3553 reflections
199 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 0.7230P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cp is the centroid of the C13–C17 ring.

Ti—O	1.794 (3)	Ti—C15	2.337 (6)
Ti—Cl2	2.243 (2)	Ti—*Cp*	2.000
Ti—Cl1	2.256 (2)	O—C1	1.378 (5)
Ti—C14	2.315 (5)	C6—C18	1.518 (6)
Ti—C13	2.331 (4)	C7—C18	1.518 (6)
Ti—C17	2.331 (5)	C13—C18	1.518 (6)
Ti—C16	2.336 (5)		
O—Ti—Cl2	104.84 (11)	Cl2—Ti—*Cp*	116.9
O—Ti—Cl1	103.45 (12)	O—Ti—*Cp*	110.7
Cl2—Ti—Cl1	103.28 (6)	C1—O—Ti	143.6 (3)
O—Ti—C14	89.8 (2)	O—C1—C2	118.0 (4)
Cl2—Ti—C14	103.30 (14)	O—C1—C6	121.0 (4)
Cl1—Ti—C14	145.97 (13)	C6—C18—C13	112.8 (4)
O—Ti—C13	81.56 (14)	C6—C18—C7	112.9 (4)
Cl1—Ti—*Cp*	116.2	C13—C18—C7	112.2 (3)

The title compound crystallized in the triclinic system. The space group $P\bar{1}$ was assumed and confirmed by analysis. H atoms were treated as riding atoms (C—H 0.93 and 0.98 Å).

Data collection: *XSCANS* (Siemens, 1994*a*). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994*b*). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1495). Services for accessing these data are described at the back of the journal.

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A copper(II) dimer: aqua(μ-2,2′-bipyrimidine-*N*,*N*′)(perchlorato)bis{[2,6-bis(2-pyridyl)pyridine-*N*,*N*′,*N*″]copper(II)} triperchlorate†

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Abstract

The title compound, $[Cu_2(ClO_4)(C_8H_6N_4)(C_{15}H_{11}N_3)_2(H_2O)](ClO_4)_3$, consists of a dinuclear copper(II) unit, the bridge being the bipyrimidine (bipym) ligand, which contains a twofold rotation axis. The Cu atoms are six-coordinated by five N atoms from the bipym and terpyridine (terpy) molecules, and by an O atom that belongs either to a water molecule or a perchlorate anion, presenting a distorted octahedral geometry. The equatorial Cu—N distances range between 1.943 (3) and 2.056 (3) Å. One apical position is occupied by a bipym N atom at a distance of 2.328 (3) Å, while the other apex of the octahedron is occupied alternatively by the O atom of the water molecule or an O atom of the perchlorate, with Cu—O distances of 2.445 (11) and 2.721 (11) Å, respectively. Most of the remaining perchlorate O atoms are disordered.

Comment

2,2′-Bipyrimidine (bipym) is known to be a versatile ligand able to coordinate transition metals in a bidentate or in a bis-bidentate bridging mode, leading to mono- or polynuclear complexes (De Munno & Julve, 1996). Several examples of dimers containing copper(II) and bipym are present in the literature (De Munno *et al.*, 1993, 1995; Castro *et al.*, 1994), together with their crystal structures and their magnetic properties. The exchange coupling between the magnetic centers can be modified by copper(II) distortions such as elongation or compression (De Munno *et al.*, 1995). The present work represents a new bipyrimidine dimer, (I), with two copper(II) ions coordinated by two 2,6-bis(2-pyridyl)-

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† Systematic name: aqua-1κO-μ-(2,2′-bipyrimidine)-1$\kappa^2 N^1,N^{1'}$:2$\kappa^2 N^3,N^{3'}$-perchlorato-2κO-bis(2,2′:6′,2″-terpyridine)-1$\kappa^3 N$,2$\kappa^3 N$-dicopper(II) triperchlorate.

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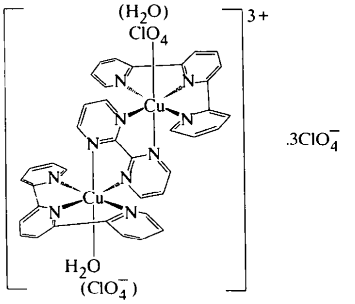
pyridine (terpy) ligands and a water molecule or a perchlorate anion.



(I)

The structure of (I) consists of discrete [Cu_2(bipym)(terpy)$_2$(H_2O)(ClO_4)]$^{3+}$ units and three ClO_4^- anions. The dimer is shown in Fig. 1 together with the labeling scheme. The two Cu^{II} atoms are coordinated by a bridging bipym ligand and related by a twofold symmetry axis. Each Cu atom is in an elongated octahedral environment, with three N atoms from the terpy ligand (N11, N22 and N23) and one N atom from the bipym ligand [N3^i; symmetry code: (i) $-x, y, \frac{1}{2}-z$] forming the basal plane. The Cu1—N distances of the terpy ligand are 1.943 (3), 2.016 (3) and 2.027 (3) Å. The fourth equatorial coordination distance (Cu1—N3^i) is 2.056 (3) Å. The Cu^{II} atom is pulled out of this basal plane toward the apical N1 atom by 0.077 (2) Å. Cu1—N1 and either Cu1—O15 or Cu1—O6 (the site occupations of O15:O6 were set at 1:1 due to the statistical disorder) represent apical distances of 2.328 (3) and 2.445 (11) or 2.721 (11) Å. Alternatively, a water or a perchlorate O atom is bonded to the Cu atom. Comparison of the positions of O15 and O6 reveals that they are 0.62 Å apart. The coordination distances of the terpy N atoms range from 1.943 (3) to 2.027 (3) Å, and are similar to those found in related complexes (Constable, 1986). Atoms N22 and N23 form bonds of approximately equal lengths (mean value 2.02 Å) to the Cu^{II} atom, while the N11 atom of the central pyridine is bonded to the Cu^{II} atom at a significantly shorter distance of 1.943 (3) Å. These values are typical of the constrained system that appears when terpy coordinates to the first transition series metals. The distorted octahedral geometry of the copper(II) coordination is due in part to the constrained geometry of the chelating bipym and terpy ligands. In the equatorial plane, the N—Cu—N angles are slightly unequal and less than 90°; the axial N1—Cu1—O15 angle is 161.2 (3)°, while the N1—Cu1—O6 angle is 168.6 (3)°. The two central pyrimidine rings are planar, with a maximum deviation of 0.021 (2) Å for C2. However, these rings are not coplanar, the angle between their planes being 9.4 (1)°. The Cu1 and Cu1^i atoms deviate by 0.377 (5) and 0.320 (5) Å, respectively, from these planes. Furthermore, the chelating geometry of the terpy ligands is as expected, with the individual pyridine rings being planar, while the ligand as a whole is not. The angles between the central plane (N11 to C61) and the neighboring planes are 3.3 (1) and 4.5 (1)°, which are comparable with literature results (Bulach *et al.*, 1997). The metal-metal separation through the bridging bipym ligand is 5.718 (1) Å and is close to distances found in analogous dimers (De Munno *et al.*, 1995).

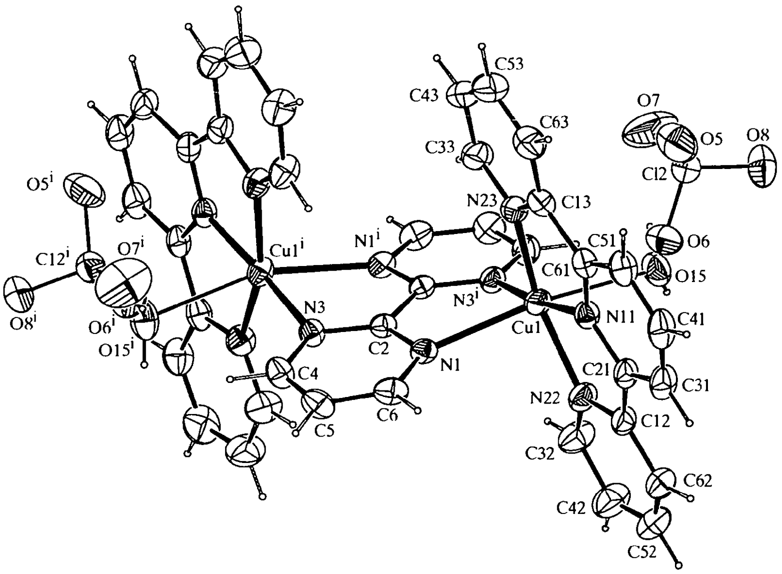


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title complex generated with *PLATON* (Spek, 1990). Displacement ellipsoids are drawn at the 30% probability level. H atoms are shown as small circles of arbitrary radii. Disordered perchlorate anions are not shown for clarity. [Symmetry code: (i) $-x, y, \frac{1}{2}-z$.]

Experimental

The title complex was prepared by adding an aqueous solution of [Cu(terpy)]Cl_2 (0.02 mmol; Henke *et al.*, 1983) to an aqueous solution of bipym (0.01 mmol). The compound was precipitated with an aqueous solution of $NaClO_4$ (4 ml) and recrystallized from a water/acetonitrile mixture (1:1) by slow evaporation of the solvent at room temperature.

Crystal data

$[Cu_2(ClO_4)(C_8H_6N_4)(C_{15}H_{11}N_3)_2(H_2O)](ClO_4)_3$
$M_r = 1167.60$
Monoclinic
$C2/c$
$a = 21.797$ (4) Å
$b = 17.904$ (4) Å
$c = 12.497$ (2) Å
$\beta = 112.59$ (3)°
$V = 4502.8$ (15) Å^3
$Z = 4$
$D_x = 1.722$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8.2$–14.3°
$\mu = 1.268$ mm^{-1}
$T = 296$ (2) K
Capped hexagonal bipyramid
0.34 × 0.32 × 0.24 mm
Blue–violet

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scan
Absorption correction: numerical (Coppens *et al.*, 1965)
$T_{\min} = 0.688$, $T_{\max} = 0.974$
11 188 measured reflections
5444 independent reflections
3208 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.051$
$\theta_{\max} = 28.01$°
$h = -28 \rightarrow 26$
$k = -23 \rightarrow 23$
$l = 0 \rightarrow 16$
3 standard reflections every 400 reflections frequency: 180 min intensity decay: 9.3% (decay correction applied)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.148$
$S = 1.029$
5444 reflections
369 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0760P)^2 + 3.4260P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.796$ e Å^{-3}
$\Delta\rho_{\min} = -0.682$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu1—N11	1.943 (3)	Cu1—N3$^{\rm i}$	2.056 (3)
Cu1—N22	2.016 (3)	Cu1—N1	2.328 (3)
Cu1—N23	2.027 (3)		
N11—Cu1—N22	80.26 (13)	N23—Cu1—N3$^{\rm i}$	96.52 (11)
N11—Cu1—N23	80.41 (12)	N11—Cu1—N1	109.83 (11)
N22—Cu1—N23	160.46 (12)	N22—Cu1—N1	91.82 (12)
N11—Cu1—N3$^{\rm i}$	174.09 (12)	N23—Cu1—N1	97.34 (11)
N22—Cu1—N3$^{\rm i}$	102.49 (12)	N3$^{\rm i}$—Cu1—N1	75.48 (11)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

Three O atoms of the Cl1 perchlorate show rotational disorder and were refined in partitioned groups with final site-occupation factors of 0.69 and 0.31. The site-occupation factors of the second perchlorate group and the adjacent water molecule were fixed at 0.50. The Cl3 and O9 atoms of the third perchlorate anion are on special positions (site symmetry 2); the site occupation factor of O11 was set to 0.50, having a similar anisotropic displacement parameter [0.207 (7) Å^2] to the O10 atom [0.214 (4) Å^2] which is fully occupied. H atoms of the bipym and terpy ligands were refined using a riding model, with $U_{\rm iso}$ values set to $1.2U_{\rm eq}$ of the parent C atoms (*SHELXL*97; Sheldrick, 1997). The relatively long O—H distances of the water molecule, which could be located from difference electron-density maps, were restrained to values of 0.865 (15) Å. There are a few weak C—H···O hydrogen-bonding interactions in the structure, the acceptor O atoms belonging to the perchlorate groups. We tried to resolve the disorder problem by refining the structure in the non-centrosymmetric space groups Cc and $C2$, however, the center of symmetry and also the twofold rotation axis remained in the structures. Furthermore, the residual electron densities in the Cc and $C2$ refinements were much higher than in the centrosymmetric ($C2/c$) refinement, and several anisotropic displacement parameters were non-positive definite. The short distance between O15 and O6, and the split positions of the perchlorates were also observed with these refinements, confirming that the centrosymmetric space group is the correct choice. The disorder can be resolved by assuming two structural models, the dimer having the connectivity ClO_4—Cu1···Cu1$^{\rm i}$—$H_2O^{\rm i}$ or H_2O—Cu1···Cu1$^{\rm i}$—$ClO_4{}^{\rm i}$, presenting two different polar directions (approximately along **c**) in distinguished non-centrosymmetric domains which results in the micro-twinned crystal of the title compound. However, twin refinements in space groups Cc and $C2$ were not successful.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97. Molecular graphics: *PLATON* and *PLUTON* (Spek, 1990). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1194). Services for accessing these data are described at the back of the journal.

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Salts of the bis(catecholato)borate anion with rhodium- and iridium–phosphine complex cations

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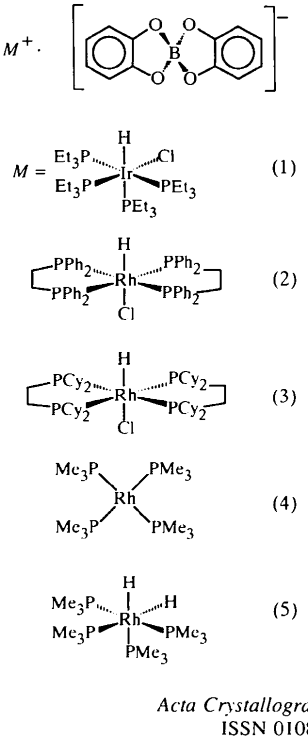
(*Received 24 November 1998; accepted 6 January 1999*)

Abstract

In a series of five salts with rhodium- or iridium–phosphine complex cations {*cis*-chlorohydridotetrakis(triethylphosphine)iridium(III) bis(pyrocatecholato-*O*,*O*′)borate, $[IrClH(C_6H_{15}P)_4](C_{12}H_8BO_4)$, (1); *trans*-chlorobis[ethylenebis(diphenylphosphine)]hydridorhodium(III) bis(pyrocatecholato-*O*,*O*′)borate dichloromethane solvate, $[RhClH(C_{26}H_{24}P_2)_2](C_{12}H_8BO_4)\cdot CH_2Cl_2$, (2); *trans*-chlorobis[ethylenebis(dicyclohexylphosphine)]hydridorhodium(III) bis(pyrocatecholato-*O*,*O*′)borate tetrakis(dichloromethane) solvate, $[RhClH(C_{26}H_{48}P_2)_2](C_{12}H_8BO_4)\cdot 4CH_2Cl_2$, (3); tetrakis(trimethylphosphine)rhodium(I) bis(pyrocatecholato-*O*,*O*′)borate, $[Rh(C_3H_9P)_4](C_{12}H_8BO_4)$, (4); and *cis*-dihydridotetrakis(trimethylphosphine)rhodium(III) bis(pyrocatecholato-*O*,*O*′)borate, $[RhH_2(C_3H_9P)_4](C_{12}H_8BO_4)$, (5)}, the bis(catecholato)borate anion has approximate D_{2d} ($\bar{4}2m$) symmetry, with the central spiro-B atom distorted from regular tetrahedral coordination geometry by reduction of the two intra-ring O—B—O bond angles. The two chelate rings show small deviations from planarity by folding about the O···O axis. The hydrido and chloro ligands in the cation of compound (1), which has four monodentate phosphine ligands, are *cis* to each other, but in compounds (2) and (3), each with two chelating diphosphine ligands, they are mutually *trans*. The cation in compound (4) has only four phosphine ligands, which are arranged in a tetragonally distorted square-planar arrangement to minimise steric crowding. Its reaction product with molecular dihydrogen, compound (5), has a *cis* arrangement of the two hydrido ligands in a distorted octahedral cation. The strong *trans* influence of the hydrido ligands is reflected in lengthened bonds to the opposite ligands in each case.

Comment

We have previously reported the structures of a series of salts of the bis(catecholato)borate [bis(benzene-1,2-diolato)borate] anion, $[B(cat)_2]^-$, with organic nitrogen and phosphorus cations (Clegg *et al.*, 1998). This anion seems to be a favoured product in many reactions of catecholborane, HB(cat), and related compounds under a wide variety of conditions, and we have encountered it numerous times in studies of catalytic hydroboration and diboration reactions of $B_2(cat)_2$ and $B_2(cat)_3$, as well as HB(cat). Few crystal structures have been reported of salts of the $[B(cat)_2]^-$ anion with metal-centred cations and of metal complexes of the anion acting as a ligand (He & Hartwig, 1996; Westcott *et al.*, 1991, 1993; Dai *et al.*, 1998). We describe here five structures with iridium- and rhodium–phosphine complex cations, which have been obtained as part of a research programme in synthesis and homogeneous catalysis.



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