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μ-Cyano-bis(2,2′:6′,2″-terpyridine-*N*,*N*′,*N*″)dicopper(II) Perchlorate Acetonitrile, $[Cu_2(CN)(C_{15}H_{11}N_3)_2](ClO_4)_3.CH_3CN$

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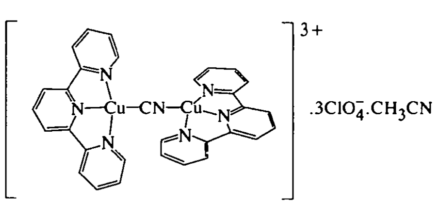
Abstract

The $[Cu_2(terpy)_2(CN)]^{3+}$ cation (terpy is 2,2′:6′,2″-terpyridine) is non-centrosymmetric and contains two Cu^{II} centres bridged by a disordered cyano group. The overall geometry around both metallic centres can be described as a distorted octahedron. The equatorial coordination plane is occupied by the N atoms of the tridentate terpy ligand and by an atom (C* or N*) of the cyanide bridge. The axial positions for one Cu atom are occupied by O atoms of two perchlorate anions while, for the other Cu atom, a perchlorate ion and an acetonitrile molecule lie in *trans* positions.

Comment

As part of our efforts to synthesize heterobimetallic Fe^{III}–Cu^{II} compounds in which the two metallic centres are bridged by various bidentate ligands (Bulach, Mandon & Weiss, 1991), we have isolated crystals of the dinuclear $[Cu_2(terpy)_2(CN)](ClO_4)_3.CH_3CN$ complex, (I).



(I)

The structure consists of asymmetric dimeric molecules in which the coordination polyhedron around each copper ion is a distorted elongated octahedron (the coordination mode is approximately '4+2' for the Cu1 atom and '4+1+1' for Cu2). A cyanide group acts as a bridging ligand between the two divalent Cu atoms. As a class, Cu^{II}–cyanide complexes are not very common, owing to the tendency of Cu^{II} to oxidize cyanide to cyanogen (Hathaway, 1987). Moreover, the Cu^{II}—CN—Cu^{II} bridge has been previously structurally authenticated for $[Cu_2([14]\text{-}4,11\text{-dieneN4})_2(CN)]^{3+}$ (Jungst & Stucky, 1974) and $[Cu_2(Me_6tren)_2(CN)]^{3+}$ (Scott, Lee & Holm, 1994) in the centrosymmetric trigonal bipyramidal geometry, and for the polymeric complex $[Cu(terpy)(CN)](NO_3).H_2O$ (Anderson, Packard & Wicholas, 1976) in the distorted square-pyramidal geometry.

The equatorial plane around each Cu atom is similar, being composed of the three N atoms of the terpyridine ligand and the cyanide group C* or N* (disordering of the bridging CN group prevented identification of the C and N atoms) (Fig. 1). The environment around the two Cu atoms differs in the nature of the ligands in the apical positions, *i.e.* two O atoms of two perchlorate anions for Cu1 [Cu1—O5 2.564 (3) Å and Cu1—O10 2.543 (4) Å],

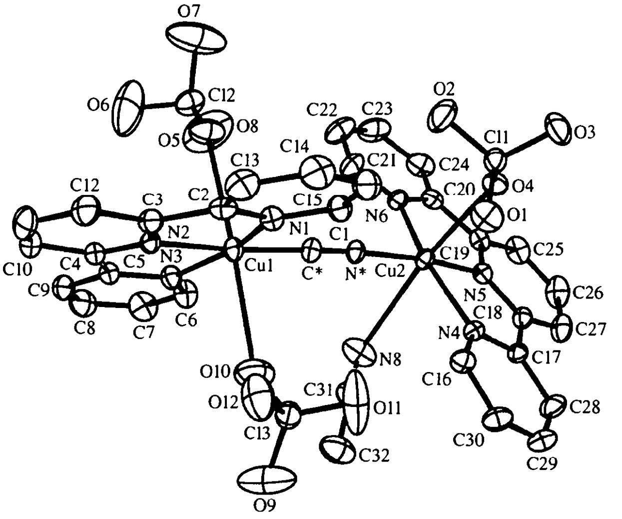


Fig. 1. *ORTEP* (Johnson, 1965) plot of the $[Cu_2(terpy)_2(CN)](ClO_4)_3.CH_3CN$ molecule showing the atom labels. Displacement ellipsoids are drawn at the 50% probability level.

but a perchlorate and an acetonitrile solvate molecule lying in *trans* positions for Cu2 [Cu2—O4 2.440 (3) Å and Cu2—N8 2.767 (4) Å]. These long axial distances are as expected for apical bond lengths in six-coordinate Cu^{II} complexes as a result of Jahn–Teller distortion.

In the equatorial plane, the Cu—C* or N* bridging distances are 1.933 (3) and 1.920 (3) Å, for Cu1 and Cu2, respectively. The metal–cyanide linkages are almost linear [178.7 (3)° and 176.2 (3)°], with a C*—N* bond length equal to 1.145 (4) Å, leading to a Cu1···Cu2 distance of 4.994 (2) Å. The Cu—N(terpy) bond distances, ranging from 1.925 (3) to 2.021 (3) Å, are similar to those found in related complexes. The N atoms of the outer pyridine rings form bonds of approximately equal length (mean value 2.02 Å) to the Cu^{II} atom, while the N atoms (N2 and N5) of the central pyridine rings are bonded to the Cu atoms at significantly shorter distances [1.935 (3) and 1.925 (3) Å, respectively]. This pattern of bond lengths is typical of the constrained system that develops when terpy coordinates to the first transition series ions (Constable, 1986). Furthermore, the geometry of the terpy chelates is as expected, with the individual pyridine rings highly planar, while the ligand as a whole is not. The maximum deviations from the least-squares planes (non-H atoms) are 0.057 (6) Å for the C13 atom and 0.153 (7) Å for C29. The angles are distorted from ideal octahedral angles, which is due in part to the constrained geometry of the chelating terpy ligand. In the equatorial plane, the N—Cu—N(*cis*) angles are slightly unequal and less than 90°, while the angles N—Cu—N* or C* are close to 100°. The dihedral angle between the two terpy chelates is 63.53 (5)°. The displacement of the Cu atoms from the mean plane of the terpy ligands is significantly greater for the Cu2 atom [0.132 (1) Å towards O4] than for Cu1 [0.035 (1) Å towards O5]. This is not surprising given the nature of the apical ligands, *i.e.* two identical anionic perchlorate ligands for the Cu1 atom, while the Cu2 atom is coordinated by a perchlorate anion and a neutral molecule of acetonitrile.

Experimental

Single crystals of $[Cu_2(terpy)_2(CN)](ClO_4)_3.CH_3CN$ were obtained by slow diffusion of diethyl ether into a solution of $[Fe(TMP)(CN)_2]^-$ (Scheidt, Haller & Hatano, 1980) (TMP is *meso*-tetramesitylporphyrinato) with an excess (10 equivalents) of $[Cu(terpy)(H_2O)](ClO_4)_2$ (Harris & Lockyer, 1970) in acetonitrile. IR (Nujol): ν(CN) 2258 and 2209 cm^{-1} (CN and/or CH_3CN).

Crystal data

$[Cu_2(CN)(C_{15}H_{11}N_3)_2]$-$(ClO_4)_3.CH_3CN$
$M_r = 959.05$
Triclinic
$P\overline{1}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 16.8$–$18.7°$

$a = 9.405 (2)$ Å
$b = 10.195 (3)$ Å
$c = 20.783 (6)$ Å
$\alpha = 89.05 (2)°$
$\beta = 78.86 (2)°$
$\gamma = 79.87 (2)°$
$V = 1924 (1)$ Å^3
$Z = 2$
$D_x = 1.66$ Mg m^{-3}
D_m not measured

$\mu = 1.387$ mm^{-1}
$T = 294$ K
Prism
0.35 × 0.30 × 0.30 mm
Blue

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.585$, $T_{max} = 0.660$
12 294 measured reflections
11 641 independent reflections

5436 reflections with $I > 3\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 30.41°$
$h = 0 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -29 \rightarrow 29$
3 standard reflections every 60 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.049$
$wR = 0.070$
$S = 1.361$
5436 reflections
523 parameters
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0064F_o^4]$

$(\Delta/\sigma)_{max} = 0.016$
$\Delta\rho_{max} = 0.700$ e Å^{-3}
$\Delta\rho_{min} = -0.522$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—N1	2.018 (3)	Cu2—N5	1.925 (3)
Cu1—N2	1.935 (3)	Cu2—N6	2.021 (3)
Cu1—N3	2.021 (3)	Cu2—N*	1.920 (3)
Cu1—C*	1.933 (3)	Cu2—O4	2.440 (3)
Cu1—O5	2.564 (3)	Cu2—N8	2.767 (4)
Cu1—O10	2.543 (4)	N*—C*	1.145 (4)
Cu2—N4	2.021 (3)		
N1—Cu1—N2	79.9 (1)	N4—Cu2—N*	100.9 (1)
N1—Cu1—C*	99.4 (1)	N4—Cu2—O4	90.4 (1)
N1—Cu1—O5	89.3 (1)	N4—Cu2—N8	81.6 (1)
N1—Cu1—O10	95.7 (1)	N5—Cu2—N6	80.3 (1)
N2—Cu1—N3	80.8 (1)	Cu2—N*—C*	176.2 (3)
N4—Cu2—N5	79.8 (1)	Cu1—C*—N*	178.7 (3)

The cyanide N and C atoms were disordered. For each atomic site, a form factor defined as (form factor for C + form factor for N)/2 was used. These atoms are labelled N* and C*. H atoms were included but not refined.

Data collection: *CAD-4 Express* (Enraf–Nonius, 1994). Cell refinement: *CAD-4 Express*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR* (Burla *et al.*, 1989). Program(s) used to refine structure: *LSFM* in *MolEN*. Software used to prepare material for publication: *BTABLE PTABLE CIF IN* in *MolEN* and *ORTEP* (Johnson, 1965).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: NA1277). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Aqua(*p*-chlorophenyl)diphenyl(*N*-phthaloylglycinato)tin(IV)

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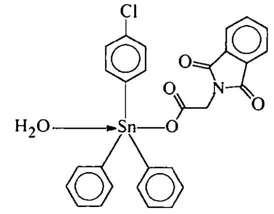
Abstract

The coordinated water molecule in the title compound, aqua(4-chlorophenyl)(1,3-dioxoisoindoline-2-acetato-*O*)diphenyltin(IV), $[Sn(C_6H_5)_2(C_6H_4Cl)(C_{10}H_6NO_4)(H_2O)]$, is hydrogen bonded to the carboxyl [O···O 2.695 (4) Å] and amido [O···O 2.900 (5) Å] O atoms of adjacent molecules, resulting in a layer structure. The Sn atom shows *trans*-C_3SnO_2 trigonal bipyramidal coordination.

Comment

The condensation of triphenyltin hydroxide and *N*-phthaloylglycine yields triphenyltin *N*-phthaloylglycinate, which crystallizes in a cyclohexameric configuration (Ng, Kumar Das, Pelizzi & Vitali, 1990), an arrangement not known among triorganotin carboxylates (Tiekink, 1991, 1994). This protected amino acid when condensed with (*p*-chlorophenyl)diphenyltin hydroxide yields the corresponding aqua carboxylate, (I); the coordinated water molecule links adjacent molecules (through hydrogen bonding *via* the carboxyl and amido O atoms) into sheets parallel to the *ac* plane.



(I)

The tin–water distance [2.413 (3) Å] is similar to those found in helical aqua(8-quinolyloxyacetato)triphenyltin [2.388 (7) and 2.391 (6) Å; Kumar Das, Chen, Ng & Mak, 1977], but exceeds that found in dinuclear aquabis[(3-oxapentamethylenethiocarbamoyl-*S*-acetato)triphenyltin] [2.298 (4) Å; Ng, 1995]. Bond dimensions involving the anionic *N*-phthaloylglycinato ligand are similar to those found in the parent carboxylic acid itself (Feeder & Jones, 1994).

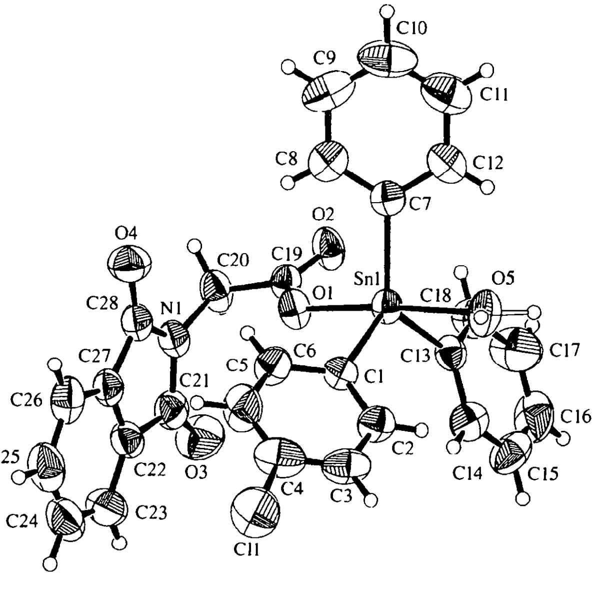


Fig. 1. *ZORTEP* (Zsolnai & Pritzkow, 1996) plot of aqua(*p*-chlorophenyl)diphenyl(*N*-phthaloylglycinato)tin(IV). Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

Experimental

The title complex was synthesized by condensing diphenyl(*p*-chlorophenyl)tin hydroxide and *N*-phthaloylglycine. Equimolar amounts of the reactants were dissolved in a small