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Bis[μ-bis(4-nitrophenyl)phosphato-κ^2O:O']bis{[bis(2-pyridylmethyl)amine-κ^3N,N',N''']copper(II)} diperchlorate acetonitrile hemisolvate

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Key indicators

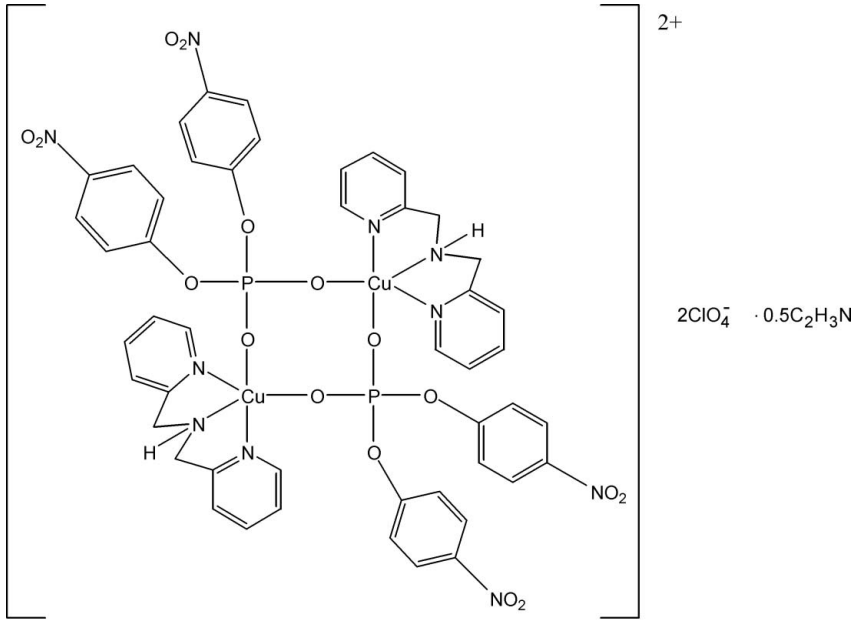
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.008 Å
Disorder in main residue
R factor = 0.065
wR factor = 0.168
Data-to-parameter ratio = 12.3

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

The title compound, $[Cu_2(bnpp)_2(bpa)_2](ClO_4)_2\cdot 0.5CH_3CN$ [bpa is bis(2-pyridylmethyl)amine ($C_{12}H_{13}N_3$) and bnpp is bis(4-nitrophenyl)phosphate ($C_{12}H_8N_2O_8P$)], contains two Cu^{II} ions, each coordinated in a distorted square-pyramidal geometry formed by the tridentate chelating ligand bpa and two O-atom donors from two bnpp ligands. Two bnpp anions bridge two Cu^{II} ions to form the dinuclear complex cation, one O-atom donor of each bnpp coordinating in a basal site and another coordinating in the apical position with a Jahn–Teller elongated bond of 2.189 (4) or 2.244 (3) Å.

Comment

Phosphate-based ligands are found in a wide variety of areas ranging from materials science to biochemistry. Their use in the preparation of new one-, two- and three-dimensional frameworks (Finn *et al.*, 2001), as well as pillared layered structures (Knight *et al.*, 2002), has received considerable attention in recent years. Their use in the synthesis of low-molecular-weight functional model complexes of phosphoesterases has also attracted great interest (Gultneh *et al.*, 1999), due to possible applications in biotechnology, molecular biology and chemotherapy (Gajda *et al.*, 2000), and the degradation of organophosphorous pesticides (Desloges *et al.*, 2004).



(I)

A number of hydrolytic metalloenzymes are activated by two or more cooperating metal ions (Lipscomb & Strater,

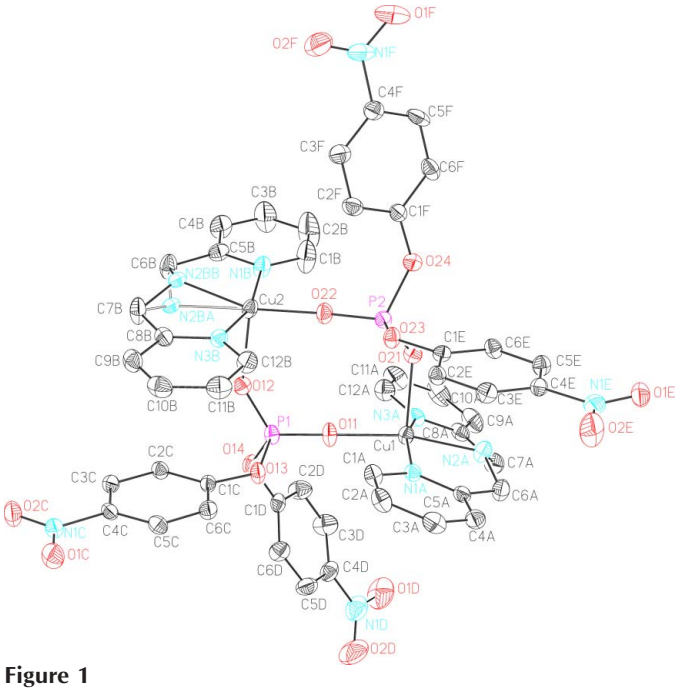


Figure 1
A view of the cation of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 20% probability level and H atoms are represented by circles of arbitrary size. H atoms have been omitted. Both disorder components are shown.

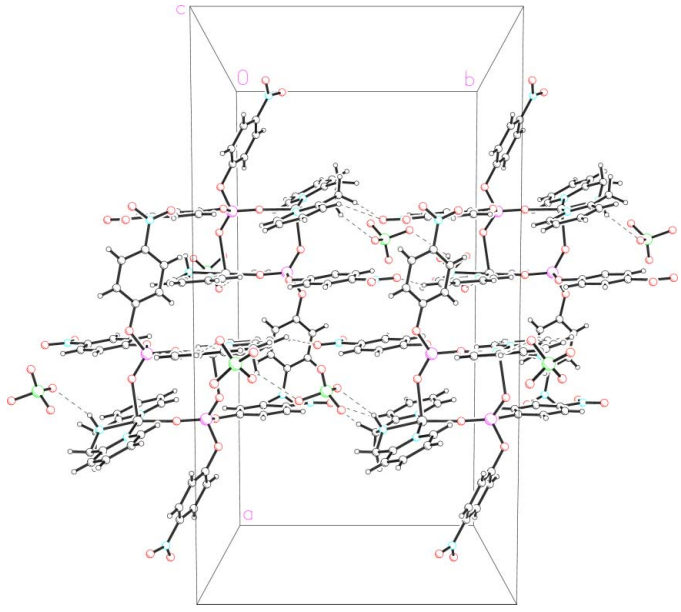


Figure 2
The molecular packing of (I), viewed along the *c* axis. Dotted lines indicate the hydrogen-bonding interactions.

1996; Wilcox, 1996). This possible cooperative effect on the hydrolysis of phosphoesters by a bimetallic core has inspired a number of model studies dealing with dinuclear complexes (Chin, 1998; Kramer & Gajda, 1999; Williams *et al.*, 1999). In particular, dinuclear complexes which incorporate the μ-1,3-bridging of a phosphoester substrate (Aoki, 1978; Bazzicalupi *et al.*, 2004; Bligh *et al.*, 1994; Clarke *et al.*, 1989; Fischer & Bau, 1978; Humphry *et al.*, 2004; Itoh, *et al.*, 2005; Kovari & Kramer, 1996; Mahroof-Tahir *et al.*, 1993; Rohovec *et al.*, 1996; Sheldrick, 1981; Wall *et al.*, 1993; Yamaguchi *et al.*, 2001) are of great interest for the light they can shed on understanding the mechanistic roles of the metal ions in phosphate ester hydrolysis.

Cu^{II} complexes of chelating *N*-donor ligands are well known to catalyze the hydrolysis of phosphate esters. The phosphate diester bis(4-nitrophenyl)phosphate (bnpp) has been used in model studies of the kinetics of the catalysis of the hydrolysis phosphate esters by Cu^{II} complexes (Deschamps *et al.*, 2002; Fry *et al.*, 2005; Linkletter & Chin, 1995; Stern *et al.*, 1990), among other complexes of transition metals (Chin & Zou, 1988). In our experiments to study the catalytic properties of the complex $[Cu(bpa)(H_2O)_2](ClO_4)_2$ (Gultneh *et al.*, 1999) formed in solution, for the hydrolysis of the diester, bnpp, under conditions of a large excess of $Na^+(bnpp)^-$ added in dimethylformamide (DMF), we isolated the title dinuclear Cu^{II} compound, (I), containing a μ-1,3-bridged activated phosphoester ligand (Jurek & Martell, 1999).

There is no crystallographically imposed symmetry on the dinuclear unit of (I), which contains two Cu^{II} centers, each of which is coordinated meridionally by the tridentate ligand, bis(2-pyridylmethyl)amine (bpa). The coordination sphere of each Cu^{II} is completed by two O donors from each of the two bridging bis(4-nitrophenyl)phosphate anions (bnpp). The charge balance requires two perchlorate anions and, in addition, the crystal structure contains acetonitrile solvent.

Fig. 1 shows the labeling within the dinuclear cation unit of (I), and Fig. 2 shows a packing diagram. The central amine N atom in one of the bpa ligands is disordered over two positions. The Cu^{II} ions are each in an approximate square-pyramidal geometry. Five-coordinate complexes span the continuum from square-pyramidal to trigonal–bipyramidal. Addison *et al.* (1984) developed a parameter, τ, which characterizes where on this continuum a particular structure lies. The values of τ for Cu1 and Cu2 of (I) are 0.09 and 0.26, respectively, meaning that both are closer to square-planar than trigonal–bipyramidal. For Cu1 and Cu2, for the four donor atoms making up the pyramidal base, the mean deviations from planarity are 0.007 (3), 0.102 (3), and 0.100 (3) Å (the latter two values include the two planes involving the disordered amine N atom). The Cu^{II} ions are each slightly drawn out of their coordination basal plane toward the apical O donor [0.220 (3) Å for Cu1, and 0.091 (3) (major component) and 0.250 (3) Å (minor component) for Cu2].

Two O donor atoms from each of the bridging bnpp ligands coordinate to two Cu^{II} atoms. One O donor occupies an apical site with a Jahn–Teller elongated Cu—O bond length and the other occupies a basal site (Table 1). In reported dinuclear copper complexes with phosphoester ligands, Cu—O bond lengths range from 1.903 (Giorgi & Cini, 1988) to 2.208 Å (Itoh *et al.*, 1999). The chelating tridentate ligand bpa coordinates meridionally in the basal sites of each Cu^{II} ion, with the two pyridyl N atoms spanning 161.3 (2) and 163.4 (2)°, respectively, about each Cu^{II} ion. In this dinuclear copper

complex, two phosphate O donors bridge the two Cu^{II} ions, as is seen in other mixed-ligand systems with phosphomonoesters (Aoki, 1978; Bazzicalupi *et al.*, 2004; Bligh *et al.*, 1994; Clarke *et al.*, 1989; Fischer & Bau, 1978; Humphry *et al.*, 2004; Itoh *et al.*, 2005; Kovari & Kramer, 1996; Mahroof-Tahir *et al.*, 1993; Rohovec *et al.*, 1996; Sheldrick, 1981; Wall *et al.*, 1993; Yamaguchi *et al.*, 2001).

A survey of the Cambridge Structural Database (Version 2.6; Allen, 2002) for phosphoester-bridged dinuclear copper complexes found 12 examples, with P—O distances ranging from 1.448 to 1.589 with a mean value of 1.50 (3) Å. The bridging P—O bond lengths in (I) are within the range found in similar complexes. Despite being a phosphodiester, the two O atoms in bnpp act as a bridge between the Cu^{II} ions, as is also seen in related dinuclear complexes with diesters. Similar bridging phosphate coordination in transition metal complexes has been invoked in intermediates in the catalytic hydrolysis of phosphate esters.

A *PLATON* analysis (Spek, 2003) shows evidence of π–π stacking interactions in (I). These are between one of the pyridine rings of bpa with the same ring on an adjoining cation, and between pyridine rings and the benzene rings of bnpp in the same cation. In the most obvious (shortest) instance, the distance between the ring centroids is 3.644 (3) Å. The amine H atoms from each of the two bpa ligands participate in hydrogen-bonding interactions with the perchlorate anions (Table 2).

Experimental

In our experiments carried out in dimethylformamide (DMF), to study the catalytic properties for the hydrolysis of the diester bnpp using the complex $[Cu(bpa)(H_2O)_2](ClO_4)_2$ under conditions of a large excess of $Na^+(bnpp)^-$, we isolated compound (I). Recrystallization from an acetonitrile solution of the residue from the catalytic reaction yielded deep blue crystals of (I) suitable for X-ray crystallography.

Crystal data

$[Cu_2(C_{12}H_8N_2O_8P)_2(C_{12}H_{13}N_3)_2](ClO_4)_2\cdot0.5C_2H_3N$
M_r = 1421.35
Monoclinic, $C2/c$
a = 26.167 (6) Å
b = 14.150 (4) Å
c = 32.116 (7) Å
β = 97.91 (2)°
V = 11778 (5) Å^3
Z = 8
D_x = 1.603 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 45 reflections
θ = 8.3–12.6°
μ = 0.96 mm^{-1}
T = 296 (2) K
Chunk, blue
0.35 × 0.27 × 0.17 mm

Data collection

Bruker P4 diffractometer
ω scans
Absorption correction: refined from ΔF (*SHELXA* in *SHELXTL*; Sheldrick, 1997)
T_{min} = 0.633, T_{max} = 0.850
10 557 measured reflections
10 331 independent reflections
5104 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 25.0°
$h = 0 \rightarrow 31$
$k = 0 \rightarrow 16$
$l = -38 \rightarrow 37$
3 standard reflections
every 97 reflections
intensity decay: 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.168
S = 1.01
10 331 reflections
839 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0626P)^2 + 22.0028P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.013
$\Delta\rho_{max}$ = 0.72 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1*A*	1.983 (4)	Cu2—O22	1.929 (3)
Cu1—N2*A*	1.998 (4)	P1—O12	1.459 (4)
Cu1—N3*A*	1.968 (4)	P1—O11	1.474 (3)
Cu1—O11	1.954 (3)	P1—O14	1.590 (3)
Cu1—O21	2.189 (4)	P1—O13	1.617 (3)
Cu2—N1*B*	1.981 (4)	P2—O22	1.471 (3)
Cu2—N2*BA*	2.066 (11)	P2—O21	1.473 (4)
Cu2—N2*BB*	1.980 (7)	P2—O24	1.594 (4)
Cu2—N3*B*	1.985 (4)	P2—O23	1.610 (3)
Cu2—O12	2.244 (3)		
O11—Cu1—N1*A*	97.38 (15)	O22—Cu2—N2*BB*	159.4 (2)
O11—Cu1—N2*A*	166.81 (18)	O22—Cu2—N3*B*	95.85 (15)
O11—Cu1—N3*A*	95.11 (15)	O22—Cu2—O12	99.52 (14)
O11—Cu1—O21	95.13 (14)	N1*B*—Cu2—N2*BA*	84.7 (3)
N1*A*—Cu1—N2*A*	82.48 (16)	N1*B*—Cu2—N2*BB*	81.9 (2)
N1*A*—Cu1—N3*A*	161.26 (17)	N1*B*—Cu2—N3*B*	163.39 (17)
N1*A*—Cu1—O21	96.90 (14)	N1*B*—Cu2—O12	95.74 (16)
N2*A*—Cu1—N3*A*	82.18 (17)	N2*BA*—Cu2—O12	79.8 (3)
N2*A*—Cu1—O21	97.99 (16)	N2*BA*—Cu2—N3*B*	83.0 (3)
N3*A*—Cu1—O21	95.83 (15)	N2*BB*—Cu2—N3*B*	82.7 (2)
O22—Cu2—N1*B*	96.48 (16)	N2*BB*—Cu2—O12	101.1 (2)
O22—Cu2—N2*BA*	178.7 (3)	N3*B*—Cu2—O12	93.15 (14)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2*A*—H2*AB*···O14*A*^{i}	0.91	2.28	3.134 (8)	156
N2*BB*—H2*BB*···O22*A*	0.91	2.10	2.934 (8)	153
N2*BA*—H2*BC*···O12	0.91	2.31	2.769 (11)	111
N2*BA*—H2*BC*···O11*A*^{ii}	0.91	2.50	3.208 (13)	135

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x+1, -y+1, -z+1$.

The central amine N donor in one of the bis(2-pyridylmethyl)-amine ligands is disordered over two positions, with occupancies of 0.585 (7) and 0.415 (7). There is also acetonitrile solvent present, which does not have full occupancy but was modeled at half occupancy. In spite of the relatively large displacement parameters for this group, its geometry did not deviate from that expected. One of the perchlorate anions was disordered. The O atoms were modeled as two idealized tetrahedra, with occupancies of 0.850 (5) and 0.150 (5). The methyl H atoms were constrained to an ideal geometry, with C—H distances of 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C), but each group was allowed to rotate freely about its C—C bond. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with the N—H distance = 0.91 Å and C—H distances in the range 0.95–1.00 Å, and with U_{iso}(H) = 1.2U_{eq}(C,*N*).

Data collection: *XSCANS* (Sheldrick, 1997); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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