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Structure of the Crystalline Phase of Composition $[N(C_4H_9)_4][CuBrCl]$

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The structure of tetrabutylammonium bromochlorocuprate(I) has been determined from single-crystal X-ray diffractometer data collected at 168 K. The compound crystallizes in space group $C2/c$ with a=13.051(5), b=9.942(8), c=15.859(9) Å, β=92.72(4)° at 168 K and Z=4. Full-matrix least-squares refinement of 156 structural parameters gave R=0.038 for 1423 observed, [$I>3.0\ \sigma(I)$], independent reflections. The complex ions show disorder: Cu is at a centre of symmetry while Br and Cl occupy their sites statistically and have been assigned occupancy 0.5. The infrared spectrum indicates the presence of $[CuCl_2]^-$ and $[CuBr_2]^-$ as well as $[CuBrCl]^-$, the most plausible description of the structure being in terms of one dichlorocuprate(I) ion, one dibromocuprate(I) ion, and two bromochlorocuprate(I) ions, with disordered orientation, per unit cell. The observed Cu–Cl and Cu–Br distances are 2.104(17) and 2.195(6) Å, respectively.

As part of an investigation concerning the configurations of dihalocuprate(I) and related ions in the solid state, the structures of tetrabutylammonium dichlorocuprate(I) and tetrabutylammonium dibromocuprate(I) have been determined.[1] Both these compounds contain linear $[CuX_2]^-$ ions, whereas the iodo counterpart contains dimeric, $[Cu_2I_4]^{2-}$, anions.[2] In this context it was of interest to investigate whether or not mixed ligand complexes, such as $[CuBrCl]^-$, could be prepared and, if so, to examine the effect of mixing ligands on the mode of copper(I) coordination and the Cu–X bond lengths.

EXPERIMENTAL

Copper(I) chloride was dissolved in molten tetrabutylammonium bromide, in the molar ratio 1:1. The melt solidified on cooling and the product was recrystallized from ethyl acetate yielding colourless rhombic plates with a pronounced tendency to polysynthetic twinning, m.p. 80–82 °C. Anal. C, H. Found: C 45.56, 45.44; H 8.68, 8.64. Calc. for $C_{16}H_{36}BrClCuN$: C 45.60, H 8.61.

Diffracted intensities from a single-crystal fragment, 0.13×0.23×0.09 mm, were measured at 168 K with a Syntex $P2_1$ diffractometer, using graphite-monochromated Mo$K\alpha$ radiation and the ω-2θ scan mode. Data were collected for $2\theta \leq 55°$ with $h \geq 0$ and $k \geq 0$, the 2θ scan rate being varied between 2.0 and 20.0° min^{-1}, depending on the intensity of the reflection. Periodical measurement of the intensity of two reflections showed no abnormal fluctuation. A 96-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis method[3] was used to calculate the intensities.[4] A total of 2623 reflections were recorded, from which a unique set of 2373 reflections was obtained, systematically absent reflections being omitted. Of these 2373 reflections, 1423 were regarded as being observed [$I>3.0\sigma(I)$] and were used in the subsequent calculations. Data were corrected for Lorentz and polarization effects but not for absorption owing to the irregular shape of the crystal. The unit-cell parameters at 168 K were determined by least-squares refinement from diffractometer setting angles for 15 reflections.

The infrared spectrum of $[N(C_4H_9)_4][CuBrCl]$ and, for comparison, the spectra of $[N(C_4H_9)_4][CuCl_2]$ and $[N(C_4H_9)_4][CuBr_2]$ were recorded on a Nicolet MX-1 spectrometer using

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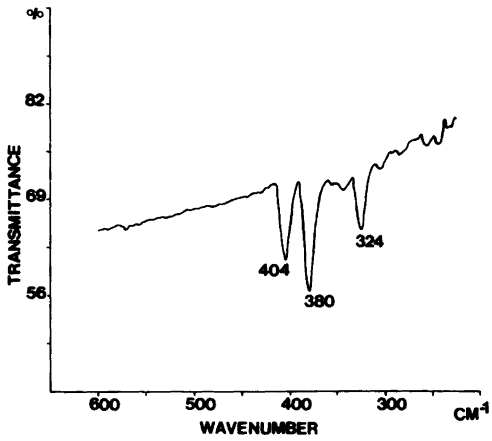

Fig. 1. The infrared spectrum of the crystalline phase of composition $[N(C_4H_9)_4][CuBrCl]$ in the region 200–600 cm^{-1}.

Nujol mulls between TlI discs. The spectrum of $[N(C_4H_9)_4][CuBrCl]$ between 600–200 cm^{-1} is depicted in Fig. 1. For $[N(C_4H_9)_4][CuCl_2]$ and $[N(C_4H_9)_4][CuBr_2]$ the antisymmetric stretching modes of the anions were observed at 406 and 325 cm^{-1}, respectively.

CRYSTAL DATA

Tetrabutylammonium bromochlorocuprate(I), $[N(C_4H_9)_4][CuBrCl]$, M_r=421.4; monoclinic, systematic absences: hkl: $h+k=2n+1$; $h0l$: $l=2n+1$, space group $C2/c$; a=13.051(5), b=9.942(8), c=15.859(9) Å, β=92.72(4)° at 168 K, Z=4, D_c=1.36 g cm^{-3}, μ(Mo$K\alpha$)=32.8 cm^{-1}. The compound crystallizes as colourless rhombic plates.

STRUCTURE DETERMINATION AND REFINEMENT

The Patterson map[5] of tetrabutylammonium bromochlorocuprate(I) showed close similarity to those of tetrabutylammonium dichlorocuprate(I) and tetrabutylammonium dibromocuprate(I).[1] Atomic coordinates for the non-hydrogen atoms in a hypothetical ordered structure in Cc were therefore calculated from those of the two known structures, taking the observed Br···C and Cl···C contacts into consideration. Full-matrix least-squares refinement[5] of positional and isotropic thermal parameters in Cc, the z coordinates for all atoms being shifted 0.1 from those in $C2/c$, yielded R=0.103, but unrealistic temperature factors for Br and Cl (B_{Br}=5.1 Å^2; B_{Cl}=1.5 Å^2). Moreover, the carbon atoms of the tetrabutylammonium ions refined to positions which gave unrealistic distances and angles, it being clear that this group required the constraint of a 2-fold axis. Despite inconsistency with the systematic absences, a trial refinement was carried out in $C2$. This also yielded $R\approx0.10$, similar temperature factors for Br and Cl and analogous anomalies in the distances and angles within the tetrabutylammonium ions. It therefore seemed that the structure would be better described in terms of a disordered model based on $C2/c$. Intensity statistics[6] were, moreover, consistent with the presence of a centre of symmetry. Refinement of atomic coordinates and isotropic thermal parameters with the calculated coordinates as starting point and occupancy 0.5 for Cu, Cl and Br yielded R=0.072, most satisfactory agreement at this stage being obtained when Cu was not confined to a centre of symmetry (R=0.081 with Cu in 4d). Allowance for anisotropic thermal motion gave R=0.060 and inclusion of the hydrogen atoms in starting positions calculated from the dibromocuprate(I) and dichlorocuprate(I) gave R=0.041 for 159 parameters. The isotropic temperature factors of the hydrogen atoms were not refined, but were reset to the equivalent isotropic values[7] of the carrying carbon atoms. A final check, however, concerning the position of the copper atom showed an improved fit to the data when Cu was replaced at the centre of symmetry (R=0.038 for 156 parameters, the e.s.d.'s of the positional parameters for Cl and Br being reduced by at least a factor of 4). When the 950 "unobserved" reflections were included with their measured F_o values R=0.081.

The chemical analysis (C, H) indicated the overall composition $[N(C_4H_9)_4][CuBrCl]$, *i.e.* 4 Cl and 4 Br per unit cell. Refinement as above but with occupancy 0.625 for Br and 0.375 for Cl, *i.e.* 5 Br and 3 Cl per unit cell [Calc. C 44.43, H 8.39] and *vice versa* [Calc. C 46.84, H 8.85] gave R=0.043 and 0.046, respectively (156 parameters), higher positional e.s.d.'s and less satisfactory temperature factors. Other Br and Cl distributions giving calc. C and H values even further from those determined experimentally were not therefore considered probable. It is, of course, not inconceivable that Br and Cl occu-

Table 1. Fractional coordinates and thermal parameters, B_{eq} or $B(Å^2)$, for $[N(C_4H_9)_4][CuBrCl]$. For the non-hydrogen atoms B_{eq} is defined as $B_{eq}=(8\pi^2/3)(U_{11}a^{*2}a^2+\cdots+U_{23}b^*c^*bc\cos\alpha)$, the anisotropic temperature factor having the form $\exp[-2\pi^2(U_{11}a^{*2}h^2+\cdots+U_{23}b^*c^*kl)]$. For the hydrogen atoms $B=B_{eq}$ of the carrying carbon atom. Estimated standard deviations are given in parentheses. Br and Cl have occupancy 0.5.

Atom	x	y	z	B_{eq} or B	Atom	x	y	z	B
Cu	0.2500	0.2500	0.5000	3.41(2)	H(22)	0.194(4)	0.215(6)	0.298(3)	2.5
Br	0.2301(4)	0.4372(7)	0.4277(3)	3.68(6)	H(31)	0.283(4)	−0.049(6)	0.277(3)	2.7
Cl	0.2686(11)	0.0717(18)	0.5706(9)	5.27(23)	H(32)	0.254(4)	0.012(6)	0.365(4)	2.7
N	0.0000	0.1496(4)	0.2500	1.95(7)	H(41)	0.376(5)	0.181(7)	0.346(4)	3.8
C(1)	0.0924(3)	0.0582(4)	0.2648(2)	2.13(6)	H(42)	0.433(5)	0.048(6)	0.342(4)	3.8
C(2)	0.1955(3)	0.1303(4)	0.2710(2)	2.48(6)	H(43)	0.398(5)	0.116(6)	0.259(4)	3.8
C(3)	0.2786(3)	0.0362(3)	0.3086(3)	2.71(7)	H(51)	−0.045(4)	0.308(5)	0.173(3)	2.0
C(4)	0.3825(3)	0.1035(6)	0.3125(3)	3.83(9)	H(52)	0.070(4)	0.300(5)	0.190(3)	2.0
C(5)	0.0141(3)	0.2421(3)	0.1743(2)	2.02(6)	H(61)	0.076(4)	0.101(6)	0.093(3)	2.5
C(6)	0.0273(3)	0.1733(4)	0.0904(2)	2.48(6)	H(62)	−0.040(4)	0.127(5)	0.071(3)	2.5
C(7)	0.0632(4)	0.2755(5)	0.0264(3)	3.23(8)	H(71)	0.011(5)	0.350(6)	0.019(3)	3.2
C(8)	0.0826(5)	0.2103(6)	−0.0584(3)	4.08(10)	H(72)	0.121(5)	0.319(6)	0.048(4)	3.2
H(11)	0.079(4)	0.011(5)	0.318(3)	2.1	H(81)	0.019(5)	0.167(7)	−0.079(4)	4.1
H(12)	0.088(4)	−0.011(5)	0.215(3)	2.1	H(82)	0.131(5)	0.146(7)	−0.055(4)	4.1
H(21)	0.221(4)	0.158(5)	0.213(3)	2.5	H(83)	0.109(5)	0.274(7)	−0.097(4)	4.1

Table 2. Comparison of the relative heights of the X···X peaks in the Patterson maps of $[N(C_4H_9)_4][CuBrCl]$, $[N(C_4H_9)_4][CuCl_2]$ and $[N(C_4H_9)_4][CuBr_2]$. The definition of n is given in the text. For $[N(C_4H_9)_4][CuCl_2]$ and $[N(C_4H_9)_4][CuBr_2]$ the theoretical ratio is given in parenthesis.

Compounds	Ratio between X···X peaks			
	Exp.	Theor., $n=0$	Theor., $n=1$	Theor., $n=2$
$[N(C_4H_9)_4][CuBrCl]:[N(C_4H_9)_4][CuCl_2]$	2.40	2.06	2.34	2.62
$[N(C_4H_9)_4][CuBrCl]:[N(C_4H_9)_4][CuBr_2]$	0.559	0.486	0.552	0.618
$[N(C_4H_9)_4][CuBr_2]:[N(C_4H_9)_4][CuCl_2]$	4.28 (4.24)			

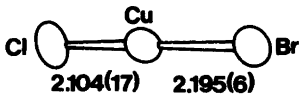

Fig. 2. The bromochlorocuprate(I) ion. The distances cited are the apparent Cu–Br and Cu–Cl bond lengths obtained in the investigation.

pancies between 0.375 and 0.625, leading to non-integral numbers on average of Cl and Br per unit cell, might give a satisfactory fit to the data, but it was not considered meaningful to examine this point further.

The model in which Cu occupies site 4*d* in *C2/c* and Br and Cl site 8*f*, each with occupancy 0.5 was thus accepted as that giving most satisfactory agreement with the experimental data. Atomic coordinates and isotropic thermal parameters are listed in Table 1. Structure factors and anisotropic thermal parameters are available from the authors on request. Atomic scattering factors for the uncharged atoms were taken from the *International Tables for X-Ray Crystallography*[8] and F_o values were weighted[9] according to $w=(29.0+F_o+0.007\ F_o^2)^{-1}$. A final difference map showed a maximum electron density of 0.3 e Å^{-3}.

DISCUSSION

Tetrabutylammonium bromochlorocuprate(I) is isomorphous with tetrabutylammonium dichlorocuprate(I) and tetrabutylammonium dibromocuprate(I). A stereoscopic view of the unit cell is given in Fig. 3 of Ref. 1. The bromochlorocuprate(I) ion is depicted in Fig. 2, the distances cited being the apparent Cu–Br and Cu–Cl bond lengths obtained in the investigation.

There are several ways in which the results of the refinement with respect to the anion might be interpreted. If Br and Cl are each assumed to have occupancy 0.5, the structure may be visualized as containing n $[CuBr_2]^-$, n $[CuCl_2]^-$ and $4-2n$ $[CuBrCl]^-$ ions per unit cell, the last ion assuming either of the two possible orientations at random. If $n=2$ the compound contains an equimolecular mixture of $[CuCl_2]^-$ and $[CuBr_2]^-$, whereas if $n=0$ only $[CuBrCl]^-$ is present.

The relative heights of the X···X peaks (X=Br,Cl) in the Patterson maps of the three compounds (see Table 2) were most consistent with $n\approx1$, which would correspond to the statistically most favourable mixture of the three anions. In order to ascertain whether or not the $[CuBrCl]^-$ entity was present, the infrared spectrum of tetrabutylammonium bromochlorocuprate(I) and, for comparison, the spectra of

Table 3. Bond lengths (Å) and angles (°) within the tetrabutylammonium ion. Angles involving hydrogen atoms are not included. Estimated standard deviations are given in parentheses. Symmetry code: (i) $-x,y,\frac{1}{2}-z$

N–C(1)	1.520(4)	N–C(5)	1.530(4)
C(1)–C(2)	1.524(5)	C(5)–C(6)	1.513(5)
C(2)–C(3)	1.532(6)	C(6)–C(7)	1.526(6)
C(3)–C(4)	1.510(6)	C(7)–C(8)	1.525(6)
C(1)–H(11)	0.99(5)	C(5)–H(51)	1.02(5)
C(1)–H(12)	1.04(5)	C(5)–H(52)	0.95(5)
C(2)–H(21)	1.03(5)	C(6)–H(61)	0.96(6)
C(2)–H(22)	0.95(6)	C(6)–H(62)	1.02(5)
C(3)–H(31)	0.98(6)	C(7)–H(71)	1.01(6)
C(3)–H(32)	1.00(6)	C(7)–H(72)	0.93(6)
C(4)–H(41)	0.94(7)	C(8)–H(81)	0.98(7)
C(4)–H(42)	0.97(6)	C(8)–H(82)	0.90(7)
C(4)–H(43)	0.90(7)	C(8)–H(83)	0.96(7)
C(1)–N–C(1^i)	106.5(4)	C(1)–N–C(5^i)	111.3(2)
C(1)–N–C(5)	110.9(2)	C(5)–N–C(5^i)	106.1(4)
N–C(1)–C(2)	114.9(3)	N–C(5)–C(6)	116.2(3)
C(1)–C(2)–C(3)	110.2(3)	C(5)–C(6)–C(7)	109.6(3)
C(2)–C(3)–C(4)	111.3(4)	C(6)–C(7)–C(8)	111.9(4)

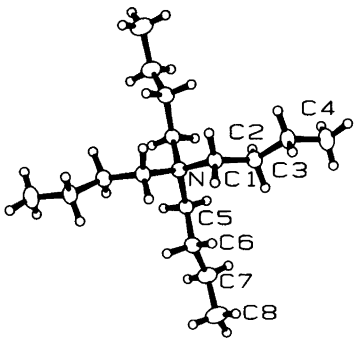

Fig. 3. The tetrabutylammonium ion in $[N(C_4H_9)_4][CuBrCl]$ showing the atomic numbering. The thermal ellipsoids of the non-hydrogen atoms are drawn[11] at the 50 % probability level while hydrogen atoms are represented as spheres of radius 0.1 Å.

tetrabutylammonium dibromocuprate(I) and tetrabutylammonium dichlorocuprate(I) were registered. For the two latter compounds, bands corresponding to the antisymmetric stretching mode were observed at 325 and 406 cm^{-1}, respectively, which is in good agreement with the findings of Bowmaker *et al.*[10] for these compounds, *viz.* 321 and 404 cm^{-1}, respectively. As is apparent from Fig. 1, the spectrum of tetrabutylammonium bromochlorocuprate(I) shows an additional band at 380 cm^{-1} which has no counterpart in the spectra of the dibromocuprate(I) and the dichlorocuprate(I) and can therefore only originate from the $[CuBrCl]^-$ ion.

It would thus seem that the $[CuBrCl]^-$ ion is indeed present and that $n=2$ can be ruled out. Nor is $n=0$ plausible, owing to the bands at 404 and 324 cm^{-1} (Fig. 1), which must originate from the dichlorocuprate(I) and dibromocuprate(I) ions, respectively. The alternative in which $n\approx1$ would thus seem to be the most satisfactory interpretation of the crystal structure. Neither is this description of the unit-cell contents, in terms of the statistically most favourable mixture of $[CuBr_2]^-$, $[CuCl_2]^-$ and $[CuBrCl]^-$, contradicted by the relative intensities of the absorption bands.

The apparent Cu–Cl distance (Fig. 2) agrees well with that determined in tetrabutylammonium dichlorocuprate(I), 2.107(1) Å.[1] The Cu–Br distance obtained in the present investigation appears, however, to be slightly shorter than that obtained in $[N(C_4H_9)_4][CuBr_2]$, 2.226(1) Å.[1] Since Cu–Br=2.195(6) Å represents an average value, it is conceivable that Cu–Br in $[CuBrCl]^-$ may be shorter than Cu–Br in $[CuBr_2]^-$. Due to the uncertainty in the determination resulting from the disorder, an estimate of the Cu–Br distance in $[CuBrCl]^-$ is not, however, warranted.

Interatomic distances and angles within the tetrabutylammonium ion are given in Table 3, the atomic numbering being in accordance with Fig. 3. As in tetrabutylammonium dichlorocuprate(I) and tetrabutylammonium dibromocuprate(I), the cation has the usual staggered conformation and there are no abnormal bond distances or angles. The shortest non-bonded approach distance between carbon and copper is C(3)···Cu=3.739(5) Å. The closest contacts between carbon and halogen are C(2)···Cl[$\frac{1}{2}-x$, $\frac{1}{2}-y$,$1-z$]=3.897(17), C(2)···Cl[x,$-y$,$z-\frac{1}{2}$]=3.916(16), C(3)···Cl[x,$-y$,$z-\frac{1}{2}$]=3.920(16) Å and C(2)···Br[$\frac{1}{2}-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$]=3.853(7), C(3)–Br[$\frac{1}{2}-x$, $y-\frac{1}{2},\frac{1}{2}-z$]=3.870(7) and C(3)···Br =3.946(7) Å. Comparison between the above values and those obtained for tetrabutylammonium dichlorocuprate(I) and for tetrabutylammonium dibromocuprate(I)[1] illustrates the flexibility of these contacts in the incorporation of $[CuCl_2]^-$, $[CuBrCl]^-$ or $[CuBr_2]^-$ in the crystal structure.

Apart from providing evidence for the existence of a linear bromochlorocuprate(I) ion, the investigation suggests that the crystalline phase contains the $[CuCl_2]^-$, $[CuBr_2]^-$ and $[CuBrCl]^-$ ions in the statistically most favourable ratio. This implies that, under the conditions for the formation of the crystalline phase, the affinity of copper(I) for bromide and chloride in linear complexation is approximately the same.

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