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## Key indicators

Single-crystal X-ray study  
T = 198 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$   
R factor = 0.036  
wR factor = 0.096  
Data-to-parameter ratio = 10.1For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Bis[ $\mu$ -bis(4-nitrophenyl) phosphato- $\kappa^2\text{O}:\text{O}$ ]-  
bis[(4,4'-dimethyl-2,2'-bipyridine)nitrato-  
copper(II)]

The title dimeric complex,  $[\text{Cu}_2(\text{L})_2(\text{BNPP})_2(\text{NO}_3)_2]$ , is formed between 4,4'-methyl-2,2'-bipyridine (*L*,  $\text{C}_{12}\text{H}_{12}\text{N}_2$ ), copper(II), and the substrate BNPP [bis-(4-nitrophenyl)-phosphate,  $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_8\text{P}$ ], with the two subunits,  $[\text{Cu}(\text{L})(\text{BNPP})\text{NO}_3]$  related by a center of inversion. The coordination geometry about the Cu atoms is square pyramidal, with phosphate O atoms occupying both an in-plane and an out-of-plane sites. While the dimeric scheme is similar to other five-coordinate copper(II) complexes of bipyridine, the alternating in-plane and out-of-plane bridging of the copper(II) centers by BNPP is unusual.

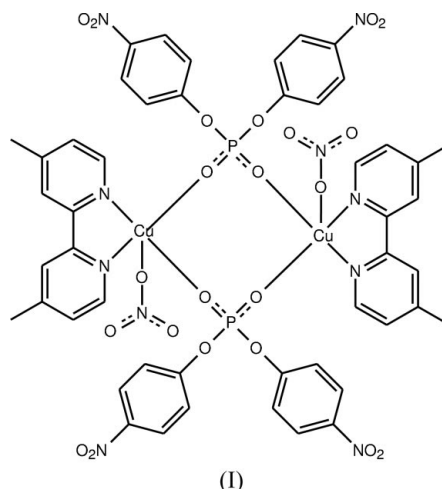
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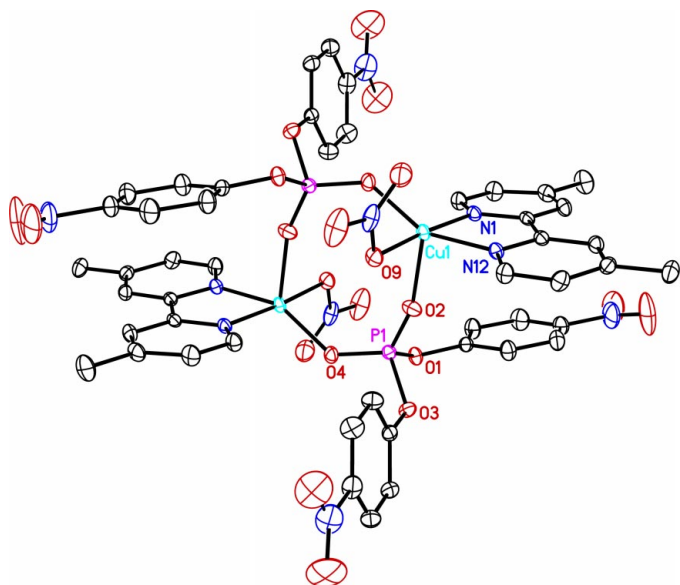
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## Comment

The role of metal ions in the enhanced hydrolysis of phosphate esters has long been known and the mechanism of these reactions extensively investigated. We have been exploring ways to incorporate these active homogeneous catalytic systems into insoluble polymers, in order to take advantage of both the fast rates of homogeneous catalysis and the ease of handling of inhomogeneous systems (Lu *et al.*, 2000; Singh *et al.*, 2000; Deschamps *et al.*, 2002; Hartshorn *et al.*, 2002).



In early research in this field, it was shown that 2,2'-bipyridyl (bpy) copper(II) complexes are among the most efficient in hydrolysing selected phosphorofluoridates, a class of compounds closely related to phosphate esters (Courtney *et al.*, 1957). A more recent report comprehensively detailed the hydrolysis of other phosphate esters with  $\text{bpy}-\text{Cu}^{\text{II}}$  (Morrow & Trogler, 1988). Since copper bipyridyl complexes are so



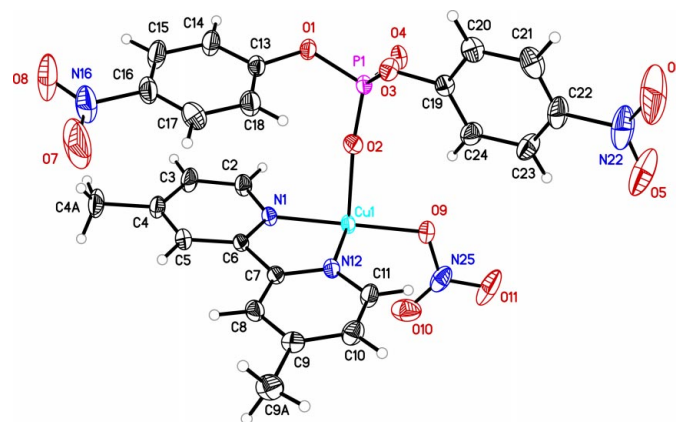
**Figure 1**

View of (I). Displacement ellipsoids are shown at the 20% probability level, H atoms have been omitted for clarity, and only selected heteroatoms are labeled.

effective across a wide range of substrates, we have sought to functionalize a 4,4'-dimethyl-2,2'-bipyridine in order to incorporate it into polymers using a cross-linker, such as 2-ethyl-2-(hydroxymethyl)propane trimethacrylate (TRIM). The resulting insoluble polymers are even more effective than the soluble monomer catalytic complexes, with catalytic rates up to  $6.7 \times 10^5$  times faster than the uncatalysed rates for methyl parathion, a phosphotriester (Hartshorn *et al.*, 2002).

A potential approach for further improving the catalytic properties of these enhanced polymeric catalysts would be to make imprinted nano-cavities within the polymers that can be customized to accommodate individual active metal-ion complexes and their targeted substrate. To this end, we have prepared a complex with copper coordinated by the dimethyl bpy molecule and a phosphodiester substrate. The complex serves as a prototype template for imprinting and also as a model to better understand the geometrical dimensions and constraints that would be necessary for making imprinted sites within polymers.

We report here the crystal structure of a  $\text{Cu}^{\text{II}}$  complex, (I), of 4,4'-dimethyl-2,2'-bipyridine (*L*) coupled to bis(4-nitrophenyl) phosphate, BNPP, a model phosphodiester. The structure is based on a dimeric complex,  $[\text{Cu}_2(\text{L})_2(\text{BNPP})_2(\text{NO}_3)_2]$  (Fig. 1), with the two subunits,  $[\text{Cu}(\text{L})(\text{BNPP})\text{NO}_3]$ , related by a center of inversion. The dimeric nature of the complex is reminiscent of other mixed-ligand systems based on bpy with phosphomonoesters (Aoki, 1978; Fischer & Bau, 1978; Glowiak *et al.*, 1986; Kovari & Kramer, 1996). Interestingly, despite being a phosphodiester, two O atoms in BNPP act as a bridge between the Cu ions, just as in the phosphomonoesters. In this case, however, the two bridging P—O bond



**Figure 2**

A view of the  $[\text{Cu}(\text{L})(\text{BNPP})\text{NO}_3]$  subunit, showing the square-pyramidal coordination around the Cu atom and BNPP in the axial position. Displacement ellipsoids are shown at the 30% probability level.

lengths of 1.466 (2) and 1.486 (2) Å (Table 1) are much shorter than that of a standard P—O single bond (1.64 Å; Cruickshank, 1961), or the bridging P—O bonds of a monophosphate (*e.g.* Fischer & Bau, 1978). A further difference is found for BNPP, which bridges the two  $\text{Cu}^{\text{II}}$  centers with alternate square-planar and axial positions. This is in contrast to the usual planar positions occupied by bridging monophosphate complexes (Aoki, 1978; Fischer & Bau, 1978; Kovari & Kramer, 1996).

The subunit  $[\text{Cu}(\text{L})(\text{BNPP})\text{NO}_3]$  (Fig. 2) is square pyramidal, with BNPP in both one axial and one basal position (not shown). The subunit exhibits some in-plane asymmetry, with one of the Cu—N bonds [*i.e.* Cu—N12 2.011 (3) Å] longer than the other, and C—O lengths of 1.961 (2) and 1.975 (2) Å. This is in contrast to the simpler  $[\text{Cu}(\text{L})(\text{NO}_3)_2]$  complex, where the two Cu—N bonds are of equal length (Deschamps *et al.*, 2002). While the Cu—O bond with nitrate forms part of the base, the rest of the nitrate ion, with a Cu—O—N angle of 111.2 (2)°, is located below the plane.

The axial phosphate C—O bond is much longer at 2.149 (2) Å, although still shorter than the average Cu—O(water) distance of 2.455 Å (Glowiak *et al.*, 1986). The P—O bonds that connect the nitrophenyl groups to the phosphate group are about the same length, at 1.598 (2) and 1.608 (2) Å, while the nitrophenyl rings are approximately at right angles to each other [92.05 (13)°].

In summary, the ternary complex,  $[\text{Cu}(\text{L})(\text{BNPP})(\text{NO}_3)]_2$ , exhibits the characteristic features, such as a five-coordinate square-pyramidal geometry, typical of previously reported mixed-ligand copper(II) complexes with monophosphate compounds. Similarly, the crystallization of the complex as a dimer conforms to the trend, even to the extent of BNPP playing the role of a bridge between the two  $\text{Cu}^{\text{II}}$  ions. The existence of a stable nitrate complex of  $\text{Cu}(\text{L})(\text{BNPP})$  is

promising both for preparing imprinted polymers and for incorporating binuclear complexes into polymers.

## Experimental

All reagents and solvents were purchased from commercial sources and used as received. To prepare the title complex,  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ , mbpy, and BNPP were mixed in ethanol in an equimolar ratio. The resulting solution was allowed to slowly evaporate, producing blue crystals suitable for single-crystal X-ray diffraction analysis.

### Crystal data

|   |   |
|---|---|
| $[\text{Cu}_2(\text{C}_{12}\text{H}_8\text{N}_2\text{O}_8\text{P})_2(\text{C}_{12}\text{H}_{12}\text{N}_2)_2(\text{NO}_3)_2]$ | $Z = 1$                                   |
| $M_r = 1297.92$   | $D_x = 1.568 \text{ Mg m}^{-3}$           |
| Triclinic, $P\bar{1}$   | Cu $K\alpha$ radiation                    |
| $a = 10.9572 (5) \text{ \AA}$   | Cell parameters from 26 reflections       |
| $b = 11.5226 (6) \text{ \AA}$   | $\theta = 3.7\text{--}27.5^\circ$         |
| $c = 12.0697 (11) \text{ \AA}$  | $\mu = 2.29 \text{ mm}^{-1}$              |
| $\alpha = 96.159 (5)^\circ$   | $T = 198 (2) \text{ K}$                   |
| $\beta = 96.421 (7)^\circ$  | Plate, blue                               |
| $\gamma = 113.044 (4)^\circ$  | $0.22 \times 0.14 \times 0.08 \text{ mm}$ |
| $V = 1374.32 (16) \text{ \AA}^3$  |   |

### Data collection

|   |   |
|---|---|
| Bruker P4 diffractometer                                    | $\theta_{\text{max}} = 58.1^\circ$      |
| $2\theta/\omega$ scans                                      | $h = -1 \rightarrow 11$                 |
| Absorption correction: by integration (XPREP; Bruker, 1997) | $k = -12 \rightarrow 11$                |
| $T_{\text{min}} = 0.702$ , $T_{\text{max}} = 0.856$         | $l = -13 \rightarrow 13$                |
| 4685 measured reflections                                   | 3 standard reflections                  |
| 3829 independent reflections                                | every 97 reflections                    |
| 3333 reflections with $I > 2\sigma(I)$                      | intensity decay: random variation of 2% |
| $R_{\text{int}} = 0.017$                                    |   |

### Refinement

|                                 |  |
|---------------------------------|--|
| Refinement on $F^2$             | $w = 1/[\sigma^2(F_o^2) + (0.0358P)^2 + 1.4102P]$    |
| $R[F^2 > 2\sigma(F^2)] = 0.036$ | where $P = (F_o^2 + 2F_c^2)/3$                       |
| $wR(F^2) = 0.096$               | $(\Delta/\sigma)_{\text{max}} < 0.001$               |
| $S = 1.07$                      | $\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$  |
| 3829 reflections                | $\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$ |
| 380 parameters                  | Extinction correction: SHELXL97                      |
| H-atom parameters constrained   | Extinction coefficient: 0.00044 (12)                 |

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

|                         |             |                          |             |
|-------------------------|-------------|--------------------------|-------------|
| Cu1—O9                  | 1.961 (2)   | P1—O2                    | 1.466 (2)   |
| Cu1—O4 <sup>i</sup>     | 1.975 (2)   | P1—O4                    | 1.486 (2)   |
| Cu1—N1                  | 1.976 (2)   | P1—O1                    | 1.598 (2)   |
| Cu1—N12                 | 2.011 (3)   | P1—O3                    | 1.608 (2)   |
| Cu1—O2                  | 2.149 (2)   |                          |             |
| O9—Cu1—O4 <sup>i</sup>  | 92.94 (9)   | O4 <sup>i</sup> —Cu1—N1  | 91.58 (9)   |
| O9—Cu1—O2               | 90.56 (9)   | O4 <sup>i</sup> —Cu1—N12 | 153.94 (10) |
| O9—Cu1—N1               | 175.44 (10) | N1—Cu1—O2                | 87.52 (9)   |
| O9—Cu1—N12              | 95.33 (10)  | N1—Cu1—N12               | 80.83 (10)  |
| O4 <sup>i</sup> —Cu1—O2 | 106.98 (9)  | N12—Cu1—O2               | 97.62 (10)  |

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

Data collection: XSCANS (Bruker, 1997); cell refinement: XSCANS; data reduction: SHELXTL (Bruker, 2000); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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