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Di-μ-phosphinato-bis[(1,10-phenanthroline)copper(II)] Nitrate, $[Cu_2(H_2PO_2)_2(phen)_2](NO_3)_2$

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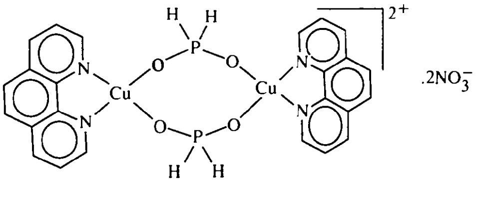
Abstract

The structure of blue $[Cu_2(H_2PO_2)_2(C_{12}H_8N_2)_2](NO_3)_2$ consists of dimeric $[Cu(H_2PO_2)(phen)]$ subunits (phen is 1,10-phenanthroline) joined by two phosphinato bridging ligands, with each metal center organized in a distorted planar arrangement. These joined subunits exist as a discrete cation, with the equivalent of two nitrates as counterions. The subunits have a four-coordinate distorted square-planar arrangement of N and O atoms from the 1,10-phenanthroline and phosphinato ligands, with the fifth and sixth positions of the Cu center occupied by neighboring O atoms of the nitrate counterions. The coordination stereochemistry around each Cu is best described as tetragonal.

Comment

The existence of compounds such as $[Cu(NCS)_2(phen)]$ (Parker & Breneman, 1993) demonstrates that the oxidation potential of copper(II) is reduced by the presence of 1,10-phenanthroline, so that ligands that would normally be oxidized by copper(II) can coexist as part of a stable complex. The phosphinato ligand, $H_2PO_2^-$, was chosen as a possible bridging ligand for copper(II) complexes. The complex, $[Cu_2(H_2PO_2)_2(phen)_2](NO_3)_2$, (I), exists as discrete pairs of $[Cu(H_2PO_2)(phen)]$ subunits linked by the phosphinato ligands to form a cation with a 2+ charge. Two nitrate ions serve as the counterions in this compound. Two related structures with phosphinato ligands bridging Mn^{II} atoms have been determined. The complexes $[Mn(H_2PO_2)_2(bipy)]_n$ (Weakley, 1978*a*), where bipy is bipyridine, and $[Mn(H_2PO_2)_2(phen)]_n$ (Weakley, 1978*b*) have structures that are bridged end-to-end through the O-atom ends of the two phosphinato ligands ($H_2PO_2^-$).



(I)

An *ORTEP* (Johnson, 1965) plot of the title complex is shown in Fig. 1, with the numbering system indicated. A stereoscopic plot of the unit cell is shown in Fig. 2. The cation, $[Cu_2(H_2PO_2)_2(phen)_2]^{2+}$, consists of discrete pairs of $[Cu(H_2PO_2)(phen)]$ subunits which are bridged by the phosphinato ligands in a symmetrical end-to-end fashion. The subunits have a four-coordinate distorted square-planar arrangement of N atoms from the 1,10-phenanthroline and O atoms from the phosphinato ligands about the central Cu atom. The cation interacts through the fifth and sixth positions on the Cu centers

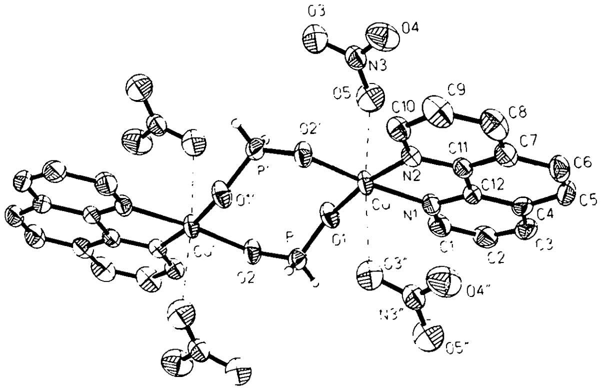


Fig. 1. Displacement ellipsoid (50% probability) plot of $[Cu_2(H_2PO_2)_2(phen)_2](NO_3)_2$ showing the atom-numbering scheme and coordination around the Cu atoms. [Symmetry codes: (′) $1-x, -y, 1-z$; (″) $1+x, 1+y, 1+z$.]

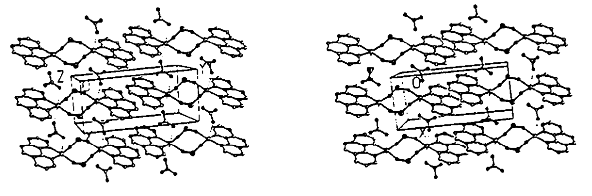


Fig. 2. Stereoscopic view of the unit-cell packing in the title compound.

with neighboring O atoms of the nitrate counterions. The coordination around each Cu center is a slightly distorted tetragonal arrangement. The structure may be described as a one-dimensional polymer of cations and anions.

The Cu—N_{phen} distances are 2.009 (2) and 1.990 (2) Å for Cu—N1 and Cu—N2, respectively, with an N1—Cu—N2 angle of 82.52 (8)°. These distances and the bite angle are similar to those found in $[Cu(NCS)_2(phen)]$ (Parker & Breneman, 1993). The Cu—O1 and Cu—O2′ distances are 1.931 (2) and 1.951 (2) Å, respectively, with an O1—Cu—O2′ angle of 93.14 (7)°. The square-planar arrangement about the Cu atom is slightly distorted, with the N1—Cu—O2′ and N2—Cu—O1 angles being 173.94 (7) and 171.99 (8)°, respectively. The fifth and sixth coordinating positions of the Cu center are occupied by $O_{nitrate}$ atoms, at distances of 2.761 (2) and 2.604 (2) Å for Cu—O3′ and Cu—O5, respectively, with an O3′—Cu—O5 angle of 172.72 (8)°. The nitrates complete the tetragonal arrangement around the central Cu atom, with slight distortion. Typical angles are: O3′—Cu—O1 90.78 (8), O3′—Cu—O2′ 97.63 (8), O3′—Cu—N1 85.44 (8) and O3′—Cu—N2 82.96 (8)°. The Cu—$O_{nitrate}$ distances are slightly longer than the Cu—O distances of 2.43 Å found in $Cu(DMG)_2$ (Frasson, Bardi & Bezzi, 1959), where DMG is dimethylglyoxime, and 2.397 (8) Å in anhydrous copper(II) formate (Barclay & Kennard, 1961). McFadden & McPhail (1975) found Cu—$O_{nitrate}$ distances ranging from 2.594 (6) to 2.863 (5) Å for $[Cu(phen)(NO_3)_2]$ and $[Cu(phen)(NO_3)(H_2O)]NO_3$.

The end-to-end bridging phosphinato ligands have P—O1 and P—O2′ distances of 1.503 (2) and 1.506 (2) Å, respectively, with an O1—P—O2 angle of 116.2 (1)°. These distances and angle are very close to those found in $[Mn(H_2PO_2)_2(bipy)]_n$ (Weakley, 1978*a*) and $[Mn(H_2PO_2)_2(phen)]_n$ (Weakley, 1978*b*).

Experimental

The title compound, $[Cu_2(H_2PO_2)_2(phen)_2](NO_3)_2$, was prepared by the slow addition of a 15 ml solution of 1,10-phenanthroline monohydrate (1.98 g, 10.0 mmol) in ethanol to a 20 ml solution of $Cu(NO_3)_2.3H_2O$ (2.41 g, 10.0 mmol) dissolved in water. To the resulting solution, which contained a yellow-green precipitate, 20 ml of a solution containing $NaH_2PO_2.H_2O$ (3.00 g, 20.0 mmol) dissolved in water was slowly added with continuous stirring. The blue solid product was dissolved in DMSO and crystals suitable for the structure determination were produced by evaporation of the solvent.

Crystal data

$[Cu_2(H_2PO_2)_2(C_{12}H_8N_2)_2]$-$(NO_3)_2$
$M_r = 741.496$
Monoclinic
$P2_1/c$
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 22.58$–$24.86°$
$a = 6.759\ (2)$ Å
$b = 13.803\ (1)$ Å
$c = 15.124\ (3)$ Å
$\beta = 109.43\ (1)°$
$V = 1330.7\ (4)$ Å^3
$Z = 2$
$D_x = 1.851$ Mg m^{-3}
$\mu = 1.79$ mm^{-1}
$T = 293$ K
Plate
0.50 × 0.40 × 0.10 mm
Blue

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans
$T_{min} = 0.663$, $T_{max} = 0.999$
2522 measured reflections
2330 independent reflections
2199 observed reflections $[I > 3\sigma(I)]$
$R_{int} = 0.015$
$\theta_{max} = 25.0°$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 17$
1 standard reflection frequency: 167 min intensity decay: 1.85%

Refinement

Refinement on F
$R = 0.029$
$wR = 0.054$
$S = 2.55$
2199 reflections
209 parameters
H atoms refined as riding
$w = 1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Atomic scattering factors from Cromer & Mann (1968) and *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cu	0.50123 (4)	0.18042 (2)	0.46019 (2)	2.544 (6)
P	0.74789 (9)	0.00741 (4)	0.58822 (5)	3.08 (1)
O1	0.5979 (3)	0.0914 (1)	0.5642 (1)	3.15 (3)
O2	0.6725 (3)	−0.0827 (1)	0.6233 (1)	2.96 (3)
O3	−0.1377 (3)	0.1508 (2)	0.4167 (2)	5.62 (6)
O4	−0.0571 (3)	0.2804 (2)	0.3573 (2)	5.10 (5)
O5	0.1533 (3)	0.2277 (2)	0.4877 (1)	4.64 (5)
N1	0.6576 (3)	0.2914 (1)	0.5386 (1)	2.52 (4)
N2	0.4431 (3)	0.2783 (1)	0.3580 (1)	2.31 (3)
N3	−0.0153 (3)	0.2200 (2)	0.4204 (2)	3.33 (4)
C1	0.7563 (4)	0.2963 (2)	0.6305 (2)	3.26 (5)
C2	0.8575 (4)	0.3801 (2)	0.6742 (2)	3.69 (5)
C3	0.8581 (4)	0.4602 (2)	0.6212 (2)	3.49 (5)
C4	0.7541 (3)	0.4583 (2)	0.5238 (2)	2.93 (4)
C5	0.7393 (3)	0.5386 (2)	0.4620 (2)	3.74 (5)
C6	0.6328 (4)	0.5306 (2)	0.3695 (2)	3.55 (5)
C7	0.5277 (3)	0.4428 (2)	0.3294 (2)	3.05 (4)
C8	0.4081 (4)	0.4311 (2)	0.2344 (2)	3.85 (5)
C9	0.3099 (4)	0.3435 (2)	0.2037 (2)	3.84 (5)
C10	0.3312 (4)	0.2687 (2)	0.2683 (2)	3.01 (5)
C11	0.5387 (3)	0.3639 (2)	0.3876 (1)	2.33 (4)
C12	0.6549 (3)	0.3711 (2)	0.4864 (2)	2.37 (4)

Table 2. *Selected geometric parameters (Å, °)*

Cu—O1	1.931 (2)	N2—C11	1.350 (3)
Cu—O2′	1.951 (2)	C1—C2	1.393 (4)
Cu—O3	2.761 (2)	C2—C3	1.366 (4)
Cu—O5	2.604 (2)	C3—C4	1.406 (4)
Cu—N1	2.009 (2)	C4—C5	1.432 (4)
Cu—N2	1.990 (2)	C4—C12	1.402 (3)
P—O1	1.503 (2)	C5—C6	1.349 (5)
P—O2	1.506 (2)	C6—C7	1.433 (4)

O3—N3	1.252 (3)	C7—C8	1.404 (4)
O4—N3	1.227 (3)	C7—C11	1.388 (3)
O5—N3	1.254 (3)	C8—C9	1.383 (5)
N1—C1	1.328 (3)	C9—C10	1.395 (4)
N1—C12	1.351 (3)	C11—C12	1.441 (3)
N2—C10	1.323 (3)		
O1—Cu—O2′	93.14 (7)	Cu—N2—C11	112.8 (2)
O1—Cu—N1	92.04 (8)	C10—N2—C11	118.4 (2)
O1—Cu—N2	171.99 (8)	O3—N3—O4	120.3 (3)
O2′—Cu—N1	173.94 (7)	O3—N3—O5	120.7 (3)
O2′—Cu—N2	92.65 (8)	O4—N3—O5	119.0 (3)
O3′—Cu—O1	90.78 (8)	N1—C1—C2	122.3 (3)
O3′—Cu—O2′	97.63 (8)	C1—C2—C3	119.4 (3)
O3′—Cu—N1	85.44 (8)	C2—C3—C4	120.1 (2)
O3′—Cu—N2	82.96 (8)	C3—C4—C5	124.8 (3)
O3′—Cu—O5	172.72 (8)	C3—C4—C12	116.4 (3)
O5—Cu—O1	96.22 (8)	C5—C4—C12	118.7 (2)
O5—Cu—O2′	84.01 (8)	C4—C5—C6	120.7 (2)
O5—Cu—N1	92.30 (8)	C5—C6—C7	121.8 (3)
O5—Cu—N2	89.89 (8)	C6—C7—C8	124.5 (3)
N1—Cu—N2	82.52 (8)	C6—C7—C11	118.7 (3)
O1—P—O2	116.2 (1)	C8—C7—C11	116.7 (3)
Cu—O1—P	134.9 (1)	C7—C8—C9	119.6 (3)
Cu—O2′—P′	123.0 (1)	C8—C9—C10	119.0 (3)
Cu—N1—C1	129.7 (2)	N2—C10—C9	122.4 (3)
Cu—N1—C12	111.9 (2)	N2—C11—C7	123.9 (2)
C1—N1—C12	118.4 (2)	N1—C12—C4	123.4 (2)
Cu—N2—C10	128.8 (2)	N1—C12—C11	116.5 (2)
N2—C11—C12	116.1 (2)	C4—C12—C11	120.0 (2)
C7—C11—C12	120.0 (2)		

Symmetry code: (′) $1 - x, -y, 1 - z$.

The displacement parameters for the H atoms range from 2.6 (5) to 5.1 (7) Å^2.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1160). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 873–876

Chloro{2-[2-(dimethylamino)ethyliminomethyl]phenol}triphenyltin(IV) Benzene Hemisolvate, $[SnCl(C_6H_5)_3(C_{11}H_{16}N_2O)].0.5C_6H_6$

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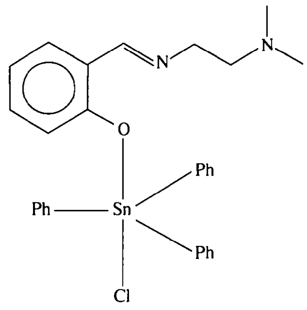
(*Received 1 August 1995; accepted 10 October 1995*)

Abstract

The coordination geometry of the Sn atom in the title compound is trigonal bipyramidal, with the *ipso* C atoms of the phenyl groups in equatorial and the Cl and O atoms in apical positions. The ligand is bonded to the Sn atom through the phenolic O atom; the hydroxy H atom is shifted towards the imino N atom to give rise to a zwitterion, *i.e.* 2-[2-(dimethylamino)ethyliminiomethyl]-phenolate.

Comment

Triorganotin halides and pseudohalides form complexes with α-amino acids (Khoo, Goh, Eng, Walen & Hazell, 1995), picolinic acid (Gabe, Lee, Khoo & Smith, 1985) and Schiff bases (Hazell, Goh & Khoo, 1994). For Schiff base derivatives of *ortho*-hydroxy phenols in particular, a zwitterionic conformation results owing to coordination by the phenolic O atom, whose proton is transferred to the imino N atom. In a continuation of studies of these Schiff base complexes of triorganotin halides, a study of the title complex, (I), was initiated, with 2-[2-(dimethylamino)ethyl]iminomethylphenol as a ligand, a Schiff base having a substituent with the potential to accept the hydroxy proton on complexation.



(I)

The coordination of the Sn atom is trigonal bipyramidal with the *ipso* C atoms of the phenyl groups in equatorial positions and the phenol O and the Cl atoms

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