Inorganica Chimica Acta, *207* (1993) 135–138

Short Communication

Phosphate ester coordination to dicopper(II) compounds; X-ray structure of a bis(4-nitrophenyl)phosphato bridged dicopper(II) complex

Mohammad Mahroof-Tahir, Kenneth D. Karlin*
Departments of Chemistry, The Johns Hopkins University, Baltimore, MD 21218 (USA)
and Department of Chemistry, SUNY at Albany, Albany, NY 12222 (USA)

Qin Chen and Jon Zubieta
Department of Chemistry, SUNY at Albany Albany, NY 12222 (USA)
and Department of Chemistry, Syracuse University, Syracuse, NY 13244 (USA)

(Received August 21, 1992; revised November 24, 1992)

The binding and reactivity of organic phosphate ester compounds with metal ion complexes has received increased recent attention [1–5]. Hydrolysis reactions with such substrates are of concern in the detoxification of phosphorous containing pesticides. In addition, naturally occurring enzymes catalyze phosphate ester (including DNA or RNA) hydrolysis processes. Recently, it has come to light that in some cases such reactions occur at enzyme active sites containing two or three metal ions, such as in alkaline phosphatase [1, 6], phopholipase C from *Bacillus cereus* [7], the Klenow fragment of *E. coli* DNA polymerase I [8], ribonuclease H of HIV-1 reverse transcriptase [9], and purple acid phosphatases [5]. Di- or trinuclear metal centers with Fe, Zn Mg or Mn are or may be involved in these biological phosphate ester hydrolysis reactions, while recent chemical model studies have most often emphasized hydrolytic chemistry with Co^{3+}, Cu^{2+} and Zn^{2+} [1–4, 10–15].

Thus, investigations of phosphate ester binding to polymetallic centers are aimed at deducing relevant coordination chemistry, mechanism(s) and structures which may occur in the enzymes, and such studies may aid efforts to design efficient synthetic hydrolysis catalysts. In initial efforts aimed at studying such chemistry at dinuclear metal centers, we thought to examine the binding and structures of phosphate esters to dicopper complex species, since with other ongoing studies in copper/dioxygen reactivity [16, 17] we have a number of types of dinuclear copper(II) complexes in hand. Here, we report the synthesis of phenolato bridged dicopper(II) complexes, each also containing a bridging bidentate bis(4-nitrophenyl)phosphato ligand.

The dicationic complex $[Cu_2(UN\text{-}O^-)(BNPP)]^{2+}$ was synthesized by the reaction of $[Cu_2(UN\text{-}O^-)(OH)](PF_6)_2$ [18] (0.30 g, 0.3 mmol) with bis(4-nitrophenyl)phosphate (BNPP) (0.11 g, 0.32 mmol) in the presence of dimethoxypropane (0.40 g, 3.8 mmol) as dehydrating agent, in CH_2Cl_2 (30 ml) under Ar. A bluish green solid separated after stirring for 20 h. Upon recrystallization from CH_3CN–Et_2O, crystalline $[Cu_2(UN\text{-}O^-)(BNPP)](PF_6)_2 \cdot CH_3CN$ (0.37 g) was obtained**. The related complex, $[Cu_2(XYL\text{-}O^-)(BNPP)](PF_6)_2 \cdot 1/2CH_2Cl_2 \cdot 1/2Et_2O$ (**2**) was synthesized by addition of bis(4-nitrophenyl)phosphate (0.17 g, 0.51 mmol) to a well stirred solution of $[Cu_2(XYL\text{-}O^-)(OH)](PF_6)_2$ [19] (0.5 g, 0.50 mmol) and dimethoxypropane (0.85 g. 8.14 mmol) in CH_2Cl_2 (30 ml). A bluish green solid separated out after stirring for 2 h whereupon diethyl ether was added for complete precipitation of the product. Recrystallization from CH_2Cl_2–Et_2O produced 0.59 g of microcrystalline product†.

Crystals of $[Cu_2(UN\text{-}O^-)(BNPP)](PF_6)_2 \cdot CH_3CN$ suitable for an X-ray diffraction study were grown by diethyl ether diffusion into a CH_3CN solution of the complex under Ar. Crystallographic data is given in Table 1. The structure of the dication $[Cu_2(UN\text{-}O^-)(BNPP)]^{2+}$ is shown in Fig. 1 and selected bond lengths and bond angles are given in the caption. It crystallizes in the triclinic space group $P\bar{1}$ with $a = 14.024(4)$, $b = 14.191(4)$, $c = 14.900(4)$ Å, $\alpha = 101.43(1)$, $\beta = 95.30(2)$, $\gamma = 105.00(2)°$, $V = 2774.8(17)$ Å^3, $Z = 2$. A total of 3930 reflections was refined to $R = 0.081$ and $R_w = 0.089$ (Mo Kα, $\lambda = 0.71073$ Å). There are two discrete molecules in the unit cell each consisting of an unsymmetrically coordinated dicopper moiety with a Cu...Cu separation of 3.773 Å. Each Cu(II) is five-coordinate with ligation from two pyridyl nitrogens, one tertiary amine nitrogen, the phenolate oxygen and one

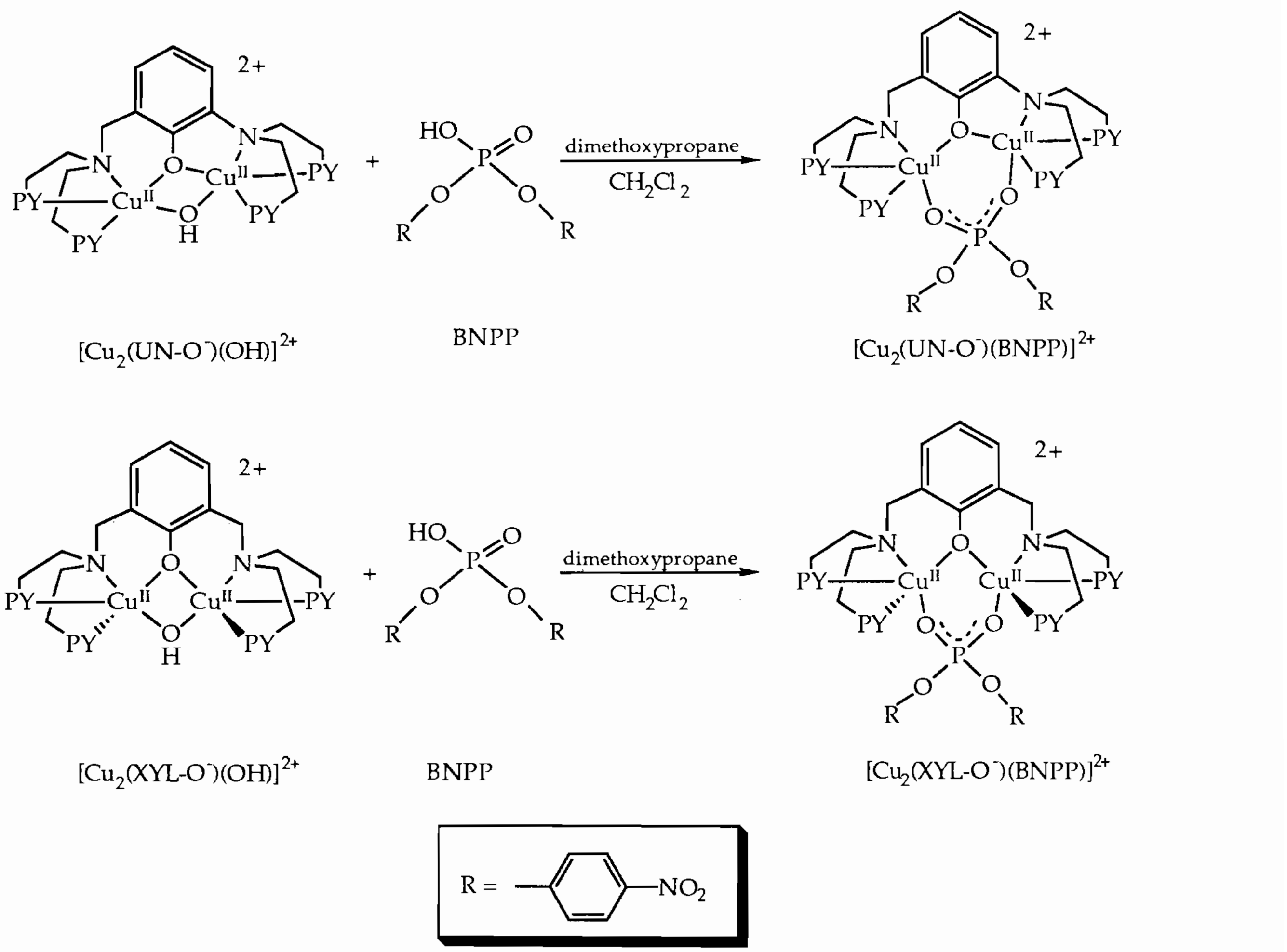
---

*Author to whom correspondence should be addressed at The Johns Hopkins University.

****Anal.* Calc. for $C_{49}H_{48}Cu_2F_{12}N_9O_9P_3$: C, 43.43; H, 3.54; N, 9.30. Found: C, 43.43; H, 3.62; N, 9.12%. UV–Vis: λ_{max} (ϵ, M^{-1} cm^{-1}): 434 (330) and 706 (180) nm.

†*Anal.* Calc. for $C_{50.5}H_{53}Cu_2Cl_1F_{12}N_8O_{9.5}P_3$: C, 43.08; H, 3.77; N, 7.96. Found: C, 43.40; H, 3.72; N, 7.90%. UV–Vis: λ_{max} (ϵ, M^{-1} cm^{-1}): 430 (1720) and 689 (220) nm.

0020-1693/93/$6.00



oxygen atom of the phosphate ester group. Addison *et al.* [23] reported a procedure to distinguish between square pyramidal and trigonal bipyramidal coordination environments based on the value of a structural parameter τ, where for an ideal trigonal bipyramidal $\tau = 1$ and for an ideal square pyramidal $\tau = 0$. In the present case the τ value was calculated to be 0.12 around Cu1 and 0.34 for Cu2, indicating that the geometry around each copper is best described as square pyramidal, with Cu2 being more highly distorted. The phenolate oxygen atom O5 occupies the axial position of Cu1, with a long Cu1–O5 bond distance of 2.241 Å. The basal plane is occupied by two pyridine nitrogen atoms (N5, N6), one amine nitrogen atom (N4) and one phosphate oxygen atom (O2). On the other hand, the N2 pyridine nitrogen atom occupies the axial position of Cu2 (Cu2–N2 = 2.225 Å), with the basal plane occupied by one pyridine nitrogen (N3), the amine nitrogen (N1), a strongly bound phenolate oxygen (O5) and the phosphate oxygen atom (O1). The distortions observed and inequivalence of Cu ion coordination environments are most likely ascribable to the unsymmetrical nature of the ligand; the five-membered chelate ring which includes Cu2, O5 and N1 forces both donor atoms to be 'in-plane', while the more flexible six-membered chelate ring with Cu1, O5 and N4 allows O5 to be axial. Note that the unsymmetrical coordination is clearly manifested by the interatomic distances Cu1–O5 = 2.241 Å and Cu2–O5 = 1.947 Å. In most Cu(II) complexes of this type, Cu–$O_{\text{phenolate}}$ distances are in the range of 1.95–2.01 Å [24].

As described, the phenolato oxygen atom (O5) which bridges the two coppers occupies an axial position with respect to one copper ion (Cu1), but an equatorial position for the other (Cu2). This may result in less efficient antiferromagnetic coupling between Cu(II) ions leading to the large room temperature magnetic moment observed, i.e. 1.9 ± 0.1 μ_B/Cu. However, in the case of $[Cu_2(XYL\text{-}O^-)(BNPP)]^{2+}$, strong coupling is indicated by the observed room temperature magnetic moment of 1.2 ± 0.1 μ_B/Cu, most likely due to a more symmetrical bridging structure.

The Cu–$O_{\text{phosphate}}$ distances are longer (2.005, 2.013 Å) than those typically found in other complexes, where Cu–$O_{\text{phosphate}}$ is 1.91–1.96 Å [25]. The six-membered ring formed by the phosphate ester and metal atoms

TABLE 1. Crystallographic data for $[Cu_2(UN\text{-}O^-)(BNPP)](PF_6)_2\cdot CH_3CN$

Formula	$C_{49}H_{48}Cu_2F_{12}N_9O_9P_3$
Temperature (K)	296
MW	1355
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)[a]	14.024(4)
b (Å)	14.191(4)
c (Å)	14.900(4)
α (°)	101.43(1)
β (°)	95.30(2)
γ (°)	105.00(2)
V (Å^3)	2775(2)
F(000)	1364
Z	2
D_{calc} (g/cm^3)	1.62
Absorption coefficient (cm^{-1})	11.70
Crystal dimensions (mm)	0.27×0.26×0.19
Scan mode	coupled θ(crystal)–2θ(counter)
Scan rate (°/min)	2–30
Scan range (°)	2.0–50.0
Scan length	$[2\theta(K_{\alpha 1})-1.0]°$ to $[2\theta(K_{\alpha 2})+1.0]°$
Background measurement	stationary crystal, stationary counter, at the beginning and end of each 2θ scan, each for half the time taken for the scan.
Reflections measured	$+h$, $+k$, $\pm l$
Reflections collected	6971
Independent reflections	3930 ($\geq 6\sigma\|F_o\|$)
No. refined parameters (N_v)	757
T_{max}/T_{min}	1.12
Reduction of intensity data and summary of structure solution and refinement[b]	
Absorption correction	not applied
Atom scattering factors[c]	neutral atomic scattering factors were used throughout the analysis.
Structure solution	Patterson synthesis yielded the copper atom position; all remaining non-hydrogen atoms were located via standard Fourier techniques
Anomalous dispersion	applied to all non-hydrogen atoms
R[e]	0.081
R_W[e]	0.089
Goodness of fig[f]	2.01

[a] From a least-squares fitting of the setting angle of 25 reflections. [b] All calculations were performed on a Micro-Vax II computer using local versions of the Nicolet SHELXTL interactive crystallographic software package as described in ref. 20. Data were collected for background, attenuators, Lorentz and polarization effects in the usual fashion. [c] Ref. 21. [d] Ref. 22. [e] $R=\Sigma[|F_o|-|F_c|/\Sigma|F_o|]$; $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w=1/\sigma^2(F_o)+g^*(F_o)^2$; $g=0.001$. [f] $GOF=[\Sigma w(|F_o|-|F_c|)^2/(NO-NV)]^{1/2}$, where *NO* is the number of observations and *NV* is the number of variables.

is distinctly non-planar. The in ring O–P–O angle has been deformed from the unstrained tetrahedral value to 121.0(6)° whereas the two other angles apart from the endocyclic one are only slightly larger (110.3, 110.6°) than tetrahedral and the three other angles are shorter (104.1, 105.0, 104.8°). This deformation of the O–P–O angle may be due to the constraint imposed by binding of two copper centers with the phenolate (O5) oxygen atom. Lippard and co-workers [26] reported a crystal structure of the dinuclear iron phosphate complex $[Fe_2O\{O_2P(OC_6H_5)_2\}_2(HBPz_3)_2]$ ($HBPz_3$ = tris(pyrazolyl)borate) in which a (μ-oxo)diiron(III) core is bridged by two bidentate phosphate ligands. This complex exhibits bridging O–P–O angles of 119.8 and 120.4° for the two phosphate groups, close to the value reported here. For comparison, additional other recent examples of phosphate ester complexes with dinuclear metal centers include examples of a terminally coordinated phosphate in a diiron(III) complex [27], bidentate coordination to a $Zn^{II}Fe^{III}$ complex [28], or bidentate bridging ligation to two mononuclear LZn^{2+} (L = HB-3,5-iPr$_2$Pz$_3$) species [15].

Future efforts will be aimed at the investigation of hydrolysis activity and synthesis of zinc and other metal ion analogues of these and related ligand complexes.

Acknowledgement

We are grateful to the National Institutes of Health for support of this research.

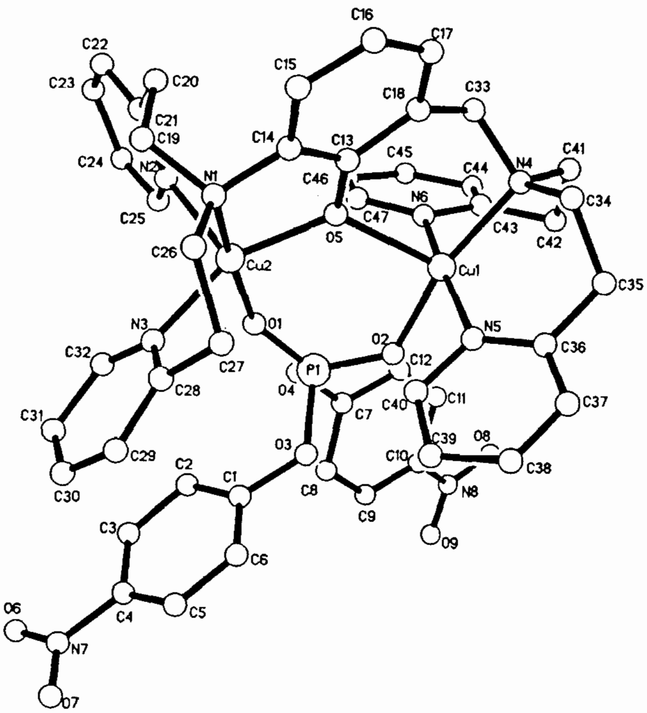


Fig. 1. ORTEP diagram of the cationic portion of $[Cu_2(UN\text{-}O)(BNPP)](PF_6)_2 \cdot CH_3CN$, showing the atom labeling scheme. Important bond lengths (Å) and bond angles (°) are as follows: Cu...Cu, 3.773(4); Cu1–O2, 2.013(9); Cu1–O5, 2.241(9); Cu1–N4, 2.063(12); Cu1–N5, 2.022(12); Cu1–N6, 1.994(13); Cu2–O1, 2.005(10); Cu2–O5, 1.947(10); Cu2–N1, 2.016(13); Cu2–N2, 2.225(11); Cu2–N3, 2.005(13); P1–O1, 1.460(9), P1–O2, 1.473(10); P1–O3, 1.601(10); P1–O4, 1.582(11); Cu1–Cu2, 3.773; O2–Cu1–O5, 99.0(4); O2–Cu1–N4, 161.3(5); O5–Cu1–N4, 98.7(4); O2–Cu1–N5, 88.4(4); O5–Cu1–N5, 98.2(4); N4–Cu1–N5, 95.0(5); O2–Cu1–N6, 85.2(4); O5–Cu1–N6, 92.2(4); N4–Cu1–N6, 88.1(5); N5–Cu1–N6, 168.6(5); O1–Cu2–O5, 91.6(4); O1–Cu2–N1, 172.7(4); O5–Cu2–N1, 86.7(5); O1–Cu2–N2, 90.8(4); O5–Cu2–N2, 102.1(4); N1–Cu2–N2, 96.5(4); O1–Cu2–N3, 86.0(5); O5–Cu2–N3, 152.3(4); N1–Cu2–N3, 92.1(5); N2–Cu2–N3, 105.5(5); O1–P1–O2, 121.0(6); O1–P1–O3, 110.6(6); O2–P1–O3, 104.1(5); O1–P1–O4, 105.0(6); O2–P1–O4, 110.3(6); O3–P1–O4, 104.8(5).

References

1 P. Handry and A. M. Sargeson, *Prog. Inorg. Chem., 38* (1990) 201–258.

2 H. Sigel, *Coord. Chem. Rev., 100* (1990) 453–539.

3 R. W. Hay, in P. S. Braterman (ed.), *Reactions of Coordinated Ligands,* Vol. 2, Plenum, New York, 1989, pp. 223–264.

4 J. Chin, M. Banazczyk, V. Jubian, J. H. Kim and K. Mrejen, *Bioorgan. Chem. Front., 2* (1991) 175–194.

5 J. B. Vincent, M. W. Crowder and B. A. Averill, *Trends Biochem. Sci., 17* (1992) 105–110.

6 E. E. Kim and H. W. Wyckoff, *J. Mol. Biol., 218* (1991) 449–464; E. E. Kim and H. W. Wyckoff, *Clin. Chim. Acta, 186* (1989) 175–188.

7 E. Hough, L. K. Hansen, B. Birknes, K. Jynge, S. Hansen, A. Hordvik, C. Little, E. Dodson and Z. Derewenda, *Nature (London), 338* (1989) 357–360.

8 L. S. Beese and T. A. Steitz, *EMBO J., 10* (1991) 25–33.

9 J. F. Davies, II, Z. Hostomska, Z. Hostomsky, S. R. Jordan and D. A. Matthews, *Science, 252* (1991) 88–95.

10 P. W. A. Hubner and R. M. Milburn, *Inorg. Chem., 19* (1980) 1267–1272.

11 J. R. Morrow and W. C. Trogler, *Inorg. Chem., 28* (1989) 2330–2333.

12 M. A. De Rosch and W. C. Trogler, *Inorg. Chem., 29* (1990) 2409–2416.

13 V. M. Shelton and J. R. Morrow, *Inorg. Chem., 30* (1991) 4295–4299.

14 P. Chaudhuri, C. Stockheim, K. Wieghardt, W. Deck, R. Gregorzik, H. Vahrenkamp, B. Nuber and J. Weiss, *Inorg. Chem., 31* (1992) 1451–1457.

15 S. Hikichi, M. Tanaka, Y. Moro-oka and N. Kitajima, *J. Chem. Soc., Chem. Commun.,* (1992) 814–815.

16 K. D. Karlin, Z. Tyeklár and A. D. Zuberbühler, in J. Reedijk (ed.), *Bioinorganic Catalysis,* Marcel Dekker, New York, 1993, Ch. 9, pp. 261–315.

17 K. D. Karlin and Z. Tyeklár, *Acc. Chem. Res., 22* (1989) 241–248.

18 M. S. Nasir, K. D. Karlin, D. McGowty and J. Zubieta, *J. Am. Chem. Soc., 113* (1991) 698–700.

19 K. D. Karlin, Y. Gultneh, J. C. Hayes, R. W. Cruse, J. Mckown, J. P. Hutchinson and J. Zubieta, *J. Am. Chem. Soc., 106* (1984) 2121–2128.

20 G. M. Sheldrick, *Nicolet SHELXTL Operations Manual,* Nicolet XRD Corporation, Cupertino, CA, 1979.

21 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect A, 24* (1968) 321.

22 *International Tables for X-ray Crystallography,* Vol. III, Kynoch, Birmingham, UK, 1962.

23 A. W. Addison, N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc. Dalton Trans.,* (1984) 1349–1356.

24 K. D. Karlin, A. Farooq, J. C. Hayes, B. I. Cohen, T. M. Rowe, E. Sinn and J. Zubieta, *Inorg. Chem., 26* (1987) 1271–1280.

25 D. R. Jones, L. F. Lindoy, A. M. Sargeson and M. R. Snow, *Inorg. Chem., 21* (1982) 4155–4160; C.-Y. Wei, B. E. Fischer and R. Bau, *Chem. Commun.,* (1978) 1053–1055; B. Anderson, R. M. Milburn, J. M. Harrowfield, G. B. Robertson and A. M. Sargeson, *J. Am. Chem. Soc., 99* (1977) 2652–2661; B. E. Fisher and R. Bau, *Inorg. Chem., 17* (1978) 27–34; K. Aoki, *J. Am. Chem. Soc., 100* (1978) 7106–7108.

26 P. N. Turowski, W. H. Armstrong, M. E. Roth and S. J. Lippard, *J. Am. Chem. Soc., 112* (1990) 681–690.

27 B. Bremer, K. Schepers, P. Fleischhauer, W. Haase, G. Henkel and B. Krebs, *J. Chem. Soc., Chem. Commun.,* (1991) 510–512.

28 K. Schepers, B. Bremer, B. Krebs, G. Henkel, E. Althaus, B. Mosel and W. Müller-Warmuth, *Angew. Chem., Int. Ed. Engl., 29* (1990) 531–533.