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Tribenzylammonium Dibenzylammonium Tetrachlorocuprate

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Abstract

In the CuCl$_4^{2-}$ anion of the title compound, (C$_{21}$H$_{22}$N)(C$_{14}$H$_{16}$N)[CuCl$_4$], the copper coordination is intermediate between tetrahedral and square planar.

Comment

Two types of metal coordination occur in compounds of the general formula (C$_n$H$_{2n+1}$NH$_3$)$_2$$MCl_4$: octahedral ($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 (C$_3$H$_7$NH$_3$)$_2$CuCl$_4$ (Barendregt & Schenk, 1970) and (C$_2$H$_5$NH$_3$)$_2$CuCl$_4$ (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 (C$_6$H$_5$CH$_2$)$_2$NH$_2^+$ and (C$_6$H$_5$CH$_2$)$_3$NH$^+$ cations are 3.234 and 3.251 Å, respectively.

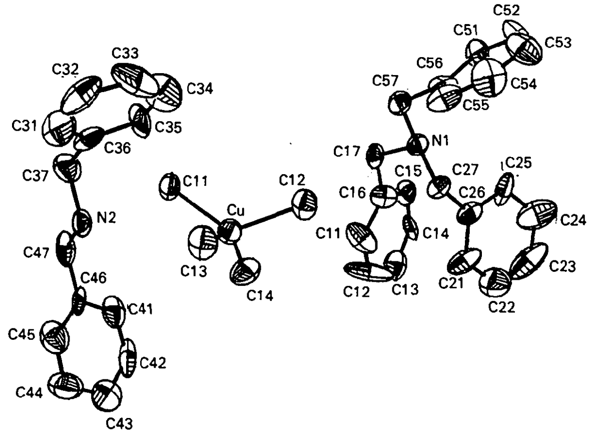

Fig. 1. Atomic numbering scheme of the non-H atoms of the title compound with 50% probability displacement ellipsoids.

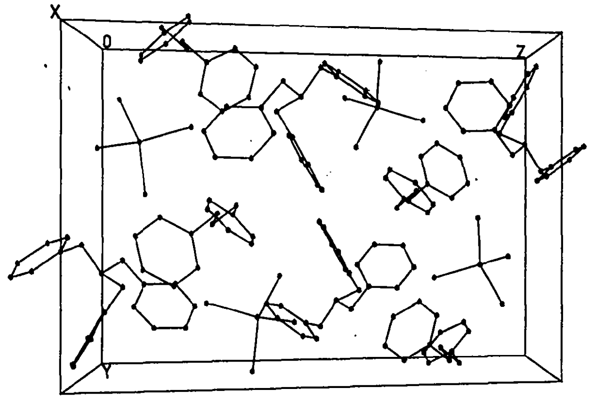

Fig. 2. Molecular packing in the unit cell of the title compound.

Experimental

Crystal data

(C$_{21}$H$_{22}$N)(C$_{14}$H$_{16}$N)[CuCl$_4$]
M_r = 692.05
Monoclinic
$P2_1/n$
a = 11.823 (5) Å
b = 14.433 (5) Å
c = 20.857 (5) Å
β = 102.65 (3)°
V = 3472.7 Å^3
Z = 4
D_x = 1.32 Mg m^{-3}

Mo $K\alpha$ 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

$R_{\rm int}$ = 0.07
$\theta_{\rm max}$ = 48°

ω scans
Absorption correction: empirical
T_{min} = 0.60, T_{max} = 0.81
5536 measured reflections
4420 independent reflections
2132 observed reflections [$I > 3\sigma(I)$]

$h = 0 \rightarrow 14$
$k = 0 \rightarrow 17$
$l = -24 \rightarrow 24$
1 standard reflection
frequency: 70 min
intensity variation: ±2%

Refinement

Refinement on F
R = 0.054
wR = 0.053
2132 reflections
379 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$ = 0.018

$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

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

	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* (Å, °)

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—C1(2)	126.5 (1)	Cl(1)—Cu—C1(3)	98.2 (1)
Cl(2)—Cu—C1(3)	99.0 (1)	Cl(1)—Cu—Cl(4)	99.4 (1)
Cl(2)—Cu—C1(4)	99.1 (1)	Cl(3)—Cu—C1(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 $(C_6H_5CH_2)_2NH.HCl$, $(C_6H_5CH_2)_3N.HCl$ and $CuCl_2.H_2O$ 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, $[CoCl_2(C_9H_{24}N_4)]ClO_4$

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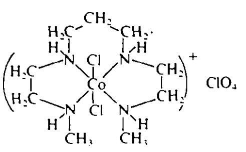
Abstract

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*-Me_2-2,3,2-tet) was prepared by the procedure described by Clay, Corr, Micheloni & Paoletti (1985). An aqueous solution of α,ω-*N*-Me_2-2,3,2-tet.4HCl (1.0 g) was passed through an anion-exchange column (Amberlite IR400, OH^- form) directly into an aqueous solution of $Na_3[Co(CO_3)_3].3H_2O$ (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 $HClO_4$ 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.



(I)

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.

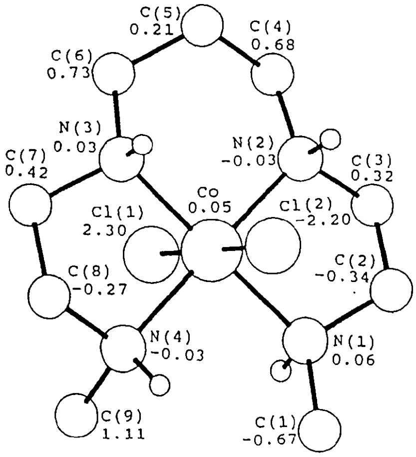


Fig. 1. A perspective view of the complex cation. The displacements from the best plane formed by atoms N(1), N(2), N(3) and N(4) are indicated.

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