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Di-μ-hypophosphito-bis[(2,2′-bipyridine)copper(II)] nitrate

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.024
wR factor = 0.070
Data-to-parameter ratio = 11.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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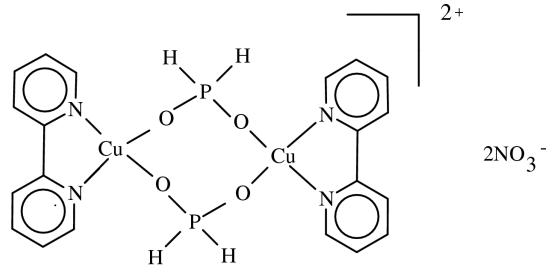
The structure of blue $[Cu_2(O_2PH_2)_2(C_{10}H_8N_2)_2](NO_3)_2$ consists of dimeric $[Cu(O_2PH_2)(bipy)]$ subunits (bipy = 2,2′-bipyridine) joined by two hypophosphite bridging ligands, with each metal center in a distorted planar arrangement. These joined subunits exist as a discrete cation with the equivalent of two nitrates as counter-ions. The subunits have a four-coordinated distorted square-planar arrangement of N and O atoms from the 2,2′-bipyridine and hypophosphite ligands, with the fifth and sixth positions of the copper coordination occupied by neighboring O atoms of the nitrate counter-ions.

Comment

The existence of compounds such as $[Cu(NCS)_2(bipy)]$ (Parker *et al.*, 1994) and the corresponding phenanthroline complex (Breneman & Parker, 1993) shows that the oxidation potential of copper(II) is reduced by the presence of 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) ligands. Compounds containing ligands such as hypophosphite which would normally be oxidized by copper(II) can co-exist as part of a stable bipyridine complex. The hypophosphite ligand, $H_2PO_2^-$, was chosen as a potential bridging ligand for copper(II) complexes. The complex, $[Cu_2(O_2PH_2)_2(bipy)_2](NO_3)_2$, exists as discrete pairs of $[Cu(O_2PH_2)(bipy)]$ subunits linked by the hypophosphite ligands to form a cation with a 2+ charge. Two nitrate ions serve as the counter-ions in this compound. The structure of a copper(II) complex, $[Cu_2(O_2PH_2)_2(phen)_2](NO_3)_2$ (Parker *et al.*, 1996), has been determined to have similar bridging by hypophosphite ligands. Two related structures, $[Mn(O_2PH_2)_2(bipy)]_n$ (Weakley, 1978*a*) and $[Mn(O_2PH_2)_2(phen)]_n$ (Weakley, 1978*b*), have been shown to involve bridging through the oxygen ends of the two hypophosphite ligands ($H_2PO_2^-$).



(I)

Selected bond distances and angles are in Table 1. A plot of the complex is shown in Fig. 1, with the numbering system indicated. The cation, $[Cu_2(O_2PH_2)_2(bipy)_2]^{2+}$, consists of

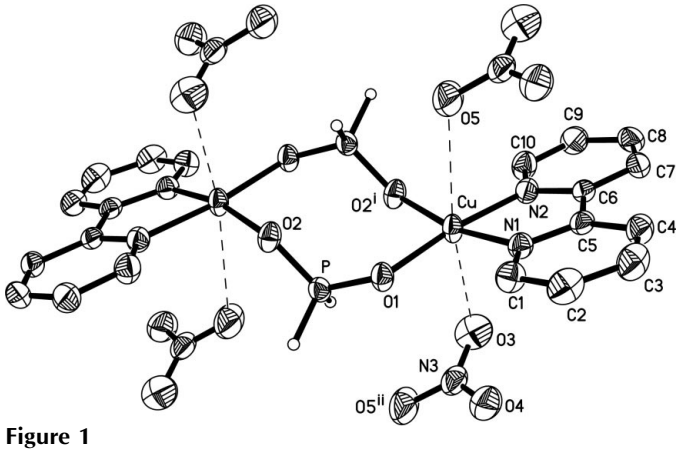


Figure 1
Displacement ellipsoid (50% probability) plot of $[Cu_2(O_2PH_2)_2(bipy)_2](NO_3)_2$, showing the atom-numbering scheme. H atoms on C atoms have been omitted. [Symmetry codes: (i) $-x, -y, 1-z$; (ii) $x-1, y, z$.]

discrete pairs of $[Cu(O_2PH_2)(bipy)]$ subunits which are bridged by the hypophosphite ligands in a symmetrical end-to-end fashion. The subunits have a four-coordinated distorted square-planar arrangement of N atoms from the 2,2′-bipyridine and O atoms from the hypophosphite ligands about the central Cu atom. The cation interacts through the fifth and sixth coordination positions on the copper with neighboring O atoms on the nitrate counter-ions. The Cu—N(bipy) distances are 1.9799 (18) and 1.9794 (19) Å for Cu—N1 and Cu—N2, respectively, with an N1—Cu—N2 angle of 81.62 (8)°. These distances and the bite angle are similar to those in $[Cu(NCS)_2(bipy)]$ (Parker *et al.*, 1994). The Cu—O1 and Cu—$O2^i$ distances are 1.9466 (15) and 1.9385 (15) Å, with an O1—Cu—$O2^i$ angle of 91.62 (7)° [symmetry code: (i) $-x, -y, 1-z$]. The square-planar arrangement about the copper is slightly distorted, the N1—Cu—$O2^i$ and N2—Cu—O1 angles being 167.45 (7) and 173.22 (7)°. The fifth and sixth coordination positions of copper have Cu—O(nitrate) distances of 2.564 (2) and 2.819 (2) Å for Cu—O3 and Cu—O5, with an O3—Cu—O5 angle of 169.39 (7)°. Typical angles are: O3—Cu—O1 85.54 (7)°; O3—Cu—$O2^i$ 97.72 (7)°; O3—Cu—N1 93.67 (8)°; and O3—Cu—N2 90.00 (8)°.

The end-to-end bridging hypophosphite ligands have P—O1 and P—$O2^i$ distances of 1.5155 (15) and 1.5085 (16) Å, with an O1—P—O2 angle of 114.79 (9)°. These distances and angle are very close to those in $[Cu_2(O_2PH_2)_2(phen)_2](NO_3)_2$ (Parker *et al.*, 1996), $[Mn(O_2PH_2)_2(bipy)]_n$ (Weakley, 1978*a*) and $[Mn(O_2PH_2)_2(phen)]_n$(Weakley, 1978*b*).

Experimental

$[Cu_2(O_2PH_2)_2(bipy)_2](NO_3)_2$ was prepared by the slow addition of a 15 ml solution of 2,2′-bipyridine (1.56 g, 10.0 mmol) in ethanol to a 20 ml solution of $Cu(NO_3)_2{\cdot}3H_2O$ (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 $NaH_2PO_2{\cdot}H_2O$ (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 X-ray analysis were obtained by evaporation of the solvent.

Crystal data

$[Cu_2(H_2PO_2)_2(C_{10}H_8N_2)_2](NO_3)_2$	$D_x = 1.851$ Mg m^{-3}
$M_r = 346.73$	Mo Kα radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 6.727$ (3) Å	$\theta = 20.0$–$24.9°$
$b = 12.8420$ (13) Å	$\mu = 1.91$ mm^{-1}
$c = 15.209$ (7) Å	$T = 295$ K
$\beta = 108.72$ (2)°	Prism, blue
$V = 1244.4$ (8) Å^3	0.50 × 0.30 × 0.20 mm
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.010$
$\theta/2\theta$ scans	$\theta_{max} = 25.0°$
Absorption correction: ψ scan *MolEN* (Fair, 1990)	$h = -7 \rightarrow 7$
$T_{min} = 0.513$, $T_{max} = 0.683$	$k = 0 \rightarrow 15$
2251 measured reflections	$l = 0 \rightarrow 17$
2165 independent reflections	1 standard reflection
2090 reflections with $I > 2\sigma(I)$	frequency: 167 min
	intensity decay: 1.1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0366P)^2 + 0.9392P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.024$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.070$	$\Delta\rho_{max} = 0.32$ e Å^{-3}
$S = 1.16$	$\Delta\rho_{min} = -0.28$ e Å^{-3}
2165 reflections	
187 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu—$O2^i$	1.9385 (15)	Cu—N1	1.9799 (18)
Cu—O1	1.9466 (15)	Cu—O3	2.564 (2)
Cu—N2	1.9794 (19)	Cu—O5	2.819 (2)
$O2^i$—Cu—O1	91.62 (7)	N1—Cu—O3	93.67 (8)
$O2^i$—Cu—N2	93.10 (7)	$O2^i$—Cu—O5	82.31 (7)
O1—Cu—N2	173.22 (7)	O1—Cu—O5	106.06 (8)
$O2^i$—Cu—N1	167.45 (7)	N2—Cu—O5	79.42 (8)
O1—Cu—N1	94.69 (7)	N1—Cu—O5	85.52 (7)
N2—Cu—N1	81.62 (8)	O3—Cu—O5	169.39 (7)
$O2^i$—Cu—O3	97.72 (7)	O2—P—O1	114.79 (9)
O1—Cu—O3	84.54 (7)	P—O1—Cu	122.18 (9)
N2—Cu—O3	90.00 (8)	P—O2—Cu^i	130.77 (10)

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

H atoms were set to ride on respective C atoms. Ideal positions were determined with C—H bond lengths = 0.96 Å, P—H bond lengths = 1.27 Å and $U_{iso} = 0.08$ Å^2.

Data collection: *CAD*-4 *Software* (Schagen *et al.*, 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: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

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