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#### Key indicators

Single-crystal X-ray study  
T = 295 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$   
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>.

## Di- $\mu$ -hypophosphito-bis[(2,2'-bipyridine)copper(II)] nitrate

The structure of blue  $[\text{Cu}_2(\text{O}_2\text{PH}_2)_2(\text{C}_{10}\text{H}_8\text{N}_2)_2](\text{NO}_3)_2$  consists of dimeric  $[\text{Cu}(\text{O}_2\text{PH}_2)(\text{bipy})]$  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.

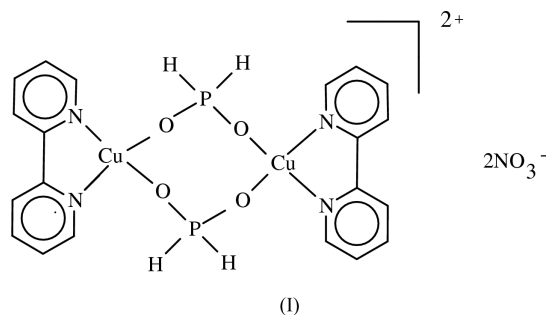
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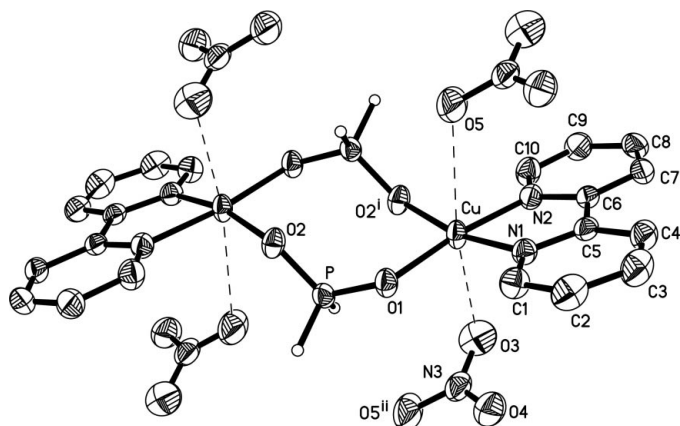
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#### Comment

The existence of compounds such as  $[\text{Cu}(\text{NCS})_2(\text{bipy})]$  (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,  $\text{H}_2\text{PO}_2^-$ , was chosen as a potential bridging ligand for copper(II) complexes. The complex,  $[\text{Cu}_2(\text{O}_2\text{PH}_2)_2(\text{bipy})_2](\text{NO}_3)_2$ , exists as discrete pairs of  $[\text{Cu}(\text{O}_2\text{PH}_2)(\text{bipy})]$  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,  $[\text{Cu}_2(\text{O}_2\text{PH}_2)_2(\text{phen})_2](\text{NO}_3)_2$  (Parker *et al.*, 1996), has been determined to have similar bridging by hypophosphite ligands. Two related structures,  $[\text{Mn}(\text{O}_2\text{PH}_2)_2(\text{bipy})]_n$  (Weakley, 1978a) and  $[\text{Mn}(\text{O}_2\text{PH}_2)_2(\text{phen})]_n$  (Weakley, 1978b), have been shown to involve bridging through the oxygen ends of the two hypophosphite ligands ( $\text{H}_2\text{PO}_2^-$ ).



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,  $[\text{Cu}_2(\text{O}_2\text{PH}_2)_2(\text{bipy})_2]^{2+}$ , consists of



**Figure 1**  
Displacement ellipsoid (50% probability) plot of  $[\text{Cu}_2(\text{O}_2\text{PH}_2)_2(\text{bipy})_2](\text{NO}_3)_2$ , 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  $[\text{Cu}(\text{O}_2\text{PH}_2)(\text{bipy})]$  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  $[\text{Cu}(\text{NCS})_2(\text{bipy})]$  (Parker *et al.*, 1994). The Cu–O1 and Cu–O2<sup>i</sup> distances are 1.9466 (15) and 1.9385 (15) Å, with an O1–Cu–O2<sup>i</sup> 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<sup>i</sup> 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<sup>i</sup> 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<sup>i</sup> distances of 1.5155 (15) and 1.5085 (16) Å, with an O1–P–O2<sup>i</sup> angle of 114.79 (9)°. These distances and angle are very close to those in  $[\text{Cu}_2(\text{O}_2\text{PH}_2)_2(\text{phen})_2](\text{NO}_3)_2$  (Parker *et al.*, 1996),  $[\text{Mn}(\text{O}_2\text{PH}_2)_2(\text{bipy})]_n$  (Weakley, 1978*a*) and  $[\text{Mn}(\text{O}_2\text{PH}_2)_2(\text{phen})]_n$  (Weakley, 1978*b*).

## Experimental

$[\text{Cu}_2(\text{O}_2\text{PH}_2)_2(\text{bipy})_2](\text{NO}_3)_2$  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  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (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  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  (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

$[\text{Cu}_2(\text{H}_2\text{PO}_4)_2(\text{C}_{10}\text{H}_8\text{N}_2)_2](\text{NO}_3)_2$   
 $M_r = 346.73$   
Monoclinic,  $P2_1/c$   
 $a = 6.727$  (3) Å  
 $b = 12.8420$  (13) Å  
 $c = 15.209$  (7) Å  
 $\beta = 108.72$  (2)°  
 $V = 1244.4$  (8) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.851$  Mg m<sup>-3</sup>  
Mo K $\alpha$  radiation  
Cell parameters from 25 reflections  
 $\theta = 20.0$ – $24.9$ °  
 $\mu = 1.91$  mm<sup>-1</sup>  
 $T = 295$  K  
Prism, blue  
0.50 × 0.30 × 0.20 mm

## Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\theta/2\theta$  scans  
Absorption correction:  $\psi$  scan  
*MolEN* (Fair, 1990)  
 $T_{\min} = 0.513$ ,  $T_{\max} = 0.683$   
2251 measured reflections  
2165 independent reflections  
2090 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.010$   
 $\theta_{\text{max}} = 25.0$ °  
 $h = -7 \rightarrow 7$   
 $k = 0 \rightarrow 15$   
 $l = 0 \rightarrow 17$   
1 standard reflection  
frequency: 167 min  
intensity decay: 1.1%

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.024$   
 $wR(F^2) = 0.070$   
 $S = 1.16$   
2165 reflections  
187 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0366P)^2 + 0.9392P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.32$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.28$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Cu–O2 <sup>i</sup>	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 <sup>i</sup> –Cu–O1	91.62 (7)	N1–Cu–O3	93.67 (8)
O2 <sup>i</sup> –Cu–N2	93.10 (7)	O2 <sup>i</sup> –Cu–O5	82.31 (7)
O1–Cu–N2	173.22 (7)	O1–Cu–O5	106.06 (8)
O2 <sup>i</sup> –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 <sup>i</sup> –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 <sup>i</sup>	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  $U_{\text{iso}} = 0.08$  Å<sup>2</sup>.

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: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

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