ units [6b].

MnCl₂(NMe₃) (I)

An insoluble precipitate was formed, the reaction taking about 1 week to consume all the pale pink manganese(II) chloride. Removal of amine gave the product as an off-white solid which was washed with n-pentane and dried *in vacuo*. *Anal.* Found: C, 19.2; H, 4.8; N, 7.6; Cl, 38.1. Calc. for C₃H₉NMnCl₂: C, 19.5; H, 4.9; N, 7.6; Cl, 38.3%.

Treatment of I (1.66 g) by Soxhlet extraction using boiling MeCN over a period of 24 h resulted in the formation of a deep green solution and an insoluble grey residue left behind in the extraction thimble. Gradual removal of solvent from the saturated green solution provided a crop of pink crystals which were carefully removed. Complete removal of solvent from the remaining mother liquor provided a dark green solid. Subsequent recrystallisations from MeCN/CH₂Cl₂ of these two separate products provided III and IV, respectively.

Yield of pink cylindrical rod crystals of [Me₃NH][MnCl₃] (III): 0.74 g. *Anal.* Calc. for C₃H₁₀NMnCl₃: C, 16.3; H, 4.6; N, 6.3; Cl, 48.0. Found: C, 16.6; H, 4.7; N, 6.6; Cl, 47.6%.

Yield of light green needle crystals of [Me₃NH]₂[MnCl₄] (IV): 0.31 g. *Anal.* Calc. for C₆H₂₀N₂MnCl₄: C, 22.7; H, 6.3; N, 8.8; Cl, 44.8. Found: C, 22.4; H, 6.0; N, 8.7; Cl, 44.3%.

CdCl₂(NMe₃) (II)

A white viscous slurry was formed over a period of 1 week. Removal of amine left the product as a white solid which was washed with n-hexane and dried *in vacuo*. *Anal.* Found: C, 14.4; H, 3.7; N, 5.2; Cl, 29.1. Calc. for C₃H₉NCdCl₂: C, 14.9; H, 3.7; N, 5.8; Cl, 29.2%.

Treatment of II (1.34 g) by Soxhlet extraction using boiling MeCN (3 days) provided a clear colourless solution and an off-white insoluble residue in the extraction thimble. Storage of the saturated solution at 0 °C resulted in the deposition of white needle crystals of [Me₃NH][CdCl₃] (0.87 g). The product was collected, washed with n-pentane and dried *in vacuo*. *Anal.* Calc. for C₃H₁₀NCdCl₃: C, 12.9; H, 3.6; N, 5.0; Cl, 38.2. Found: C, 12.8; H, 3.6; N, 5.2; Cl, 38.1%.

*Crystal structure determination of [Me₃NH][MnCl₃] (III)**Crystal data*

MnCl₃NC₃H₁₀, *M_r* = 221.4, orthorhombic, *a* = 8.938(7), *b* = 6.474(8), *c* = 14.396(14) Å, *V* = 833.0 Å³, *F*(000) = 444, *D_c* = 1.76 g cm⁻³, *Z* = 4, Mo Kα radiation (λ = 0.7107 Å), μ (Mo Kα) = 25.17 cm⁻¹, space group *Pcmm* from systematic absences *hk0*, *h + k = 2n + 1*, *0kl*, *k = 2n + 1* (non-standard setting of *Pnma*, No. 62).

A crystal of approximate size 0.25 × 0.20 × 0.15 mm was set up to rotate about the *b* axis on a Stoe Stadi2 diffractometer and data were collected via variable width *w* scan. Background counts were for 20 s and a scan rate of 0.0333° s⁻¹ was applied to a width of (1.5 + sin μ/tan θ). A total of 839 independent reflections was measured up to a 2θ maximum of 50° of which 603 with *I* > 2σ(*I*) were used in subsequent refinement. The structure was determined by Patterson and Fourier methods. All non-hydrogen atoms were in special positions apart from one carbon atom. Hydrogen atoms on this carbon were included as a rigid group. Other hydrogen atoms were introduced in positions compatible with the difference Fourier map and refined using distance constraints. Calculations were performed using full-matrix least-squares methods with a weighting scheme *w* = 1/[σ²(*F*) + 0.003*F*²]. Calculations were performed using SHELX76 [7] on the Amdahl V7 Computer at the University of Reading. The final *R* values were 0.077 (*R_w* = 0.079). In the final cycle of refinement the maximum shift/error ratio was 0.2

TABLE 1. Atomic coordinates (×10⁴) with e.s.d.s. in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Mn(1)	0	0	0
Cl(1)	1482(3)	2500	1042(2)
Cl(2)	721(3)	2500	-1283(2)
Cl(3)	-2121(5)	2500	279(2)
N(1)	4732(13)	7500	1957(10)
C(2)	5161(11)	5573(21)	1414(8)
C(3)	3178(15)	7500	2238(9)

TABLE 2. Molecular dimensions: distances (Å) and angles (°)

Anionic polymer chain		
Mn(1)–Cl(1)		2.573(2)
Mn(1)–Cl(2)		2.539(2)
Mn(1)–Cl(3)		2.525(2)
Cl(1)–Mn(1)–Cl(2)		83.83(8)
Cl(1)–Mn(1)–Cl(3)		83.71(7)
Cl(2)–Mn(1)–Cl(3)		84.12(8)
Mn(1)–Cl(1)–Mn(1 [*])		77.93(8)
Mn(1)–Cl(2)–Mn(1 [*])		79.21(8)
Mn(1)–Cl(3)–Mn(1 [*])		79.74(8)
Cation		
N(1)–C(2)		1.521(14)
N(1)–C(3)		1.447(17)
C(2)–N(1)–C(2 [*])		110.2(11)
C(2)–N(1)–C(3)		112.7(7)

*Symmetry element *x*, 0.5 – *y*, *z*.

and in the final difference Fourier map, maximum and minimum peaks were 0.62 and $-0.54 \text{ e } \text{\AA}^{-3}$, respectively. Positional coordinates are given in Table 1 and molecular dimensions in Table 2. See also 'Supplementary material'.

Results and discussion

Reaction of trimethylamine with anhydrous manganese(II) chloride provides the mono-adduct $\text{MnCl}_2(\text{NMe}_3)$ (I) which is assumed, by comparison with tertiary phosphine analogues $[\text{MnX}_2\text{L}]$ where X=halogen, NCS; L=tertiary phosphine, to have a polymeric or, at the least, an oligomeric structure in the solid state [8]. IR bands at $1255 \nu_{\text{as}}(\text{CN})$, $989 \rho(\text{CH}_3)$, $811 \nu_{\text{s}}(\text{CN})$ and $509 \delta_{\text{as}}(\text{CN}) \text{ cm}^{-1}$ confirm the presence of coordinated amine. One interesting facet of the tertiary phosphine complexes is their general ability to reversibly coordinate dioxygen and other small molecules such as NO, CO etc., under quite mild conditions [9]. With dioxygen and $\text{MnCl}_2(\text{PMe}_3)$, which is the direct trimethylamine counterpart, there is an irreversible oxidation reaction to produce the Mn(III) complex $\text{MnCl}_3(\text{PMe}_3)_2$ along with other products [10]. From our investigations I shows no reaction with dioxygen under various conditions.

An attempted crystallisation of I via Soxhlet extraction with boiling MeCN provides a green solution from which two products, both chloro-anions, were isolated: red $[\text{Me}_3\text{NH}][\text{MnCl}_3]$ (III) ($\nu(\text{NH}^+)$ 2786, $\nu(\text{MnCl})$ 225 cm^{-1}) and green $[\text{Me}_3\text{NH}]_2[\text{MnCl}_4]$ (IV) ($\nu(\text{NH}^+)$ 2735, $\nu(\text{MnCl})$ 286, 265, 240 cm^{-1}). Whereas the Vis-UV spectrum of III ($\lambda_{\text{max}}(\text{MeCN})$ 444, 430, 360, 307 nm) is only partially resolved, due

to limited solubility in MeCN, that of IV ($\lambda_{\text{max}}(\text{MeCN})$ 687, 664(sh), 630(sh), 590, 446, 430, 357, 306 nm) is indicative of octahedral Mn(II) species in solution. Recrystallisation of III from MeCN/ CH_2Cl_2 gave red cylindrical rod crystals of suitable quality for an X-ray structure determination. In addition to the present species, MnCl_3^- [11] and MnCl_4^{2-} [12], other chloro-anions of Mn(II) include MnCl_8^{6-} and $\text{Mn}_3\text{Cl}_8^{2-}$ [13], MnCl_6^{4-} [14] and $\text{Mn}_2\text{Cl}_7^{3-}$ [15] but there is no direct analogue of the tetrahedral zinc(II) species $[\text{ZnCl}_3\text{Y}]^-$ (above).

Structure of $[\text{Me}_3\text{NH}][\text{MnCl}_3]$

The structure of $[\text{Me}_3\text{NH}][\text{MnCl}_3]$ (Fig. 1) is similar to that observed for $[\text{Me}_3\text{NH}][\text{CdCl}_3]$ [16] in that it contains $[\text{Me}_3\text{NH}]^+$ cations and one-dimensional $[\text{MnCl}_3]^{n-}$ polymeric chains in comparable unit cells. However, for our Mn salt, it proved possible to refine the cation as ordered rather than disordered around the crystallographic mirror planes.

The Mn-Cl bond lengths in the $[\text{MnCl}_3]^{n-}$ anion (Table 2) can be compared to the unique value of 2.560(2) \AA found in similar chains in $[\text{NMe}_4][\text{MnCl}_3]$ [11]. However, of the three unique bonds in the anion, Mn-Cl(1) at 2.573(2) \AA is significantly longer than the other two (Mn-Cl(2) 2.539(2), Mn-Cl(3) 2.525(2) \AA). It seems likely that this elongation is due to the formation of the N(1)-H...Cl(1) hydrogen bond (N...Cl 3.28(2), H...Cl 2.46 \AA). Similar variations in the M-Cl distances are observed in the $[\text{CdCl}_3]^{n-}$ anion [16] (see 'Additional comment').

Direct treatment of CdCl_2 with an excess of trimethylamine over a period of several days gives the white amine-insoluble adduct $\text{CdCl}_2(\text{NMe}_3)$ (II). Typically CdX_2L complexes (X=halogen, L=substi-

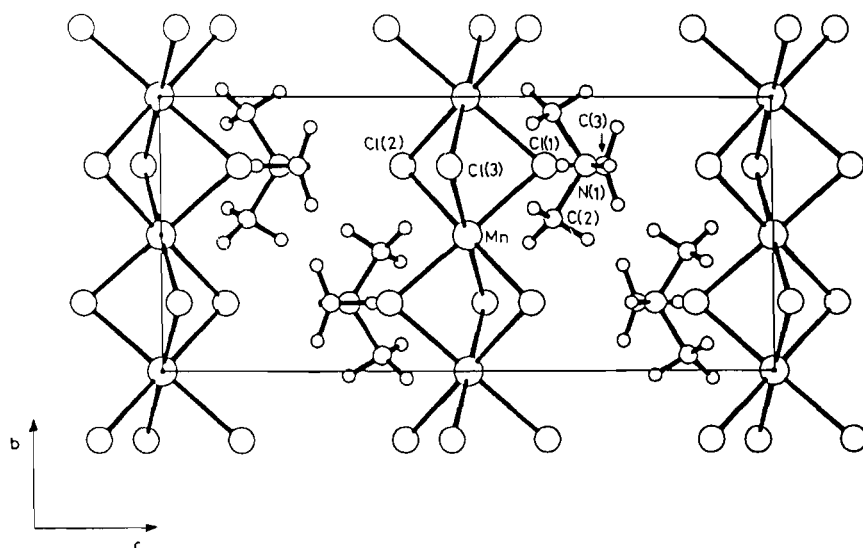


Fig. 1. Unit cell of $[\text{Me}_3\text{NH}][\text{MnCl}_3]$ in the a projection.

tuted phosphine) are dimeric with tetrahedral metal ions linked by halogen bridges, e.g. X=Cl, Br; L=^tBu₃P [17], X=I, L=PEt₃ [18], and the same structure is assumed for **I**. The IR spectrum contains bands at 1260 $\nu_{as}(\text{CN})$, 1012 $\rho(\text{CH}_3)$, 825 $\nu_3(\text{CN})$ and 488 $\delta_{as}(\text{CN}) \text{ cm}^{-1}$ associated with coordinated trimethylamine and also two bands below 400 cm^{-1} which are assigned as $\nu(\text{CdCl})_{\text{terminal}} 244 \text{ cm}^{-1}$ and $\nu(\text{CdCl})_{\text{bridge}} 210 \text{ cm}^{-1}$, cf. $[\text{CdCl}_2(^t\text{Bu}_3\text{P})_2]$ $\nu(\text{CdCl})$ 285 and 208 cm^{-1} [17]. An attempted crystallisation of **II** by Soxhlet extraction with boiling MeCN leads to the formation of $[\text{Me}_3\text{NH}][\text{CdCl}_3]$ (see 'Additional Comment') and an insoluble light-brown Cd^{II}-containing residue. The IR spectrum of this product contains a characteristic $\nu(\text{NH}^+)$ band, 2778 cm^{-1} , and the room temperature ¹H NMR spectrum shows a sharp singlet δ_{CH_3} 2.78 and a much broader signal at δ_{NH^+} 11.75 ppm. Both signals show a perceptible downfield shift (δ_{CH_3} 2.84, δ_{NH^+} 12.20) on cooling from 298–230K. Various chloro-anions of Cd(II) are known, for example, CdCl_3^- [19], CdCl_5^{3-} [20], CdCl_6^{4-} [21] and $\text{Cd}_2\text{Cl}_6^{2-}$ [22] but again there is no tetrahedral equivalent to $[\text{ZnCl}_3\text{Y}]^-$.

General considerations

There are several factors common to these $\text{MCl}_2\text{-NMe}_3$ systems, M=Cd, Mn (present study) and M=Zn (previous) [1]: the complete insolubility of $\text{ZnCl}_2(\text{NMe}_3)_2$, $\text{CdCl}_2(\text{NMe}_3)$ and $\text{MnCl}_2(\text{NMe}_3)$ in parent trimethylamine denies the usual extraction *in situ*, so effective for the tervalent metal halide systems $\text{MCl}_3\text{-NMe}_3$ (M=Ti, V, Cr, Fe, In), which provide the respective bis-adducts as amine-soluble mononuclear five coordinate (D_{3h}) species (Fe [1]; Sc [23a]; Ti [23b]; V [23c]; Cr [23d]; In [23e]); subsequent attempts to crystallise the M(II) adducts using polar coordinating solvents results in the formation of soluble complex anions together with insoluble (M^{II}-containing) residues; the resulting cation is always trimethylammonium.

How the $\text{MCl}_2(\text{NMe}_3)$ complexes rearrange in MeCN to give the corresponding anions is open to question. Studies by Goel *et al.* [6a, 17] of the M(II) halide-^tBu₃P systems (M=Co, Ni, Zn, Cd) lend emphasis to the importance of the choice of solvent, e.g. with 1-butanol anionic complexes $[\text{Bu}_3\text{PH}][\text{MX}_3\text{P}^t\text{Bu}_3]$ are isolated following phosphine protonation by the solvent; in aprotic solvents the neutral $\text{MX}_2\text{P}^t\text{Bu}_3$ adducts are formed. In our present study, solvent (MeCN) abstraction is a possible but extremely unlikely source of protons.

We believe traces of water in the solvent play a crucial role in initiating limited solvolysis of M–Cl bonds to give molecular rearrangement with incipient halide transfer and loss of coordinated trimethyla-

mine. The latter provides the trimethylammonium cation following proton capture; the formation of insoluble residues, most likely $[\text{M}^{\text{II}}(\text{oxo})(\text{hydroxo})(\text{chloro})](?)$ species, is seen to preserve the overall balance of metal:halogen.

Additional comment

Chapius and Zuniga [16] have reported the X-ray crystal structures of three phases of $[\text{Me}_3\text{NH}][\text{CdCl}_3]$. The basic structure is made up of one-dimensional chains of face-fused CdCl_6 octahedra with disordered trimethylammonium cations located in the free space between the chains. Additionally the organic cation is involved in a strong hydrogen bond N–H...Cl with a chlorine atom. The X-ray crystal structure of our product, carried out as an independent study, is similar to those at 174 and 295 K; all three structures have equivalent dimensions for the polymeric CdCl_3 anion.

Cell data. $\text{CdCl}_3\text{NC}_3\text{H}_{10}$: $M_r = 278.9$, orthorhombic, $a = 8.855(7)$, $b = 6.689(6)$, $c = 14.308(10)$ Å, $V = 847.5$ Å³, $Z = 4$, $D_c = 2.18 \text{ g cm}^{-3}$, Mo K α radiation ($\lambda = 0.7107$ Å), $\mu(\text{Mo K}\alpha) = 34.0 \text{ cm}^{-1}$, space group *Pcmn* (non-standard setting of *Pnma*, No. 62) from the systematic absences, $hk0$, $h+k=2n+1$, $0kl$, $k+1=2n+1$, and from the successful structure determination.

Supplementary material

Tables of thermal parameters and hydrogen atom positions are available from the authors on request.

Acknowledgements

We thank the SERC for financial support and Mr. A. W. Johans for his assistance with the crystallographic investigations.

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