

References

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Tribenzylammonium Dibenzylammonium Tetrachlorocuprate

GUANG-FU ZENG,* MEI QIN, YONG-HUA LIN AND SHI-QUAN XI

Changchun Institute of Applied Chemistry,
Academia Sinica, 130022 Changchun,
People's Republic of China

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Abstract

In the CuCl₄²⁻ anion of the title compound, (C₂₁H₂₂N)(C₁₄H₁₆N)[CuCl₄], the copper coordination is intermediate between tetrahedral and square planar.

Comment

Two types of metal coordination occur in compounds of the general formula (C_nH_{2n+1}NH₃)₂MCl₄: octahedral (*M* = Cu, Cd, Mn, Fe, Hg) or tetrahedral (*M* = Zn, Co) (Ciajolo, Corradini & Pavone, 1977). However, square-planar copper coordination is found in anilinium tetrachlorocuprate (Larsen, 1974). The distorted-tetrahedral copper coordination in the title compound, (I), contrasts with the structures of (C₃H₇NH₃)₂CuCl₄ (Barendregt & Schenk, 1970) and (C₂H₅NH₃)₂CuCl₄ (Steadman & Willet, 1970), which contain octahedrally coordinated metal atoms, and also differs from the structure of anilinium tetrachlorocuprate (Larsen, 1970). In addition, the average Cu—Cl distance in (I) is shorter than the corresponding values in the octahedral complexes. In

(I) the shortest N...Cl distances involving the (C₆H₅CH₂)₂NH₂⁺ and (C₆H₅CH₂)₃NH⁺ cations are 3.234 and 3.251 Å, respectively.

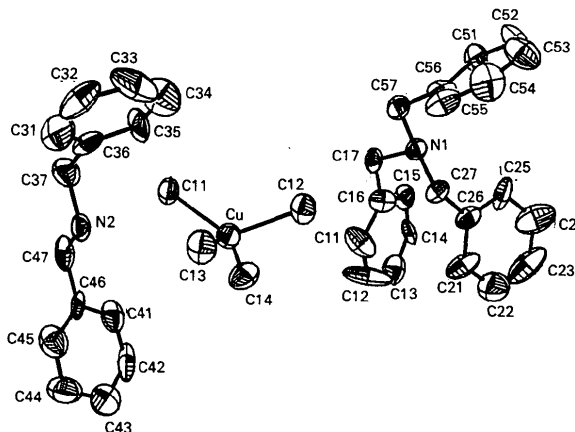


Fig. 1. Atomic numbering scheme of the non-H atoms of the title compound with 50% probability displacement ellipsoids.

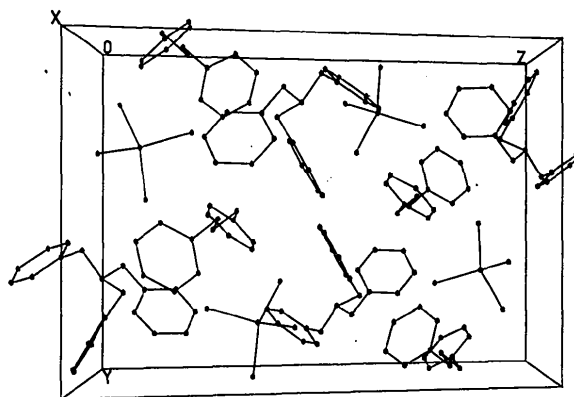


Fig. 2. Molecular packing in the unit cell of the title compound.

Experimental

Crystal data

(C₂₁H₂₂N)(C₁₄H₁₆N)[CuCl₄]

M_r = 692.05

Monoclinic

*P*2₁/*n*

a = 11.823 (5) Å

b = 14.433 (5) Å

c = 20.857 (5) Å

β = 102.65 (3)°

V = 3472.7 Å³

Z = 4

D_x = 1.32 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 2.3–12.4°

μ = 0.956 mm⁻¹

T = 298 K

Lamina

0.62 × 0.46 × 0.12 mm

Brownish yellow

Data collection

Nicolet R3m/E diffractometer

*R*_{int} = 0.07

θ_{max} = 48°

ω scans $h = 0 \rightarrow 14$
 Absorption correction: $k = 0 \rightarrow 17$
 empirical $l = -24 \rightarrow 24$
 $T_{\min} = 0.60$, $T_{\max} = 0.81$ 1 standard reflection
 5536 measured reflections frequency: 70 min
 4420 independent reflections intensity variation: $\pm 2\%$
 2132 observed reflections
 $[I > 3\sigma(I)]$

Refinement

Refinement on F $\Delta\rho_{\max} = 0.41 \text{ e } \text{\AA}^{-3}$
 $R = 0.054$ $\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$
 $wR = 0.053$ Atomic scattering factors
 2132 reflections from *International Tables*
 379 parameters for *X-ray Crystallography*
 $w = 1/\sigma^2(F)$ (1974, Vol. IV)
 $(\Delta/\sigma)_{\max} = 0.018$

The main computer program used was *SHELXTL* (Sheldrick, 1983). The H atoms were included in idealized positions with U fixed at $0.08 \text{ \AA}^2$.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Cu	0.7408 (1)	0.3168 (1)	0.1296 (1)	0.050 (1)
Cl(1)	0.6314 (2)	0.1932 (2)	0.0828 (1)	0.055 (1)
Cl(2)	0.6770 (2)	0.4654 (2)	0.1375 (1)	0.058 (1)
Cl(3)	0.7643 (2)	0.2746 (2)	0.2347 (1)	0.067 (1)
Cl(4)	0.8443 (2)	0.3388 (2)	0.0556 (1)	0.079 (1)
C(11)	0.7606 (7)	0.5864 (6)	-0.0098 (4)	0.062 (4)
C(12)	0.8539 (8)	0.6001 (7)	-0.0394 (4)	0.075 (5)
C(13)	0.8424 (7)	0.6560 (7)	-0.0944 (4)	0.075 (4)
C(14)	0.7403 (8)	0.6965 (7)	-0.1194 (4)	0.074 (5)
C(15)	0.6432 (8)	0.6829 (7)	-0.0903 (4)	0.061 (4)
C(16)	0.6529 (7)	0.6287 (6)	-0.0335 (4)	0.046 (4)
C(17)	0.5530 (7)	0.6113 (5)	0.0002 (4)	0.042 (3)
C(21)	0.8169 (8)	0.7962 (7)	0.0642 (4)	0.071 (5)
C(22)	0.8802 (11)	0.8643 (10)	0.0385 (6)	0.099 (6)
C(23)	0.8281 (13)	0.9349 (10)	0.0066 (6)	0.099 (7)
C(24)	0.7073 (11)	0.9482 (7)	-0.0019 (5)	0.091 (6)
C(25)	0.6416 (8)	0.8791 (6)	0.0250 (4)	0.067 (4)
C(26)	0.6966 (6)	0.8016 (7)	0.0578 (4)	0.053 (4)
C(27)	0.6349 (6)	0.7313 (6)	0.0900 (4)	0.046 (3)
N(1)	0.5279 (5)	0.6961 (4)	0.0390 (3)	0.038 (2)
C(31)	-0.0117 (8)	0.5337 (7)	0.1857 (4)	0.081 (5)
C(32)	0.0473 (8)	0.5838 (8)	0.1444 (4)	0.089 (5)
C(33)	0.0819 (8)	0.6697 (7)	0.1593 (5)	0.091 (5)
C(34)	0.0655 (8)	0.7120 (7)	0.2142 (4)	0.085 (5)
C(35)	0.0064 (8)	0.6636 (7)	0.2571 (4)	0.074 (5)
C(36)	-0.0325 (7)	0.5736 (7)	0.2448 (4)	0.059 (4)
C(37)	-0.0906 (7)	0.5195 (7)	0.2924 (4)	0.064 (4)
C(41)	-0.4394 (8)	0.5863 (6)	0.3531 (4)	0.074 (4)
C(42)	-0.5590 (8)	0.6094 (7)	0.3463 (5)	0.087 (5)
C(43)	-0.6361 (9)	0.5716 (7)	0.2972 (5)	0.099 (6)
C(44)	-0.6037 (8)	0.5076 (7)	0.2554 (5)	0.090 (5)
C(45)	-0.4849 (8)	0.4830 (7)	0.2642 (4)	0.076 (5)
C(46)	-0.4035 (8)	0.5238 (6)	0.3132 (4)	0.054 (4)
C(47)	-0.2754 (7)	0.4954 (6)	0.3242 (4)	0.059 (4)
C(51)	0.3196 (7)	0.8034 (6)	0.0913 (4)	0.063 (4)
C(52)	0.2872 (8)	0.8705 (7)	0.1319 (4)	0.080 (5)
C(53)	0.3306 (8)	0.8669 (8)	0.1984 (5)	0.080 (5)
C(54)	0.4044 (9)	0.8001 (7)	0.2248 (4)	0.073 (5)
C(55)	0.4379 (7)	0.7312 (6)	0.1839 (4)	0.060 (4)
C(56)	0.3993 (6)	0.7323 (6)	0.1164 (4)	0.046 (4)
C(57)	0.4357 (7)	0.6587 (5)	0.0736 (4)	0.049 (4)
N(2)	-0.2194 (5)	0.5506 (4)	0.2782 (3)	0.045 (3)

Table 2. Selected geometric parameters ($\text{\AA}$, $^\circ$)

Cu—Cl(1)	2.291 (2)	Cu—Cl(2)	2.292 (2)
Cu—Cl(3)	2.233 (2)	Cu—Cl(4)	2.192 (3)
C(11)—C(12)	1.391 (14)	C(11)—C(16)	1.402 (12)
C(12)—C(13)	1.384 (13)	C(13)—C(14)	1.339 (12)
C(14)—C(15)	1.425 (14)	C(15)—C(16)	1.404 (12)
C(16)—C(17)	1.521 (12)	C(17)—N(1)	1.532 (10)
C(21)—C(22)	1.410 (17)	C(21)—C(26)	1.402 (12)
C(22)—C(23)	1.296 (19)	C(23)—C(24)	1.413 (20)
C(24)—C(25)	1.450 (16)	C(25)—C(26)	1.396 (12)
C(26)—C(27)	1.493 (12)	C(27)—N(1)	1.550 (8)
N(1)—C(57)	1.531 (11)	C(31)—C(32)	1.419 (15)
C(31)—C(36)	1.428 (13)	C(32)—C(33)	1.322 (15)
C(33)—C(34)	1.349 (14)	C(34)—C(35)	1.432 (14)
C(35)—C(36)	1.383 (14)	C(36)—C(37)	1.539 (13)
C(37)—N(2)	1.552 (10)	C(41)—C(42)	1.429 (14)
C(41)—C(46)	1.358 (13)	C(42)—C(43)	1.329 (13)
C(43)—C(44)	1.381 (15)	C(44)—C(45)	1.422 (14)
C(45)—C(46)	1.374 (11)	C(46)—C(47)	1.537 (12)
C(47)—N(2)	1.507 (11)	C(51)—C(52)	1.395 (13)
C(51)—C(56)	1.413 (11)	C(52)—C(53)	1.370 (12)
C(53)—C(54)	1.335 (14)	C(54)—C(55)	1.423 (14)
C(55)—C(56)	1.381 (11)	C(56)—C(57)	1.509 (12)
Cl(1)—Cu—Cl(2)	126.5 (1)	Cl(1)—Cu—Cl(3)	98.2 (1)
Cl(2)—Cu—Cl(3)	99.0 (1)	Cl(1)—Cu—Cl(4)	99.4 (1)
Cl(2)—Cu—Cl(4)	99.1 (1)	Cl(3)—Cu—Cl(4)	139.6 (1)
C(12)—C(11)—C(16)	122.0 (8)	C(11)—C(12)—C(13)	120.5 (8)
C(12)—C(13)—C(14)	119.6 (9)	C(13)—C(14)—C(15)	121.1 (8)
C(14)—C(15)—C(16)	120.8 (8)	C(11)—C(16)—C(15)	116.1 (8)
C(11)—C(16)—C(17)	120.2 (7)	C(15)—C(16)—C(17)	123.7 (7)
C(16)—C(17)—N(1)	111.8 (6)	C(22)—C(21)—C(26)	122.5 (9)
C(21)—C(22)—C(23)	120.7 (12)	C(22)—C(23)—C(24)	121.7 (13)
C(23)—C(24)—C(25)	118.0 (10)	C(24)—C(25)—C(26)	120.7 (9)
C(21)—C(26)—C(25)	116.4 (9)	C(21)—C(26)—C(27)	120.3 (8)
C(25)—C(26)—C(27)	123.0 (7)	C(26)—C(27)—N(1)	108.6 (6)
C(17)—N(1)—C(27)	113.6 (5)	C(17)—N(1)—C(57)	102.0 (6)
C(27)—N(1)—C(57)	110.5 (5)	C(32)—C(31)—C(36)	121.3 (9)
C(31)—C(32)—C(33)	120.1 (9)	C(32)—C(33)—C(34)	122.0 (10)
C(33)—C(34)—C(35)	119.3 (9)	C(34)—C(35)—C(36)	122.0 (9)
C(31)—C(36)—C(35)	115.2 (9)	C(31)—C(36)—C(37)	122.5 (9)
C(35)—C(36)—C(37)	122.2 (8)	C(36)—C(37)—N(2)	106.7 (6)
C(42)—C(41)—C(46)	121.9 (8)	C(41)—C(42)—C(43)	118.6 (10)
C(42)—C(43)—C(44)	121.5 (10)	C(43)—C(44)—C(45)	119.3 (8)
C(44)—C(45)—C(46)	120.0 (9)	C(41)—C(46)—C(45)	118.7 (9)
C(41)—C(46)—C(47)	121.0 (7)	C(45)—C(46)—C(47)	120.2 (8)
C(46)—C(47)—N(2)	108.7 (6)	C(52)—C(51)—C(56)	121.8 (7)
C(51)—C(52)—C(53)	119.8 (8)	C(52)—C(53)—C(54)	120.7 (10)
C(53)—C(54)—C(55)	120.0 (8)	C(54)—C(55)—C(56)	122.0 (8)
C(51)—C(56)—C(55)	115.5 (8)	C(51)—C(56)—C(57)	123.0 (7)
C(55)—C(56)—C(57)	121.4 (7)	N(1)—C(57)—C(56)	110.8 (6)
C(37)—N(2)—C(47)	105.9 (6)		

The title compound (I) was prepared by the reaction of stoichiometric amounts of $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{NH}\cdot\text{HCl}$, $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{N}\cdot\text{HCl}$ and $\text{CuCl}_2\cdot\text{H}_2\text{O}$ in methanol solution. Crystals were obtained by slow evaporation at room temperature.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71509 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1039]

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***trans*-Dichloro[(2*RS*,5*RS*,9*SR*,12*RS*)-
 2,5,9,12-tetraazatridecane]cobalt(III)
 Perchlorate, [CoCl₂(C₉H₂₄N₄)]ClO₄**

TIAN-HUEY LU*

*Department of Physics, National Tsing Hua University,
 Hsinchu, Taiwan 30043*

CHUNG-YU LAI AND CHUNG-SUN CHUNG

*Department of Chemistry, National Tsing Hua
 University, Hsinchu, Taiwan 30043*

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Abstract

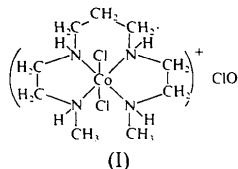
The coordination geometry about Co^{III} is slightly distorted octahedral. The four donor N atoms of the tetraamine form the equatorial plane of the coordination octahedron and two Cl ligands occupy the apices. The alternate five-, six- and five-membered chelate rings have stable skew, chair and skew conformations, respectively. The perchlorate group binds the tetraamine groups through weak hydrogen bonds.

Comment

Previous studies indicate that the chelate ring sizes of the cobalt(III) complexes of tetraamines have significant effects on their structures; *cis* isomers (*cis*- α and *cis*- β) are more stable than *trans* isomers for the dichloro(triethylenetetraamine)cobalt(III) ion (Basolo, 1948) and the dinitro(1,4,7,10-tetraazacyclododecane)cobalt(III) ion (Iitaka, Shina & Kimura, 1974). On the other hand, the dichloro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) ion (Bosnich, Poon & Tobe, 1965) and the dichloro(1,10-diamino-4,7-diazadecane)cobalt(III) ion (Payne, 1973) exhibit *trans* configurations.

The ligand 2,5,9,12-tetraazatridecane (α,ω -N-Me₂-2,3,2-tet) was prepared by the procedure described by Clay, Corr, Micheloni & Paoletti (1985). An aqueous solution of α,ω -N-Me₂-2,3,2-tet.4HCl (1.0 g) was passed through an anion-exchange

column (Amberlite IR400, OH⁻ form) directly into an aqueous solution of Na₃[Co(CO₃)₃].3H₂O (1.08 g) (Bauer & Drinkard, 1960). The resulting solution was heated to 373 K with stirring. A small amount of HCl was added, cooled to room temperature and a few drops of HClO₄ added. The precipitate was filtered and washed with ethanol. Green single crystals of the title complex (I) were obtained by slow evaporation from aqueous solution.



The crystal is comprised of discrete ions, linked by weak hydrogen bonds between the perchlorate ion and the amine groups of the complex ion. The coordination geometry about Co^{III} is slightly distorted octahedral. The four donor N atoms of the tetraamine in the equatorial plane are coplanar within ± 0.06 (2) Å. The four Co—N distances are in a relatively large range of 1.93 (1)–2.03 (1) Å. The two *trans* Cl atoms occupy the apices, with a mean Co—Cl distance of 2.250 (2) Å, which agrees well with the mean Co—Cl distance of 2.255 (8) Å found in the *trans*-dichloro(1,10-diamino-4,7-diazadecane)-cobalt(III) cation (Payne, 1973).

The complex has 2*RS*, 5*RS*, 9*SR*, 12*RS* configurations at the chiral N centres. The alternate five-, six- and five-membered chelate rings have the stable skew, chair and skew conformations, respectively. Consequently, the four donor N atoms in this complex nearly match the symmetry properties of the Co^{III} orbitals; a very stable *trans* complex is found.

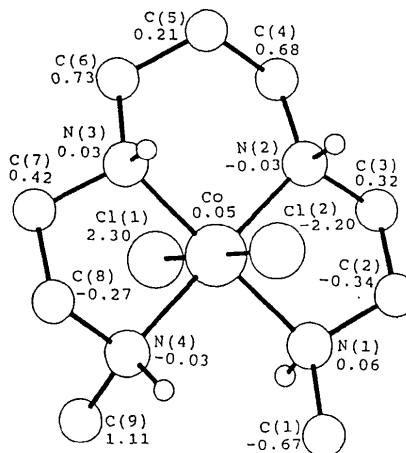


Fig. 1. A perspective view of the complex cation. The displacements from the best plane formed by atoms N(1), N(2), N(3) and N(4) are indicated.