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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55371 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1009]

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## Tetraethylammonium Tetrachlorocuprate(II), [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]<sub>2</sub>[CuCl<sub>4</sub>]

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### Abstract

The structure has been determined by single-crystal X-ray diffraction at 120 K. There are two independent copper sites, one at 4 and the other very close to the fourfold axis with positional disorder. The structures of the [CuCl<sub>4</sub>]<sup>2-</sup> ions have a *D*<sub>2d</sub> type distortion from tetrahedral symmetry with the larger Cl—Cu—Cl bond angles 122.3 (1)–128.1 (5)°.

### Comment

The [CuCl<sub>4</sub>]<sup>2-</sup> ion in the solid state adopts various geometries from planar through tetrahedral to trigo-

nal bipyramidal (Smith, 1976). Several spectroscopic studies have been carried out to establish the relationships between the geometry and the electronic reflectance spectra (Lamotte-Brasseur, 1974; Battaglia, Bonamartini Corradi, Marcotrigiano, Menabue & Pellacani, 1979), paramagnetic susceptibilities (Lamotte-Brasseur & Van den Bossche, 1974) and X-ray absorption spectra (Sano, Komorita & Yamatera, 1992). An X-ray structure analysis of the title compound by Lamotte-Brasseur (1973) was not completed, possibly because of difficulties in modelling the positional disorder of the Cu(2) atom.

The flattening of the [CuCl<sub>4</sub>]<sup>2-</sup> ion from a regular tetrahedron can be measured by taking the average of the two larger Cl—Cu—Cl angles,  $\theta$  (Willett, Haugen, Lebsack & Morrey, 1974), or by the dihedral angle between the two Cl—Cu—Cl planes (Battaglia *et al.*, 1979). As speculated by Lamotte-Brasseur & Van den Bossche (1974), the *D*<sub>2d</sub> type distortion of the [CuCl<sub>4</sub>]<sup>2-</sup> ion in this [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]<sub>2</sub>[CuCl<sub>4</sub>] salt [ $\theta = 124.7 (5)^\circ$ ] is smaller than in [N(CH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>[CuCl<sub>4</sub>] [ $\theta = 129.3 (3)^\circ$ ; Morosin & Lingafelter, 1961; Clay, Murray-Rust & Murray-Rust, 1975], [NH(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>[CuCl<sub>4</sub>] [ $\theta = 132.9 (1)^\circ$ ; Williams, Brown & Taylor, 1992], [NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[CuCl<sub>4</sub>] [ $\theta = 135.8 (2)^\circ$ ; Willett & Larsen, 1971], [NH(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>[CuCl<sub>4</sub>] [ $\theta = 134.8 (2)^\circ$ ; Lamotte-Brasseur, Dideberg & Dupont, 1973] and [N(CH<sub>3</sub>)<sub>3</sub>(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>[CuCl<sub>4</sub>] [ $\theta = 132.5 (1)^\circ$ ; Bonamico, Dessy & Vaciago, 1967].

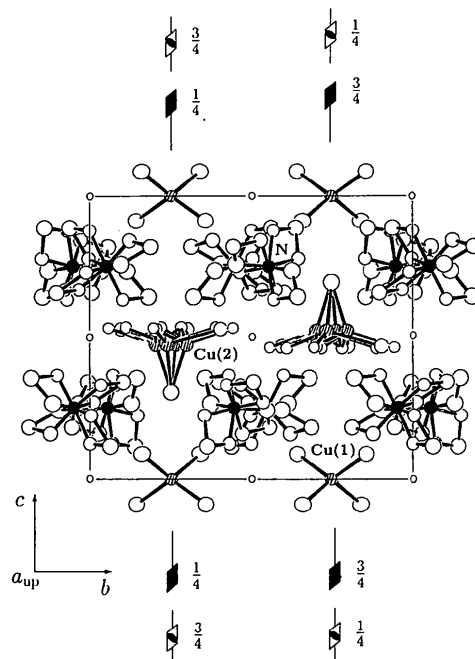


Fig. 1. Projection of the crystal structure along *a*. Black and hatched spheres represent N and Cu atoms respectively.

## Experimental

## Crystal data

[N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]<sub>2</sub>[CuCl<sub>4</sub>]M<sub>r</sub> = 465.86

Tetragonal

P4/n

a = 13.984 (3) Å

c = 12.232 (5) Å

V = 2392 (1) Å<sup>3</sup>

Z = 4

D<sub>x</sub> = 1.29 Mg m<sup>-3</sup>

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 30 reflections

θ = 10–15°

μ = 1.368 mm<sup>-1</sup>

T = 120 (1) K

Prism

0.45 × 0.25 × 0.15 mm

Orange-red

## Data collection

Rigaku AFC-5 four-circle diffractometer

ω scans

Absorption correction:

by integration from crystal shape

T<sub>min</sub> = 0.716, T<sub>max</sub> = 0.822

2969 measured reflections

2752 independent reflections

1172 observed reflections

[|F<sub>o</sub>| > 3σ(|F<sub>o</sub>|)]R<sub>int</sub> = 0.028θ<sub>max</sub> = 27.5°

h = 0 → 18

k = 0 → 18

l = 0 → 15

3 standard reflections

monitored every 50

reflections

intensity variation: 0.982–

1.008

## Refinement

Refinement on F

Final R = 0.107

wR = 0.083

S = 3.62

1172 reflections

83 parameters

H atoms not located

w = 1/σ

(Δ/σ)<sub>max</sub> = 0.365Δρ<sub>max</sub> = 0.868 e Å<sup>-3</sup>Δρ<sub>min</sub> = -1.254 e Å<sup>-3</sup>

Atomic scattering factors

from *International Tables*for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>)The origin of the unit cell is located at  $\bar{1}$ .  $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ .

	Occupancy	x	y	z	U <sub>eq</sub>
Cu(1)	1	0.25	0.75	0.0	0.0323 (8)
Cl(1)	1	0.1598 (3)	0.6429 (3)	0.0882 (3)	0.049 (1)
Cu(2)*	0.25	0.2643 (8)	0.2970 (4)	0.4774 (4)	0.038 (2)
Cl(2)*	1	0.25	0.25	0.3056 (6)	0.051 (2)
Cl(3)*	0.25	0.4040 (9)	0.2002 (9)	0.530 (1)	0.038 (4)
Cl(4)*	0.25	0.3045 (8)	0.4429 (8)	0.5340 (9)	0.023 (3)
Cl(5)*	0.25	0.1107 (9)	0.2821 (9)	0.5366 (9)	0.027 (3)
N*	1	0.0498 (7)	0.5533 (7)	0.7509 (8)	0.031 (3)
C(1)*	0.80	-0.011 (1)	0.464 (1)	0.730 (1)	0.035 (5)
C(2)*	1	-0.103 (1)	0.494 (1)	0.659 (1)	0.043 (4)
C(3)*	0.80	0.101 (1)	0.570 (1)	0.635 (1)	0.031 (4)
C(4)*	1	0.180 (1)	0.645 (1)	0.645 (1)	0.050 (4)
C(5)*	0.80	0.121 (1)	0.529 (1)	0.842 (1)	0.039 (5)
C(6)*	1	0.187 (1)	0.444 (1)	0.820 (1)	0.044 (4)
C(7)*	0.80	-0.004 (1)	0.646 (1)	0.778 (1)	0.034 (5)
C(8)*	1	-0.0620 (9)	0.6384 (9)	0.886 (1)	0.047 (4)
C(O1)*	0.20	-0.033 (4)	0.577 (4)	0.669 (5)	0.03 (2)
C(O3)*	0.20	0.114 (5)	0.627 (5)	0.735 (5)	0.05 (2)
C(O5)*	0.20	0.095 (5)	0.452 (5)	0.759 (5)	0.05 (2)
C(O7)*	0.20	-0.001 (4)	0.568 (4)	0.877 (5)	0.03 (2)

\*Refined isotropically.

Table 2. Bond lengths (Å) and angles (°)

Cu(1)—Cl(1)	2.236 (4)	Cu(2)—Cl(4)	2.23 (1)
Cu(2)—Cl(2)	2.211 (9)	Cu(2)—Cl(5)	2.28 (2)
Cu(2)—Cl(3)	2.46 (2)		
Cl(1)—Cu(1)—Cl(1) <sup>i</sup>	122.3 (1)	Cl(2)—Cu(2)—Cl(5)	100.9 (5)
Cl(1)—Cu(1)—Cl(1) <sup>ii</sup>	103.5 (1)	Cl(3)—Cu(2)—Cl(4)	102.9 (6)
Cl(2)—Cu(2)—Cl(3)	98.9 (4)	Cl(3)—Cu(2)—Cl(5)	128.1 (5)
Cl(2)—Cu(2)—Cl(4)	126.2 (4)	Cl(4)—Cu(2)—Cl(5)	102.9 (5)

Symmetry codes: (i)  $\frac{1}{2} - x, \frac{3}{2} - y, z$ ; (ii)  $-\frac{1}{2} + y, -x, -z$ .

The compound was prepared according to Gill & Nyholm (1959) by mixing ethanol solutions of [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]Cl and CuCl<sub>2</sub>. Orange-red prismatic crystals were grown from the filtrate. An X-ray intensity measurement was carried out at room temperature to confirm the Laue group 4/m, and the systematic absences, *hk0*, *h + k* odd, which had been reported by Lamotte-Brasseur (1973). As radiation damage of the crystal was severe, the crystal was kept at 120 K by blowing cold nitrogen gas over it. There was no phase transition in the temperature range 300–120 K but a pronounced contraction of the *c* axis was observed [*a* = 14.04(3), *c* = 12.38(3) Å at 260 K, 13.984(3) and 12.232(5) Å at 120 K]. The positions of Cu(1) and Cl(1) could be easily deduced from the Patterson function. However, the structure determination was not straightforward. The *R* value stopped at 22% for the structure model in which the other Cu atom lies on a crystallographic fourfold axis. After several trials, it was revealed that one of the Cl atoms, Cl(2), is located on the fourfold axis and that the Cu(2) atom deviates from the axis. The positions of the N and terminal C atoms of the tetraethylammonium group are ordered but the C atoms bonded to the N atom have two possible positions suggesting that the [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]<sup>+</sup> ion is orientationally disordered as observed in [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]<sub>2</sub>[InCl<sub>5</sub>] (Brown, Einstein & Tuck, 1969). Anisotropic thermal parameters were not introduced except for Cu(1) and Cl(1) in order to avoid a non-positive-definite mean-square displacement matrix. The relatively large *R* value (0.107) may be due to the disorder of the CuCl<sub>4</sub><sup>2-</sup> ion. Calculations were performed using *Xtal3.0* (Hall & Stewart, 1990) on a MIPS RS3230 workstation.

Lists of structure factors, anisotropic thermal parameters, and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55509 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1014]

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### Structure of 1-[(*R*)-1',2-Bis(diphenylphosphino)ferrocenyl]-(*S*)-*N,N*-dimethylethylamine

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#### Abstract

In the ferrocene moiety, the cyclopentadienyl rings are planar and slightly staggered with a dihedral angle of 2.8°. The average Fe—C and C—C distances are 2.042 (4) and 1.417 (7) Å respectively. The P—C—C angles are asymmetric and the C—C distances in the phenyl rings range from 1.347 (9) to 1.413 (7) Å.

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#### Comment

Although the structures of several transition-metal complexes containing the 1-[(*R*)-1',2-bis(diphenylphosphino)ferrocenyl]-(*S*)-*N,N*-dimethylethylamine ligand have been determined (Hayashi, Kumada, Higuchi & Hirotsu, 1987; Hayashi *et al.*, 1989), the crystal structure of the ligand has not been determined. This may provide useful comparative data for understanding the activity of the asymmetric catalyst. The compound was prepared from optically resolved 1-ferrocenyl-*N,N*-dimethylethylamine (Marquarding, Klusacek, Gokel, Hoffmann & Ugi, 1970) according to the method of Hayashi *et al.*, (1980). Dark-orange crystals suitable for X-ray work were grown from a dichloromethane/ethanol mixture by slow solvent-diffusion techniques. The structural study indicates that the cyclopentadienyl rings in the ferrocene moiety are planar with a dihedral angle of 2.8°. The cyclopentadienyl rings are slightly staggered with torsion angles about the centroids of the two rings ranging from 17.2–19.0°. The Fe—C distances of 2.024 (5)–2.050 (4) Å for the C(1)–C(5) ring and 2.027 (5)–2.058 (4) Å for C(6)–C(10) ring are similar to those found for ferrocene (Seiler & Dunitz, 1982) and its derivatives (Krukoni, Silverman & Yannoni, 1972; Einstein & Willis, 1980). The average C—C distance in the ferrocene moiety is 1.417 (7) Å. In the diphenylphosphino groups, the C—P—C angles are smaller than the ideal tetrahedral angle of 109.5°. The resultant crowding of the phenyl and cyclopentadienyl rings causes the P—C—C angles to be asymmetric. The C—C distances within the phenyl rings range from 1.347 (9) to 1.413 (7) Å. The C(17)–C(22) and C(23)–C(28) phenyl rings are nearly coplanar whereas C(11)–C(16) and C(29)–C(34) rings are stacked at an angle of 141.9°. The N atom adopts a pyramidal configuration.

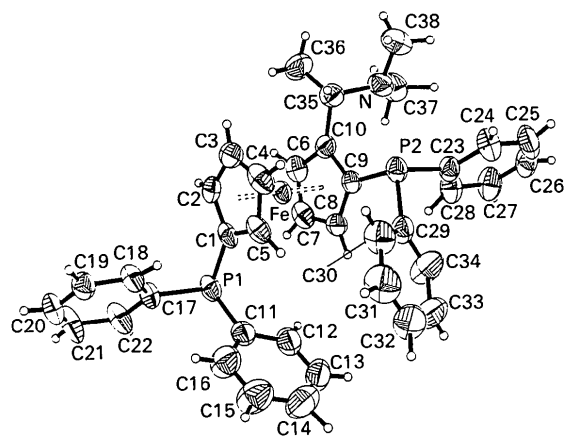


Fig. 1. A view of the molecule showing the labelling of the non-H atoms. Thermal ellipsoids are shown at 50% probability levels.