Cl—Zn—Cl^{i}	109.91 (7)	C2—N—C4	111.2 (12)
Cl—Zn—Cl^{ii}	108.60 (14)	C3—N—C4	103.6 (12)
C1—N—C2	116.8 (14)	N—C1—C11	112.9 (13)
C1—N—C3	116.0 (13)	N—C2—C22	111.6 (13)
C1—N—C4	104.1 (12)	N—C3—C33	115.3 (14)
C2—N—C3	104.5 (12)	N—C4—C44	118.2 (15)

Symmetry codes: (i) $-y, \frac{1}{2}+x, \frac{1}{2}-z$; (ii) $-\frac{1}{2}-x, \frac{1}{2}-y, z$.

The structures were solved by the Patterson method using *SHELXS*86 (Sheldrick, 1990) and from subsequent difference Fourier calculations using *SHELXL*93 (Sheldrick, 1993), and refined by full-matrix least-squares techniques, with isotropic displacement parameters for non-H atoms, except for Hg and Cl which were refined anisotropically. Because of disorder of the tetraethylammonium group, the bond lengths were constrained [N—C = 1.50 (1) and C—C = 1.54 (1) Å]. The H atoms were idealized with the standard methods in *SHELXL*93 and included in the least-squares process as fixed contributors, with a common freely refining isotropic displacement parameter. The figure was prepared using *ORTEP*II (Johnson, 1976) adapted for the Macintosh by André & Michalowicz (1991).

For all compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: local program; program(s) used to refine structures: *SHELXL*93; software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MD1004). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetraethylammonium Tetramethylammonium Tetrachlorocuprate(II), $[(C_2H_5)_4N][(CH_3)_4N][CuCl_4]$

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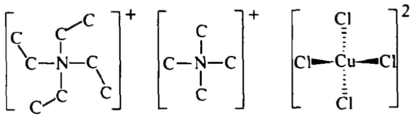
Abstract

The title compound contains four isolated and discrete moieties, *i.e.* two independent $[(CH_3)_4N]^+$ cations, with one ordered on a $\bar{4}$ axis and the other disordered with the central N atom on a 2_z axis, one $[(C_2H_5)_4N]^+$ cation, on a mirror plane and in a *trans* conformation, and one distorted tetrahedral $[CuCl_4]^{2-}$ anion on another mirror. The crystal structure is isomorphous with that of $[(C_2H_5)_4N][(CH_3)_4N][ZnCl_4]$ [Caëtano, Lapasset & Saint Grégoire (1995). *Acta Cryst.* C**51**, 220–222].

Comment

As part of our studies of structural instabilities in the $[(C_2H_5)_4N]_2[MX_4]$ family (Mahoui, Lapasset, Moret & Saint Grégoire, 1994; Mahoui, Lapasset, Sannikov, Moret & Saint Grégoire, 1996; Mahoui, Lapasset, Moret, Lopez & Saint Grégoire, 1995; Caëtano, Lopez, Mahoui, Lapasset, Moret, Assih & Saint Grégoire, 1995), we have investigated the single-crystal structure of the title compound, (I), which belongs to a sub-family of $[(C_2H_5)_4N]_2[MX_4]$, where one $[(C_2H_5)_4N]^+$ (TEA) cation has been substituted by a $[(CH_3)_4N]^+$ (TMA) cation and MX_4 corresponds to $CuCl_4$.



(I)

The crystal structure analysis of (I) shows a structure isomorphous with (TEA)(TMA)$[ZnCl_4]$ (Caëtano, Lapasset & Saint Grégoire, 1995). In this compound, the substitution of zinc by copper does not modify the structure, unlike in $(TEA)_2[ZnCl_4]$ (Mahoui, Lapasset, Moret & Saint Grégoire, 1996) and $(TEA)_2[CuCl_4]$ (Mahoui, Lapasset, Sannikov, Moret & Saint Grégoire, 1996), where the TEA cations possess different disorders.

The crystal structure of (I) consists of discrete $[CuCl_4]^{2-}$, TEA and TMA moieties. The mutual arrangement of the different moieties is illustrated in

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Fig. 1. The structure is organized into alternating layers, in the sequence —TMA–TMA–$[CuCl_4]^{2-}$–TEA–TEA–$[CuCl_4]^{2-}$—, stacked along [001]. The Cu, Cl2 and Cl3 atoms of the anion lie in a diagonal mirror plane, whereas the Cl1 atom is in a general position; the corresponding tetrahedra present a distorted geometry with bond lengths and angles in the ranges 2.242 (5)–2.264 (5) Å and 105.5 (1)–118.9 (2)°, respectively. The Cu—Cl bond lengths are larger than those observed for $[CuCl_4]^{2-}$ in the corresponding $(TEA)_2[CuCl_4]$ crystal (Mahoui *et al.*, 1994) [Cu—Cl 2.225 (6) Å] and the tetrahedral geometry less distorted [Cl—Cu—Cl 102.5 (3)–113.1 (2)°]. All $[CuCl_4]$ tetrahedra, facing one another, have one of their threefold axes, *i.e.* that lying in the Cu—Cl2 bond direction, tilted slightly away from the crystallographic *c* axis. As for the anion, two chains of the TEA group, namely, N1—C121—C122 and N1—C131—C132, lie in the same diagonal mirror plane, whereas atoms C111 and C112 are in general positions, all leading to a *trans* conformation. The central N atoms (N2 and N3) of the two independent TMA groups are situated in special positions, (0,0,0) and $(0,\frac{1}{2},0.0054)$ for the ordered and disordered groups, respectively, on the $\bar{4}$ and 2_z axes. The bond lengths and angles in the different cations are close to the expected values (Table 2).

The organization of the moieties in the (TEA)(TMA)-$[CuCl_4]$ crystal is similar to that in $(TEA)_2[CdBr_4]$ (Geselle & Fuess, 1994). In fact, the $[CdBr_4]^{2-}$ anions have the same geometry and symmetry positions as $[CuCl_4]^{2-}$. One of the three independent TEA groups in $(TEA)_2[CdBr_4]$ presents the same *trans* conformation and symmetry position as the corresponding one in (TEA)(TMA)$[CuCl_4]$, while the two remaining TEA groups in $(TEA)_2[CdBr_4]$ have a 'swastiska' conformation (nordic-cross shape) and are situated on the same 2_z axes as for the two TMA groups in compound (I). In addition, the corresponding TEA of disordered TMA in (I), namely, that situated on the axis with $(0,\frac{1}{2},z)$ coordinates, is also disordered in $(TEA)_2[CdBr_4]$.

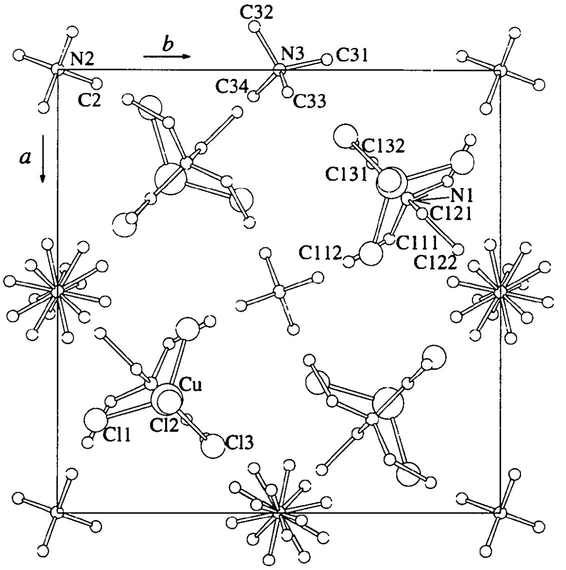

Fig. 1. An *ORTEP*II (Johnson, 1976; André & Michalowicz, 1991) drawing with atomic labelling scheme viewed along [001]. Atoms are drawn as spheres of arbitrary radii. Only one position of the disordered TMA cation at $(0,\frac{1}{2},0.0054)$ is shown.

Experimental

A stoichiometric mixture of anhydrous $(C_2H_5)_4NCl$, $CuCl_2$ and $(CH_3)_4NCl$ dissolved in absolute ethanol afforded single crystals of (I) on slow cooling.

Crystal data

$(C_8H_{20}N)(C_4H_{12}N)[CuCl_4]$
$M_r = 409.74$
Tetragonal
$P\bar{4}2_1m$
$a = 13.078 (10)$ Å
$c = 11.871 (10)$ Å
$V = 2030.3 (28)$ Å^3
$Z = 4$
$D_x = 1.340$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 20 reflections
$\theta = 42–55°$
$\mu = 6.280$ mm^{-1}
$T = 293 (2)$ K
Prism
0.34 × 0.29 × 0.20 mm
Yellow–orange

Data collection

Enraf–Nonius CAD-3 diffractometer
$\theta/2\theta$ scans
Absorption correction: *SHELX76* Gaussian (Sheldrick, 1976)
$T_{min} = 0.1783$, $T_{max} = 0.4250$
1765 measured reflections
952 independent reflections

866 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0238$
$\theta_{max} = 65.12°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 13$
2 standard reflections monitored every 40 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0702$
$wR(F^2) = 0.1763$
$S = 1.097$
952 reflections
73 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0838P)^2 + 5.7928P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.492$ e Å^{-3}
$\Delta\rho_{min} = -0.484$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = −0.14 (10)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Cu	0.74605 (10)	0.24605 (10)	0.80803 (15)	0.0507 (5)
Cl1	0.7926 (3)	0.0865 (2)	0.7612 (3)	0.0951 (12)
Cl2	0.7517 (4)	0.2517 (4)	0.9967 (3)	0.106 (2)

Cl3	0.8503 (2)	0.3503 (2)	0.7081 (3)	0.0801 (12)
N1	0.2897 (6)	0.7897 (6)	0.3923 (8)	0.045 (2)
C111	0.3802 (8)	0.7492 (9)	0.3248 (9)	0.067 (3)
C112	0.4323 (10)	0.6571 (10)	0.3765 (11)	0.092 (4)
C121	0.3227 (9)	0.8227 (9)	0.5087 (14)	0.076 (4)
C122	0.4039 (10)	0.9039 (10)	0.5107 (16)	0.089 (5)
C131	0.2095 (10)	0.7095 (10)	0.4090 (16)	0.087 (5)
C132	0.1659 (11)	0.6659 (11)	0.3019 (15)	0.090 (5)
N2	0	0	0	0.064 (5)
C2	0.0321 (10)	0.0869 (10)	−0.0709 (11)	0.081 (3)
N3	0	1/2	0.0054 (14)	0.056 (5)
C31†	−0.023 (5)	0.607 (3)	−0.031 (5)	0.105 (10)
C32†	−0.100 (3)	0.443 (4)	0.024 (4)	0.105 (10)
C33†	0.051 (4)	0.518 (4)	0.114 (3)	0.105 (10)
C34‡	0.060 (2)	0.441 (2)	−0.076 (4)	0.105 (10)

† Site occupancy = 0.25. ‡ Site occupancy = 0.50.

Table 2. *Selected geometric parameters (Å, °)*

Cu—Cl1	2.243 (3)	C121—C122	1.50 (2)
Cu—Cl2	2.242 (5)	C131—C132	1.51 (3)
Cu—Cl3	2.264 (5)	N2—C2	1.48 (1)
N1—C111	1.52 (1)	N3—C31	1.49 (4)
N1—C121	1.51 (2)	N3—C32	1.52 (4)
N1—C131	1.50 (2)	N3—C33	1.47 (3)
C111—C112	1.51 (2)	N3—C34	1.47 (3)
Cl1—Cu—Cl1^{i}	116.3 (2)	C132—C131—N1	115 (1)
Cl1—Cu—Cl2	105.6 (1)	C2—N2—C2^{iii}	110.4 (10)
Cl1—Cu—Cl3	105.5 (1)	C2—N2—C2^{iv}	109.0 (5)
Cl2—Cu—Cl3	118.9 (2)	C31—N3—C32	109 (4)
C111—N1—C111^{ii}	105.3 (10)	C31—N3—C33	101 (3)
C111—N1—C121	111.0 (7)	C31—N3—C34	114 (3)
C111—N1—C131	111.7 (7)	C32—N3—C33	110 (3)
C121—N1—C131	106.2 (11)	C32—N3—C34	107 (2)
C112—C111—N1	114.4 (9)	C33—N3—C34	115 (3)
C122—C121—N1	115 (1)		

Symmetry codes: (i) $\frac{1}{2}+y, x-\frac{1}{2}, z$; (ii) $y-\frac{1}{2}, \frac{1}{2}+x, z$; (iii) $-x, -y, z$; (iv) $-y, x, -z$.

The title structure was solved by the Patterson method, from subsequent difference-Fourier calculations and refined by full-matrix least-squares techniques with isotropic displacement parameters for non-H atoms, except Cu and Cl atoms which were refined anisotropically. The bond lengths of the disordered tetramethylammonium group were constrained [N—C = 1.45 (5) Å]. The H atoms were idealized with the standard methods in *SHELXL*93 (Sheldrick, 1993) and included in the least-squares process as fixed contributors; their isotropic displacement parameters were set at $1.5U_{iso}$ of the corresponding C atoms.

Data collection: Enraf–Nonius CAD-3 software. Cell refinement: Enraf–Nonius CAD-3 software. Data reduction: local program. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SK1018). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis[4-(5-chloro-2-hydroxyphenylimino-*N*,*O*:*O*)-2-penten-2-olato(2–)-*O*]dicopper(II)

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Abstract

In the title complex, $[Cu_2(C_{11}H_{10}ClNO_2)_2]$, the Cu atoms have two phenolic oxygen bridges resulting in centrosymmetric Cu dimers. The coordination around copper is distorted square planar, with an average Cu—O distance of 1.921 (5) and a Cu—N distance of 1.910 (5) Å. Two additional O atoms belonging to adjacent dimers at distances of 2.986 (6) and 3.139 (6) Å complete the distorted octahedron about copper.

Comment

Doubly oxygen-bridged dimeric copper(II) complexes with subnormal magnetic moments are known to exhibit super-exchange interaction (Kato, Jonassen & Fanning, 1964; Butcher & Sinn, 1976; Kato & Muto, 1988). The