Refinement

Refinement on F
$R = 0.0361$
$wR = 0.0584$
$S = 1.67$
1029 reflections
131 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F) + 0.03F^2]$
$(\Delta/\sigma)_{\max} = 0.0001$
$\Delta\rho_{\max} = 2.15$ e Å^{-3}
$\Delta\rho_{\min} = -3.20$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *The SDS System* (Petříček & Malý, 1992)

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

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

	x	y	z	$B_{\rm eq}$
Ni	0.08590 (4)	1/4	0.0146 (3)	2.0 (1)
O1	−0.0620 (2)	1/4	−0.0523 (2)	2.8 (1)
O2	−0.1363 (2)	1/4	−0.1937 (2)	3.8 (1)
O3	−0.0033 (2)	1/4	0.1233 (1)	2.9 (1)
O4	0.0214 (3)	1/4	0.2737 (2)	5.4 (1)
N1	0.1772 (2)	1/4	−0.0965 (2)	2.2 (1)
N2	0.2380 (2)	1/4	0.0835 (2)	2.2 (1)
N3	0.3585 (1)	0.0726 (3)	−0.0333 (1)	2.3 (1)
C1	−0.0478 (3)	1/4	−0.1398 (2)	2.6 (1)
C2	0.0856 (2)	1/4	−0.1740 (2)	3.3 (1)
C3	0.0640 (3)	1/4	0.1965 (2)	3.0 (1)
C4	0.2045 (3)	1/4	0.1818 (2)	3.3 (1)
C5	0.3146 (1)	0.0681 (3)	0.0600 (1)	2.4 (1)
C6	0.2595 (2)	0.0664 (3)	−0.1003 (1)	2.5 (1)
C7	0.4344 (2)	1/4	−0.0470 (2)	2.4 (1)

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

Ni—O1	1.852 (2)	N1—C6	1.517 (2)
Ni—O3	1.856 (2)	N2—C4	1.485 (4)
Ni—N1	1.899 (2)	N2—C5	1.512 (3)
Ni—N2	1.905 (2)	N3—C5	1.447 (3)
O1—C1	1.293 (4)	N3—C6	1.441 (3)
O2—C1	1.229 (4)	N3—C7	1.456 (2)
O3—C3	1.291 (4)	C1—C2	1.504 (4)
O4—C3	1.221 (4)	C3—C4	1.508 (4)
N1—C2	1.496 (4)		
O1—Ni—O3	91.3 (1)	C4—N2—C5	110.5 (1)
O1—Ni—N1	88.7 (1)	C5—N3—C6	114.3 (2)
O1—Ni—N2	180.0 (0)	C5—N3—C7	109.0 (2)
O3—Ni—N1	180.0 (0)	C6—N3—C7	109.5 (2)
O3—Ni—N2	88.6 (1)	O1—C1—O2	123.4 (3)
N1—Ni—N2	91.4 (1)	O1—C1—C2	116.2 (3)
Ni—O1—C1	115.4 (2)	O2—C1—C2	120.4 (3)
Ni—O3—C3	115.6 (2)	O3—C3—O4	124.6 (3)
Ni—N1—C2	108.8 (2)	O3—C3—C4	115.4 (3)
Ni—N1—C6	109.0 (1)	O4—C3—C4	120.0 (3)
C2—N1—C6	110.3 (1)	N2—C4—C3	112.1 (2)
Ni—N2—C4	108.2 (2)	N2—C5—N3	111.9 (2)
Ni—N2—C5	109.6 (1)	N1—C6—N3	111.8 (2)

Preliminary lattice parameters and space-group symmetry were determined from Weissenberg photographs. The structure was solved by the heavy-atom method using *SHELXS*86 (Sheldrick, 1985). All atoms, except H atoms, were refined anisotropically by block-diagonal-matrix least-squares procedures using *SDS* (Petříček & Malý, 1992). Absorption corrections were not applied. We tried to make an empirical absorption correction from diffraction data (ψ scan). The $R_{\rm int}$ factor before correction was 0.0171 for all data; after correction it was 0.0119. The influence of the whole correction on the final R factor and the e.s.d.'s of the refined parameters was negligible.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances involving H atoms have been deposited with the IUCr (Reference: VS1010). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1994). C**50**, 1212–1214

Bis(tetrapropylammonium) Hexachlorodicuprate(II)

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(*Received* 15 *November* 1993; *accepted* 4 *February* 1994)

Abstract

Bis(tetrapropylammonium) di-μ-chlorobis(dichlorocuprate)(2−), $(C_{12}H_{28}N)_2[Cu_2Cl_6]$, contains a centrosymmetric hexachlorodicuprate group in which each Cu atom shows coordination to two bridging Cl atoms [Cu—Cl 2.314 (1) Å] and two terminal Cl atoms [average Cu—Cl 2.198 (1) Å] in flattened tetrahedral geometry. There are no interactions between neighboring $[Cu_2Cl_6]^{2-}$ groups.

Comment

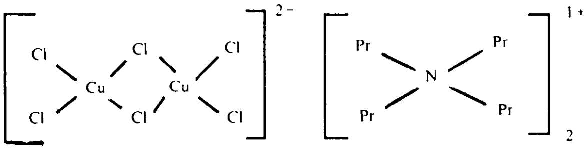
Structural observations for $[Cu_2Cl_6]^{2-}$ groups reported in the literature may be divided into three groups depending upon the size of the cation present. All show a pair of Cu$^{\rm II}$ atoms bridged by two Cl atoms, each Cu atom showing further coordination to two terminal Cl atoms. Terminal Cu—Cl distances are typically 2.20 Å and bridging Cl—Cu distances are slightly longer.

When the cation is large, *e.g.* Ph_4P^+ (Textor, Dubler & Oswald, 1974) or Ph_4As^+ (Willett & Chow, 1974), the geometry at each tetracoordinate Cu atom may be described as flattened tetrahedral and no interactions between the dianionic groups are found. When the cationic group is smaller in size, an additional 'long' bond (approximately 3 Å) between Cu and a terminal Cl atom of a neighboring dimer is observed and the geometry at the Cu atom becomes square pyramidal, as seen for the cations $(CH_3)_2NH_2^+$ (Willett, 1966), $(CH_3)_2CHNH_3^+$ (Roberts, Bloomquist, Willett & Dodgen, 1981) and $C_3N_6H_8^+$ (melaminium) (Colombo, Menabue, Motori, Pellacani, Porzio, Sandrolini & Willett, 1985), or distorted trigonal bipyramidal, as seen for the cations $PhCH_2CH_2N(CH_3)H_2^+$ (Harlow, Wells, Watt & Simonsen, 1974), 4-benzylpiperidinium (Battaglia, Bonamartini Corradi, Marcotrigiano, Menabue & Pellacani, 1980) and *N*,*N*′-dimethyl-4,4′-bipyridylium (Murray-Rust, 1975).

On further diminution of the cation size, *e.g.* NH_4^+ or K^+ (Willett, Dwiggins, Kruh & Rundle, 1963), two 'long' interdimer Cu—Cl bonds result in near octahedral geometry at the Cu atom.

When the cation or included organic molecules present ligation or hydrogen-bonding possibilities, the fifth and sixth sites of copper(II) may be involved. The structure of $Li_2Cu_2Cl_6.2H_2O$ (Vossos, Fitzwater & Rundle, 1963) contains square-planar $CuCl_4$ units made octahedral by the addition of a long Cu—Cl bond (2.922 Å) *trans* to a Cu—OH_2 interaction. (Purinium)Cu_2Cl_6 (Sheldrick, 1981) shows one Cu atom with octahedral coordination geometry due to a long chloride bond *trans* to a bond to an N atom of the purine base, whereas the second Cu atom has only an additional long chloride bond and has square-pyramidal coordination geometry.

The geometry of the title compound, bis(tetrapropylammonium)Cu_2Cl_6, (I), thus appears to resemble that of the family of complexes in which the cation is large and the $[Cu_2Cl_6]^{2-}$ groups are isolated and without intergroup interactions.



(I)

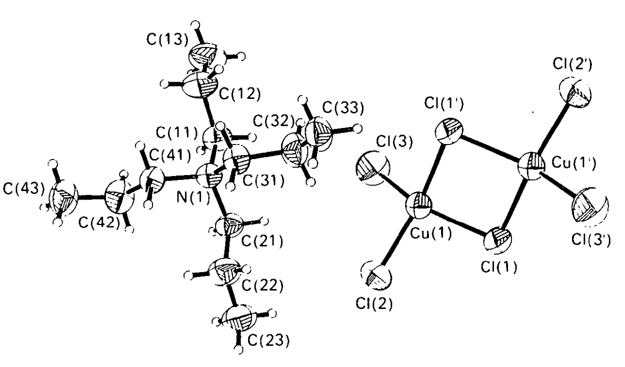


Fig. 1. Projection view of $(C_{12}H_{28}N)_2[Cu_2Cl_6]$. Displacement ellipsoids are shown at the 50% probability level. [Symmetry code: (i) $-x, 2-y, 2-z$.]

Experimental

Tetrapropylammonium chloride (9 mmol) and 0.25 g (2.5 mmol) CuCl were mixed in 40 ml of EtOH. The resulting solution was heated under reflux for 5 h, cooled, filtered and evaporated slowly under nitrogen. After 48 h, colorless prismatic crystals of Pr_4NCuCl_2 were obtained. After 30 days brown rhombohedral crystals of the title compound were formed.

Crystal data

$(C_{12}H_{28}N)_2[Cu_2Cl_6]$
$M_r = 712.47$
Triclinic
$P\bar{1}$
$a = 9.368$ (2) Å
$b = 9.382$ (2) Å
$c = 11.881$ (3) Å
$\alpha = 100.12$ (1)°
$\beta = 106.37$ (2)°
$\gamma = 113.30$ (2)°
$V = 869.9$ (3) Å^3
$Z = 1$
$D_x = 1.360$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.107–12.690$°
$\mu = 1.707$ mm^{-1}
$T = 293$ (2) K
Rhombohedron
0.4 × 0.2 × 0.2 mm
Brown

Data collection

Siemens *P*4 four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.720$, $T_{max} = 0.967$
4238 measured reflections
3992 independent reflections
2674 observed reflections [$F > 4\sigma(F)$]

$R_{int} = 0.0225$
$\theta_{max} = 30.00$°
$h = -12 \rightarrow 11$
$k = 0 \rightarrow 12$
$l = -15 \rightarrow 15$
3 standard reflections monitored every 97 reflections
intensity variation: 0.01%

Refinement

Refinement on F^2
$R(F) = 0.0467$
$wR(F^2) = 0.1040$
$S = 1.109$
3988 reflections
159 parameters
H-atom parameters refined using a riding model
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0326P)^2 + 1.4540P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.269$
$\Delta\rho_{max} = 0.604$ e Å^{-3}
$\Delta\rho_{min} = -0.398$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1994)
Extinction coefficient: 0.0000 (12)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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(1)	0.05237 (7)	0.94742 (7)	0.87894 (5)	0.0505 (2)
Cl(1)	0.0810 (2)	1.18365 (14)	1.00336 (12)	0.0614 (3)
Cl(2)	0.2915 (2)	1.0650 (2)	0.85492 (13)	0.0719 (4)
Cl(3)	−0.0924 (2)	0.7425 (2)	0.70297 (12)	0.0845 (4)
N(1)	0.2973 (4)	0.5097 (4)	0.7414 (3)	0.0443 (8)
C(11)	0.1185 (5)	0.3958 (5)	0.6476 (4)	0.0539 (11)

C(12)	0.0327 (6)	0.2276 (6)	0.6593 (5)	0.0722 (14)
C(13)	−0.1379 (7)	0.1261 (7)	0.5550 (6)	0.091 (2)
C(21)	0.3533 (5)	0.6685 (5)	0.7091 (4)	0.0508 (10)
C(22)	0.5300 (6)	0.8001 (6)	0.7866 (5)	0.0698 (14)
C(23)	0.5773 (8)	0.9398 (6)	0.7354 (6)	0.084 (2)
C(31)	0.3058 (5)	0.5413 (5)	0.8735 (4)	0.0492 (10)
C(32)	0.1969 (7)	0.6122 (7)	0.9051 (5)	0.0663 (13)
C(33)	0.2264 (6)	0.6386 (6)	1.0406 (4)	0.0657 (13)
C(41)	0.4137 (5)	0.4356 (5)	0.7364 (4)	0.0470 (10)
C(42)	0.4342 (7)	0.3974 (7)	0.6152 (4)	0.0678 (13)
C(43)	0.5478 (7)	0.3194 (7)	0.6235 (5)	0.0753 (15)

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

Cu(1)—Cl(2)	2.1979 (14)	C(11)—C(12)	1.514 (6)
Cu(1)—Cl(3)	2.1983 (15)	C(12)—C(13)	1.504 (7)
Cu(1)—Cl(1)	2.3076 (14)	C(21)—C(22)	1.496 (6)
Cu(1)—Cl(1^i)	2.3241 (13)	C(22)—C(23)	1.503 (7)
N(1)—C(41)	1.516 (5)	C(31)—C(32)	1.513 (6)
N(1)—C(11)	1.517 (5)	C(32)—C(33)	1.511 (7)
N(1)—C(31)	1.518 (5)	C(41)—C(42)	1.506 (6)
N(1)—C(21)	1.529 (5)	C(42)—C(43)	1.503 (7)
Cl(2)—Cu(1)—Cl(3)	98.91 (6)	C(11)—N(1)—C(21)	105.8 (3)
Cl(2)—Cu(1)—Cl(1)	96.17 (5)	C(31)—N(1)—C(21)	111.3 (3)
Cl(3)—Cu(1)—Cl(1)	147.64 (6)	C(12)—C(11)—N(1)	116.5 (4)
Cl(2)—Cu(1)—Cl(1^i)	145.99 (6)	C(13)—C(12)—C(11)	109.9 (4)
Cl(3)—Cu(1)—Cl(1^i)	97.37 (6)	C(22)—C(21)—N(1)	116.2 (4)
Cl(1)—Cu(1)—Cl(1^i)	85.48 (5)	C(21)—C(22)—C(23)	111.0 (4)
Cu(1)—Cl(1)—Cu(1^i)	94.52 (5)	C(32)—C(31)—N(1)	117.0 (3)
C(41)—N(1)—C(11)	111.7 (3)	C(33)—C(32)—C(31)	109.0 (4)
C(41)—N(1)—C(31)	105.2 (3)	C(42)—C(41)—N(1)	116.5 (3)
C(11)—N(1)—C(31)	111.6 (3)	C(43)—C(42)—C(41)	110.1 (4)
C(41)—N(1)—C(21)	111.3 (3)		

Symmetry code: (i) $-x, 2-y, 2-z$.

Data collection, cell refinement and data reduction: *SHELXL XSCANS* (Sheldrick, 1994). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*. Molecular graphics: *SHELXL XP*. Software used to prepare material for publication: *SHELXL*.

The authors acknowledge NSF grant EHR-9108771

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BR1067). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1994). **C50**, 1214–1217

cis-Ammine(benzoylhydrazine-*N*)-dichloroplatinum(II)

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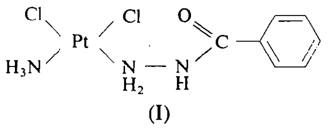
(*Received* 24 *November* 1993; *accepted* 8 *February* 1994)

Abstract

In the title compound, *cis*-ammine(benzohydrazide-*N*′)-dichloroplatinum(II), *cis*-$[PtCl_2(C_7H_8N_2O)(NH_3)]$, the benzoylhydrazine ligand is bonded to the Pt atom through its amino group. The Pt—Cl and Pt—N distances are in the ranges 2.293 (5)–2.318 (5) and 2.01 (1)–2.08 (1) Å, respectively. The arrangement of molecules in the monoclinic unit cell approximates $P2_1/c$ space-group patterns; however, the true space-group symmetry is $P2_1$. The two crystallographically independent molecules have significantly different conformations about the Pt—N(hydrazine) bond. The structure is held together by a complicated network of N—H···O and N—H···Cl hydrogen bonds.

Comment

The considerable success of *cis*-$[PtCl_2(NH_3)_2]$ (cisplatin) in the clinical treatment of tumours (Carter, 1984) has stimulated the design of analogous complexes with modified ligands (Hides & Russell, 1988; Lippert, 1992). Recently, Dodoff, Grancharov, Gugova & Spassovska (1994) described the preparation, characterization and *in vitro* cytotoxic effects of a series of Pt^{II} complexes of benzoylhydrazine and 3-methoxybenzoylhydrazine. Crystals could be obtained only for the title compound (I).



(I)

The asymmetric unit of the title compound contains two *cis*-$[PtCl_2(bh)(NH_3)]$ (bh = benzoylhydrazine) molecules (Fig. 1) related by a pseudo symmetry centre at $(0,0,\frac{1}{4})$. Corresponding atoms of the two independent molecules are labelled identically, except those of the second molecule are distinguished by primes (see