Anion design by choice of cation: isolation of a dinuclear chlorocuprate(I) anion containing trigonally coordinated copper(I) using the tetraethylphosphonium cation

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Abstract

A centrosymmetric di-μ-chloro-dichlorodicuprate(I) ion, $[Cu_2Cl_4]^{2-}$, has been prepared by selecting the tetraethylphosphonium cation as counter-ion, on the basis of its size in comparison with those of related symmetrically substituted phosphonium and ammonium cations. The copper(I) centres in $[Cu_2Cl_4]^{2-}$ exhibit distorted trigonal coordination and the anion can be seen as a loose association of $[CuCl_2]^-$ moieties, in which the Cu–Cl bonds are 2.112(3) and 2.136(3) Å, joined by two long Cu$\cdots$Cl interactions of 2.922(3) Å. The Cu$\cdots$Cu and Cl$\cdots$Cl separations are 3.515(2) and 3.722(5) Å, respectively. $[P(C_2H_5)_4]_2[Cu_2Cl_4]$ crystallizes in space group $P2_1/n$ with $a = 11.881(4)$, $b = 7.976(3)$, $c = 14.296(2)$ Å, $\beta = 112.46(2)°$, at $-150\,°C$, and $Z = 2$. Full-matrix least-squares refinement yielded a final $R = 0.051$ ($R_w = 0.066$) for 109 parameters and 1266 observed reflections.

Introduction

The coordination number of the metal in crystalline halogenocuprates(I) and, to a lesser extent, in halogenoargentates(I) has been shown to be dependent on the properties, and, in particular, on the size of the cation with which co-precipitation occurs [1]. We have prepared a series of chlorocuprates(I) crystallizing with symmetrical tetraalkylammonium, tetraphenylphosphonium and tetraalkylphosphonium cations in which the coordination number of copper(I) increases regularly from two to four with decreasing cation size [2–7]. Two dinuclear di-μ-chloro-dichlorodicuprate(I) ions have been described previously [8, 9]. The aim of the present investigation was to demonstrate the possibility of preparing a $[Cu_2Cl_4]^{2-}$ anion in the solid state by selecting an alkylammonium or alkylphosphonium cation of appropriate size. Since with tetrapropylammonium a mononuclear, digonal $[CuCl_2]^-$ anion is obtained [4], whereas an infinite chain anion, $[Cu_7Cl_{10}]^{3-}$, composed of four three-coordinated copper(I) centres, two with $(3+1)$ coordination, and one with $(2+2)$ coordination [5], is precipitated with tetraethylammonium, tetraethylphosphonium, intermediate in size between these two cations, was considered a likely candidate for the preparation of $[Cu_2Cl_4]^{2-}$.

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Experimental

Preparation of $[P(C_2H_5)_4]_2[Cu_2Cl_4]$

All operations were carried out under nitrogen or argon, using standard Schlenk or special low-temperature techniques [10]. Copper(I) chloride was purified as described in ref. 11, and dried *in vacuo*. Tetraethylphosphonium chloride (Aldrich) (0.18 g, 1.0 mmol) was dissolved in a mixture of 40 ml ethanol and 10 ml dichloromethane and 0.099 g (1.0 mmol) copper(I) chloride was added at ambient temperature under stirring. The resulting solution was evaporated to the point of saturation and allowed to stand at 4 °C. Colourless irregular-shaped prisms of $[P(C_2H_5)_4]_2[Cu_2Cl_4]$ were deposited after 1–2 days. Crystals of $[P(C_2H_5)_4]_2[Cu_2Cl_4]$ are unstable and undergo rapid oxidation on exposure to the atmosphere at ambient temperature.

Crystallography

A colourless, prismatic crystal was mounted at -150 °C under argon in a glass capillary, using a device specially constructed for this purpose [10], and was transferred, at the same temperature, to a Rigaku AFC6R diffractometer. Diffracted intensities were measured (Table 1) using graphite-monochromated radiation from a RU200 rotating anode source operated at 9 kW (50 kV; 180 mA). The ω–2θ scan mode was employed with an ω scan rate of 32° min^{-1} and a scan

width of $(1.47+0.30 \tan \theta)°$. Weak reflections ($I<10\sigma(I)$) were rescanned up to three times and counts accumulated to improve counting statistics. Stationary background counts were recorded on each side of the reflection, the ratio of peak counting time versus background counting time being 2:1. Three reflections monitored at regular intervals (after every 150 reflections measured) showed no evidence of crystal decay. Intensities were corrected for Lorentz and polarization effects but not for absorption. Of the 2381 unique reflections measured, 1266 had $I>3\sigma(I)$ and were considered observed. Cell constants were determined from the setting angles of 25 reflections in the range $25.1<2\theta<29.8°$.

The structure was solved by direct methods (MITH-RIL [12]) confirming near isostructurality with $[P(C_2H_5)_4]_2[Cu_2Br_4]$ [13]. Full-matrix least-squares refinement including anisotropic thermal parameters for the non-hydrogen atoms and with the H atoms in calculated positions (C–H = 0.95 Å, $B=1.2\times B_{eq}$ of the carrying carbon atom) gave a final $R=0.051$ ($R_w=0.066$) for 109 parameters and 1266 observed reflections Further details concerning the refinement are given in Table 1.

Fractional coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table 2. Atomic scattering factors and anomalous dispersion corrections were taken from ref. 14; all calculations were performed using the TEXSAN [15] software package. Structural illustrations were drawn with ORTEP [16].

Results and discussion

The $[Cu_2Cl_4]^{2-}$ anion (Fig. 1) is less symmetrical than the counterparts whose geometries have been determined previously [8, 9] and can be seen as a loose association of two $[CuCl_2]^-$ moieties joined by long $Cu\cdots Cl$ interactions of 2.922(3) Å. This results in a long $Cu\cdots Cu^i$ distance of 3.515(2) Å, while the $Cl\cdots Cl^i$ separation is 3.722(5) Å (for symmetry code see Fig. 1). The coordination geometry of the copper(I) centre in the present $[Cu_2Cl_4]^{2-}$ ion is thus severely distorted from trigonal planar. This contrasts with the geometry of copper(I) in the $[Cu_2Br_4]^{2-}$ anion in $[P(C_2H_5)_4]_2[Cu_2Br_4]$ [13], with which $[P(C_2H_5)_4]_2[Cu_2Cl_4]$ is nearly isostructural. The $[Cu_2Cl_4]^{2-}$ anion is centrosymmetric and the copper(I) centres are displaced 0.032 Å above and below the plane through the chloride ligands.

Similar geometry, i.e. a loose association of MX_2^- monomers, has been noted for those silver(I) analogues, $[Ag_2Cl_4]^{2-}$, crystallizing with the tetraphenylphosphonium [17] and tetraphenylarsonium [18] cations. The flexibility of the $Cu(\mu-X)_2Cu$ rhombus in $[Cu_2X_4]^{2-}$ anions has been addressed in a recent theoretical study,

TABLE 1. Crystal and experimental data for $[P(C_2H_5)_4]_2[Cu_2Cl_4]$

Formula	$C_{16}H_{40}Cu_2Cl_4P_2$
Molecular weight	563.3
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
Temperature (°C)	−150
a (Å)	11.881(4)
b (Å)	7.976(3)
c (Å)	14.296(2)
β (°)	112.46(2)
Volume (Å³)	1252(1)
Z	2
Calculated density (g/cm³)	1.49
$F(000)$	584
μ (cm⁻¹)	22.6
Approx. crystal dimensions (mm)	$0.20\times0.10\times0.10$
Radiation	graphite-monochromated Mo Kα (0.71069 Å)
Data collected	$h, k, \pm l$
$2\theta_{max}$ (°)	51
Scan mode	ω–2θ
ω Scan rate (°/min)	32.0
No. unique reflections	2381
No. observed reflections	1266
No. parameters refined	109
R	0.051
R_w	0.066
Max.; min. residual electron density (e/Å³)	0.99; −0.52

TABLE 2. Positional and equivalent isotropic thermal parameters, B_{eq} (Å^2), for the non-hydrogen atoms in $[P(C_2H_5)_4]_2[Cu_2Cl_4]$

Atom	x	y	z	B_{eq}
Cu	0.4218(1)	0.0759(2)	0.5737(1)	2.48(5)
Cl(1)	0.2584(2)	0.0250(3)	0.5945(2)	2.54(10)
Cl(2)	0.5959(2)	0.1657(3)	0.5850(2)	2.31(9)
P	−0.0096(2)	0.1078(3)	0.7629(2)	1.33(8)
C(11)	0.1147(8)	0.0420(11)	0.8725(6)	2.0(4)
C(12)	0.2364(9)	0.0084(14)	0.8598(7)	2.8(4)
C(21)	0.0434(8)	0.2441(11)	0.6882(7)	1.8(3)
C(22)	−0.0574(9)	0.3165(13)	0.5949(7)	2.5(4)
C(31)	−0.0882(7)	−0.0707(11)	0.6885(6)	1.7(3)
C(32)	−0.0112(9)	−0.1820(12)	0.6503(7)	2.5(4)
C(41)	−0.1151(8)	0.2223(11)	0.8015(7)	1.7(3)
C(42)	−0.1646(9)	0.1204(12)	0.8672(7)	2.5(4)
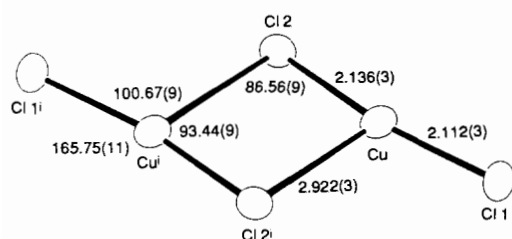
Fig. 1. The $[Cu_2Cl_4]^{2-}$ anion in $[P(C_2H_5)_4]_2[Cu_2Cl_4]$. Distances are in Å and angles in °. Symmetry code: [i] $1-x$, $-y$, $1-z$.
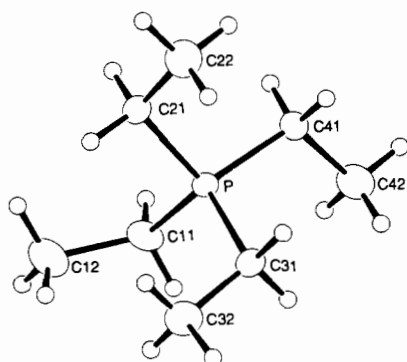

Fig. 2. The tetraphenylphosphonium cation in $[P(C_2H_5)_4]_2[Cu_2Cl_4]$, showing the crystallographic numbering of the non-hydrogen atoms. The hydrogen atoms are at calculated positions (C–H = 0.95 Å).

the energy variation associated with both angular and bond length distortions within the rhombus being shown to be slight [19]. Thus the $[Cu_2X_4]^{2-}$ system is particularly soft, i.e. associated with a flat potential surface, resulting in a near-continuum of possible structures and extreme sensitivity of the anion to crystal packing environments [19].

The tetraethylphosphonium cation (Fig. 2; Table 3) exhibits no anomalous features. The shortest cation–anion contacts are: $Cu\cdots C(41^{ii}) = 3.644(9)$;

TABLE 3. Bond distances (Å) and angles (°) within the tetraethylphosphonium cation

P–C(11)	1.773(9)	P–C(31)	1.809(9)
P–C(21)	1.798(8)	P–C(41)	1.799(9)
C(11)–C(12)	1.55(1)	C(31)–C(32)	1.52(1)
C(21)–C(22)	1.53(1)	C(41)–C(42)	1.52(1)
C(11)–P–C(21)	109.9(4)	C(21)–P–C(31)	110.2(4)
C(11)–P–C(31)	110.8(4)	C(21)–P–C(41)	108.6(4)
C(11)–P–C(41)	108.8(4)	C(31)–P–C(41)	108.5(4)
P–C(11)–C(12)	116.6(6)	P–C(31)–C(32)	115.2(6)
P–C(21)–C(22)	114.3(6)	P–C(41)–C(42)	113.4(6)

$Cu\cdots C(42^{iii}) = 3.650(10)$; $Cl(1)\cdots C(21) = 3.741(8)$; $Cl(2)\cdots C(41^{iv}) = 3.668(9)$ Å (symmetry code: [ii] $\frac{1}{2}-x$, $y-\frac{1}{2}$, $\frac{3}{2}-z$; [iii] $\frac{1}{2}+x$, $\frac{1}{2}-y$, $z-\frac{1}{2}$; [iv] $1+x$, y, z). See also 'Supplementary material'.

The present investigation provides a further example in which the adaptability of halogenocuprates(I) to cation dictates has been exploited for the preparation of a species with a desired copper(I) coordination number. For halogenocuprates(I) crystallizing with bulky unipositive ions with well-screened positive charge, the coordination number of copper(I) has been found to increase with decreasing size of the cation with which the halogenocuprate(I) is precipitated [1, 4]. This is contrary to the usual principle of matching large anions with large cations and vice versa [20, 21].

For both halogenocuprates(I) and halogenoargentates(I) crystallizing with comparable unipositive ions, there is a correlation between the coordination number of copper(I) or silver(I) and the concentration of halogenide ligand in the solid [1, 4]. This has been interpreted as suggesting that cation–halogenide packing is a determinative factor for the attainment of a particular metal(I) coordination number and consequently for the resulting anionic configuration [1, 4]. With decreasing cation size in chlorocuprates(I) crystallizing with symmetrically substituted phosphonium or ammonium cations, the copper(I) coordination number and the concentration of chloride in the solid are seen to increase (Table 4). Only in one case, i.e. with the tetramethylphosphonium cation, was a small amount of a second phase, $[P(CH_3)_4]_2[CuCl_3]$, obtained at the end of the crystallization process [6]. Formation of the major product, an infinite $[Cu_2Cl_3]^-$ chain composed of one three-coordinated and one four-coordinated copper(I) centre, consumed excess copper(I) over the total Cu:Cl molar ratio in the system, i.e. 1:2, the minor crystalline product thus containing an anion with excess chloride over the total Cu:Cl molar ratio of 1:2 [6].

In the search for a $[Cu_2Cl_4]^{2-}$ dimer within this system of halogenocuprates(I) of tetraalkylammonium and related cations, it seemed reasonable to investigate a cation intermediate in size between tetrapropylam-

TABLE 4. Coordination of copper(I) in chlorocuprates(I) crystallizing with symmetrically substituted ammonium and phosphonium cations

Cation	Anion	Coord. no. of copper(I)	[Cl][a]	Ref.
As(C$_6$H$_5$)$_4$$^+$	[CuCl$_2$]$^-$	2	6.0	2
P(C$_6$H$_5$)$_4$$^+$	[CuCl$_2$]$^-$	2	6.1	2
N(C$_4$H$_9$)$_4$$^+$	[CuCl$_2$]$^-$	2	6.6	3
N(C$_3$H$_7$)$_4$$^+$	[CuCl$_2$]$^-$	2	7.8	4
P(C$_2$H$_5$)$_4$$^+$	[Cu$_2$Cl$_4$]$^{2-}$	3	10.6	this work
N(C$_2$H$_5$)$_4$$^+$	([Cu$_7$Cl$_{10}$]$^{3-}$)$_\infty$	1×(2+2) 4×3 2×(3+1)	15.7	5
P(CH$_3$)$_4$$^+$	([Cu$_2$Cl$_3$]$^-$)$_\infty$	1×3 1×4	17.9	6
	[CuCl$_3$]$^{2-}$	3	11.7	6
N(CH$_3$)$_4$$^+$	([Cu$_2$Cl$_3$]$^-$)$_\infty$	4	20.3	7
NH$_4$$^+$	([CuCl$_3$]$^{2-}$)$_\infty$	4	30.1	22

[a][Cl] is the concentration of chloride ligand (mol dm^{-3}) in the solid.

monium and tetraethylammonium. As is seen from Table 4, with the former cation a discrete two-coordinated [CuCl$_2$]$^-$ ion is obtained [4], whereas a [Cu$_7$Cl$_{10}$]$^{3-}$ chain polymer was isolated with tetraethylammonium [5]. The [Cu$_7$Cl$_{10}$]$^{3-}$ anion can be seen as being composed of one two-coordinated and six three-coordinated copper(I) centres, the presence of some long Cu···Cl interactions ($\approx$3.0 Å) permitting the alternative formulation presented in Table 4.

That the desired [Cu$_2$Cl$_4$]$^{2-}$ anion is, in fact, precipitated with tetraethylphosphonium provides further evidence for the importance of cation–halogenide packing in the formation of crystalline halogenocuprates(I). Previously, it has been shown that the halogenocuprate(I) species in solution at the onset of crystallization can differ from that precipitated [23]. Thus, an IR spectroscopic investigation of solutions ([Br$^-$]$_{max}$ $\approx$ 0.16 M) from which the [Cu$_4$Br$_6$]$^{2-}$ cluster, composed of three-coordinated copper[I], crystallizes as the tetrapropylammonium salt demonstrates that the centrosymmetric [CuBr$_2$]$^-$ monomer is the dominant and probably the sole bromocuprate(I) species in solution [23]. In media permitting higher concentrations of halogenocuprates(I), e.g. in which the total halogenide concentrations approach those estimated for the relevant halogenocuprate(I) species in the solid, such as for [Cu$_2$I$_4$]$^{2-}$ [4, 24–26], dimeric anions have, however, been shown to be present in solution [27].

Further support for the role of cation–halogenide packing in determining the coordination number of copper(I) and silver(I) in crystalline halogenocuprates(I) and halogenoargentates(I) has been furnished by the successful preparation of the heteronuclear clusters [Ag$_2$Cu$_2$I$_8$]$^{4-}$ and [Ag$_3$CuI$_8$]$^{4-}$ in which copper(I) is three-coordinated, whereas silver(I) is four-coordinated or both three- and four-coordinated, respectively, simply by dissolving the metal(I) iodides and tetraphenylphosphonium iodide in acetonitrile solution [28]. From the individual metal iodides and tetraphenylphosphonium iodide in acetonitrile, a dinuclear [Cu$_2$I$_4$]$^{2-}$ ion in which copper(I) is three-coordinated [26] and an [Ag$_4$I$_8$]$^{4-}$ ion containing both three- and four-coordinated silver(I) [18] are precipitated, respectively.

For crystalline halogenocuprates(I), it has been suggested that cation–halogenide packing is the primary process occurring during nucleation, copper(I) attaining the appropriate coordination number by occupation of available interstices, subsequent adjustment then resulting in the specific anion [23]. The tuning of the copper(I) coordination environment in halogenocuprates(I) to cation properties undoubtedly reflects the flexibility of the bonding requirements not only of the metal [19, 29, 30] but also of the ligands [31].

Supplementary material

Anisotropic thermal parameters for the non-hydrogen atoms, observed and calculated structure factors and a diagram of the unit cell are available from the authors on request.

Acknowledgement

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