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A study of the copper(II) chloride–trimethylamine system. Crystal and molecular structure of bis[trimethyl(chloromethyl)ammonium]tetrachlorocuprate(II), $[Me_3NCH_2Cl]_2[CuCl_4]$

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Abstract

Treatment of anhydrous $CuCl_2$ with excess NMe_3 at room temperature gives the yellow mono-adduct $CuCl_2 \cdot 1.1NMe_3$ (**I**). Attempted recrystallization of **I** from CH_2Cl_2 provides the orange tetrachlorocuprate(II) salt $[Me_3NCH_2Cl]_2[CuCl_4]$ (**II**). The same product is obtained from direct treatment of $CuCl_2$ with a mixture of NMe_3/CH_2Cl_2. The structure of **II** has been determined by conventional X-ray diffraction techniques: crystals are monoclinic, space group $P2_1/n$ with cell constants $a = 17.20(1)$, $b = 11.78(1)$, $c = 9.067(7)$ Å, $\beta = 90.5(1)°$, $U = 1837.0$ Å^3, $Z = 4$. The final R value for 1620 unique reflections ($I > 2\sigma(I)$) is 0.062 ($R_w = 0.064$). The structure consists of two independent $[Me_3NCH_2Cl]^+$ cations and one discrete $[CuCl_4]^{2-}$ anion whose geometry is intermediate between tetrahedral and square planar with *trans* Cl–Cu–Cl angles of 132.5(1) and 134.4(1)° and Cu–Cl distances in the range 2.232(3)–2.253(3) Å.

Introduction

As befits a powerful, monodentate N-donor trimethylamine forms a wide variety of transition and post-transition metal (M) complexes. Tetrahalide metal complexes include $TiX_4 \cdot NMe_3$, X = Cl, Br [1a]**; $ZrX_4 \cdot 2NMe_3$, X = Cl, Br, I [2]; $HfX_4 \cdot 2NMe_3$, X = Cl, Br, I [3]; $ThCl_4 \cdot 3NMe_3$ [4]; $UCl_4 \cdot 2NMe_3$ [5]. With tervalent halides the resulting bis-adducts $MX_3 \cdot 2NMe_3$, M = Sc [6a], Ti [6b], V [6c], Cr [6d], Fe [6e], In [6f]; X = Cl, Br are amine-soluble and share a common five coordinate trigonal bipyramidal structure. By way of contrast metal dihalides invariably give oligomeric/polymeric complexes $[MX_2 \cdot NMe_3]$ which are insoluble in the parent amine; subsequent attempts to recrystallize these materials from typical organic solvents leads to the formation of trimethylammonium salts involving complex haloanions, e.g.

$$ZnCl_2 \cdot NMe_3 \longrightarrow [Me_3NH][ZnCl_3(NMe_3)]\ [6e]$$

$$CdCl_2 \cdot NMe_3 \longrightarrow [Me_3NH][CdCl_3]$$

$$MnCl_2 \cdot NMe_3 \longrightarrow [Me_3NH][MnCl_3]\ \text{and}\ [Me_3NH]_2[MnCl_4]\ [7]$$

Specifically for Cu(II), Lane and Yoke [8] have reported that anhydrous $CuCl_2$ and trimethylamine react at 0 °C to provide an initial blue–green solid (presumed as $CuCl_2 \cdot 2NMe_3$) which rapidly changes to the brown–yellow mono-adduct following pumping *in vacuo* at room temperature. At temperatures above 75 °C, oxidation of trimethylamine occurs with the formation of a dark red tar.

As part of our systematic structural study of such MX_2/NMe_3 systems we have re-examined the reaction with Cu(II) chloride and herein report the formation and structural characterization of the tetrachlorocuprate(II) salt $[Me_3NCH_2Cl]_2[CuCl_4]$.

Experimental

Trimethylamine was stored over P_4O_{10} and NaOH pellets and distilled into reaction vessels using a

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**With an excess of amine present, Ti(IV) and V(IV) are reduced to the tervalent state, see ref. 1b.

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conventional all-glass high vacuum system. Organic solvents were stored over CaH_2 and distilled under nitrogen prior to use. Anhydrous $CuCl_2$ was used as supplied commercially. Details of the spectroscopic instrumentation and experimental techniques as used in this study have been previously described [7].

Addition of excess trimethylamine (~ 30 cm^3) to anhydrous copper(II) chloride (~ 2 g) in a double ampoule vessel initially gave a very pale green mixture which changed to a yellow–brown colour after several days. Removal of amine gave a yellow solid which was washed with n-hexane and then Soxhlet extracted with boiling benzene to provide the bright yellow mono-adduct based on $CuCl_2 \cdot 1.1NMe_3$. *Anal.* Calc. for this composition: C, 19.87; H, 5.00; N, 7.72; Cu, 31.85; Cl, 35.55. Found: C, 20.01; H, 5.06; N, 7.69; Cl, 35.45%. m.p. (uncorrected) 154–155 °C. (Our microanalytical data are, in fact, identical to those of Lane and Yoke [8] viz., C, 19.76; H, 5.09; N, 7.69; Cu, 31.92%.)

TABLE 1. Atomic coordinates ($\times 10^4$) with e.s.d.s. in parentheses

Atom	*x*	*y*	*z*
Cu(1)	3951(1)	2024(2)	2940(1)
Cl(1)	3542(2)	250(3)	2473(3)
Cl(2)	5042(2)	2716(3)	3999(4)
Cl(3)	4171(2)	2612(3)	641(3)
Cl(4)	3109(2)	2519(3)	4702(4)
Cl(10)	3836(2)	5972(3)	−555(3)
C(11)	3816(9)	7304(17)	2332(13)
C(12)	4749(6)	5717(14)	2413(14)
C(13)	3480(7)	5533(12)	1128(14)
C(15)	3538(8)	5579(16)	3772(14)
N(14)	3943(6)	6064(12)	2353(9)
Cl(20)	7312(2)	1446(4)	3947(5)
C(20)	6501(7)	520(11)	3853(13)
N(21)	6379(6)	67(9)	2361(9)
C(22)	6226(10)	955(14)	1258(13)
C(23)	7057(8)	−669(13)	1864(14)
C(24)	5683(8)	−685(15)	2494(16)

TABLE 2. Dimensions in the anion

Distances (Å)	
Cu(1)–Cl(1)	2.245(4)
Cu(1)–Cl(2)	2.253(3)
Cu(1)–Cl(3)	2.232(3)
Cu(1)–Cl(4)	2.243(3)
Angles (°)	
Cl(1)–Cu(1)–Cl(2)	132.52(15)
Cl(1)–Cu(1)–Cl(3)	99.71(13)
Cl(2)–Cu(1)–Cl(3)	97.98(14)
Cl(1)–Cu(1)–Cl(4)	99.94(14)
Cl(2)–Cu(1)–Cl(4)	98.21(14)
Cl(3)–Cu(1)–Cl(4)	134.44(16)

Treatment of **I** with boiling dichloromethane in the presence of charcoal gave an orange solution from which small orange cubic crystals of the product $[Me_3NCH_2Cl]_2[CuCl_4]$ (**II**) were obtained following partial removal of solvent and storage at 0 °C. *Anal.* Calc. for $C_8H_{22}N_2CuCl_6$: C, 22.74; H, 5.25; N, 6.63; Cu, 15.04; Cl, 50.34. Found: C, 22.59; H, 5.20; N, 6.61; Cl, 50.19%. m.p. (uncorrected) melts with decomposition 239–241 °C.

Crystal data for **II**, $[Me_3NCH_2Cl]_2[CuCl_4]$, $CuCl_6C_8H_{22}N_2$, $M=422.42$, monoclinic, $a=17.20(1)$, $b=11.78(1)$, $c=9.067(7)$ Å, $\beta=90.5(1)°$, $U=1837.0$ Å^3, $F(000)=860$, $D_m=1.53$ g cm^{-3}, $D_c=1.53$ g cm^{-3}, $Z=4$, Mo Kα radiation ($\lambda=0.7107$ Å), μ(Mo Kα)$=$ 20.80 cm^{-1}, spacegroup $P2_1/n$.

A crystal of approximate size $0.3\times0.4\times0.2$ mm was set up to rotate about the *a* axis on a Stoe Stadi2 diffractometer and data were collected via variable width ω scan. Background counts were for 20 s and a scan rate of 0.0333°/s was applied to a width of $(1.5+\sin\mu/\tan\theta)$. A total of 2620 independent reflections was measured of which 1620 with $I>2\sigma(I)$ were used in subsequent refinement. The structure was determined by the heavy atom method. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon were included in fixed positions. The methyl hydrogen atoms were refined as rigid groups. The structure was given a weighting scheme in the form $w=1/[\sigma^2(F)+0.003F^2]$. The final R value was 0.062 ($R_w=0.064$). In the final cycle of refinement all shift/error ratios were $<0.3\sigma$. The final difference Fourier map showed maximum and minimum peaks of 0.41 and -0.32 e Å^{-3}. Calculations were carried out using SHELX76 [9] and some of our own programs on the Amdahl 5870 at the University of Reading. Positional parameters are given in Table 1 and anion dimensions in Table 2. See also 'Supplementary material'.

Discussion

Direct treatment of anhydrous $CuCl_2$ with an excess of trimethylamine at room temperature provides a brown–yellow solid which on Soxhlet extraction in boiling benzene gives the mono-adduct **I** as a golden yellow solid with a sharp melting point 154–155 °C. Analytical data correspond with a $CuCl_2 \cdot 1.1NMe_3$ formulation identical with that proposed by Lane and Yoke [8]. The IR spectrum of **I** shows bands at 1265 ν_{as}(CN), 999 $\rho(CH_3)$, 830 ν_s(CN), 564 $\delta(NMe_3)$ typical for coordinated amine and two broad bands at 250, 204 cm^{-1} assigned as ν(CuCl) stretching modes. The electronic spectrum features a 'd–d' band at 11 494 cm^{-1} with a broad shoulder at higher energy 13 089 cm^{-1}. We have been unable to identify the structure of this mono-adduct; various attempts to obtain crystals from benzene, acetonitrile and other non-chlorinated solvents proved unsuccessful. However with CH_2Cl_2 orange needle crystals of suitable quality for an X-ray structure determination were isolated. This recrystallized product turns out to be the salt $[Me_3NCH_2Cl]_2[CuCl_4]$ (**II**) which melts with decomposition at 239–241 °C. The low IR (400–200 cm^{-1}) spectrum features two broad symmetric bands at 281, 237 cm^{-1} ($\nu_3(Cu–Cl)_{str}$) characteristic of the tetrachlorocuprate(II) anion [10]. A single broad 'd–d' band, λ_{max} 9090 cm^{-1}, is observed in the near IR region of the electronic spectrum; resolution into $^2B_2 \rightarrow {}^2A_1$, $^2B_2 \rightarrow {}^2B_1$, $^2B_2 \rightarrow {}^2E'$ components was not possible.

Structure of II

The structure which is shown in Fig. 1 together with the atomic numbering scheme consists of two independent $[Me_3NCH_2Cl]^+$ cations and one $[CuCl_4]^{2-}$ anion. The conformation of the cations is as expected. In the anion there is a significant deviation from both of the two ideal geometries, square planar and tetrahedral, in that the Cl–Cu–Cl angles around the metal atom are 98.0(1), 98.2(1), 99.7(1), 99.9(1), 132.5(1) and 134.4(1)°. The Cu–Cl bond lengths are however regular at 2.232(3), 2.243(3), 2.245(4) and 2.253(3) Å.

In general terms the structure of the $CuCl_4{}^{2-}$ anion in salts of the type A_2CuCl_4 is sensitive to the nature of the cation. Thus for small cations there is octahedral (4 + 2) coordination, e.g. $[EtNH_3]_2CuCl_4$ [11] but with large and non-spherical cations four coordination commensurate with a flattened tetrahedral geometry is found, e.g. [*N*-(2-ammonioethyl)morpholinium]$[CuCl_4]$ [12]. In a recent publication, Halvorson *et al.* [13] have analysed over 60 crystal structure determinations containing the $[CuCl_4]^{2-}$ anion. Variations in angular deformation of the $[CuCl_4]^{2-}$ anion between these known structures have been examined from a plot of the *trans* Cl–Cu–Cl angle against frequency of occurrence which shows (i) the majority of the structures contain *trans* angles between 125 and 145° and (ii) there is a maximum around 135° with a secondary maximum at 180°. Halvorson *et al.* also note that the occurrence of hydrogen bonds to the chlorine atoms in the anion tends to decrease the *trans* angle. Typically values range from *c.* 130° for large non-hydrogen bonding cations through to 180° (planar) for those cations which can form extensive hydrogen bond interactions. Significantly there are necessarily no such contacts in the present structure and indeed the closest C–H···Cl contact is 2.73 Å so it is appropriate that the present angles at 133, 134° are almost identical to the maximum frequency value.

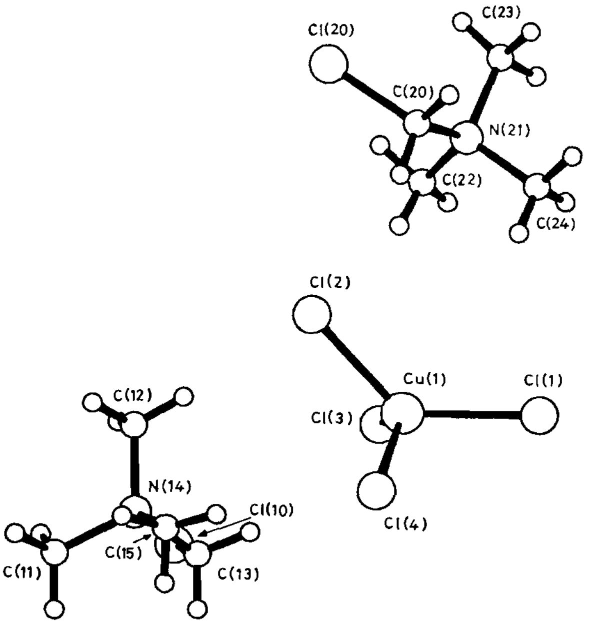

Fig. 1. Structures of the $[Me_3NCH_2Cl]^+$ cations and $[CuCl_4]^{2-}$ anion in **II**.

Halvorson *et al.* also correlate the value of the 'd–d' electronic absorption energy with the *trans* Cl–Cu–Cl angle. From the straight line plot obtained our observed *trans* angle of 134° corresponds to a predicted energy of 9500 cm^{-1}; the experimental value, 9090 cm^{-1}, provides an excellent fit.

Formation of the tetrachlorocuprate(II) ion (**II**) during the attempted recrystallization of **I** in CH_2Cl_2 clearly involves halide abstraction from solvent molecules most likely via free trimethylamine. Partial dissolution/decomposition of **I** in CH_2Cl_2 — in the absence of a definitive structure we presume some oligomeric/polymeric arrangement for **I** involving halogen-bridged Cu(II) centres with coordinated trimethylamine — provides the source of free amine. There is no Cu^{II}–Cu^{I} redox behaviour. In a separate reaction we have confirmed the formation of $[Me_3NCH_2Cl][Cl]$ directly from a mixture of CH_2Cl_2 and NMe_3 in a sealed tube at room temperature; m.p. 163.5–164.5 °C, lit. [14] 165–166 °C. Again in a separate reaction we have confirmed that direct treatment of anhydrous $CuCl_2$ with a CH_2Cl_2/NMe_3 mixture also provides **II** along with some residual $[Me_3NCH_2Cl][Cl]$.

Supplementary material

Dimensions in the cations, anisotropic thermal parameters, hydrogen atom positions and observed and calculated structure factor tables are available from the authors on request.

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