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Article

Macrocyclic Copper(II) and Zinc(II) Complexes Incorporating Phosphate Esters

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Slow evaporation of solutions prepared by adding either $Cu(ClO_4)_2 \cdot 6H_2O$ or $Zn(ClO_4)_2 \cdot 6H_2O$ to solutions containing appropriate proportions of Me_3tacn (1,4,7-trimethyl-1,4,7-triazacyclononane) and sodium phenyl phosphate (Na_2PhOPO_3) gave dark blue crystals of $[Cu_3(Me_3tacn)_3(PhOPO_3)_2](ClO_4)_2 \cdot {}^1/_2H_2O$ (**1**) and colorless crystals of $[Zn_2(Me_3tacn)_2(H_2O)_4(PhOPO_3)](ClO_4)_2 \cdot H_2O$ (**2**), respectively. Blue crystals of $[Cu(tacn)_2](BNPP)_2$ (**3**) formed in an aqueous solution of $[Cu(tacn)Cl_2]$, bis(*p*-nitrophenyl phosphate) (BNPP), and HEPES buffer (pH 7.4). Compound **1** crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with $a = 9.8053(2)$ Å, $b = 12.9068(2)$ Å, $c = 22.1132(2)$ Å, $\alpha = 98.636(1)°$, $\beta = 99.546(1)°$, $\gamma = 101.1733(8)°$, and $Z = 2$ and exhibits trinuclear Cu(II) clusters in which square pyramidal metal centers are capped by two phosphate esters located above and below the plane of the metal centers. The trinuclear cluster is asymmetric having Cu···Cu distances of 4.14, 4.55, and 5.04 Å. Compound **2** crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 13.6248(2)$ Å, $b = 11.6002(2)$ Å, $c = 25.9681(4)$ Å, $\beta = 102.0072(9)°$, and $Z = 4$ and contains a dinuclear Zn(II) complex formed by linking two units of $[Zn(Me_3tacn)(OH_2)_2]^{2+}$ by a single phosphate ester. Compound **3** crystallizes in the monoclinic space group $C2/c$ (No. 15) with $a = 24.7105(5)$ Å, $b = 12.8627(3)$ Å, $c = 14.0079(3)$ Å, $\beta = 106.600(1)°$, and Z = 4 and consists of mononuclear $[Cu(tacn)_2]^{2+}$ cations whose charge is balanced by the $BNPP^-$ anions.

Introduction

One successful approach to the investigation of metalloenzymes that catalyze the hydrolysis of phosphate ester bonds in biological molecules[1−4] has been to develop model complexes that reproduce the function, structure, and/or reactivity of the active site.[5−12] The systematic variation of ligands and coordination environments in these biological analogues has provided a valuable insight into the structure and function of enzymes that can be difficult to obtain through the direct study of the protein. Polydentate ligands have been widely applied in the synthesis of discrete metal complexes that offer comparable structural and/or functional metal environments to those found in the enzyme, enable the substrate to bind, and facilitate the formation of a nucleophile to attack the substrate. The complexes applied in the study of the cleavage of phosphate ester bonds range from mononuclear to polynuclear and incorporate a variety of metals, including the d-block transition metals[5−10,12] and the lanthanides.[11,12] Since phosphatases often have two or more coordinatively unsaturated metal centers in the active sites,[1−4] polynuclear mimics are attracting interest. An important finding to emerge from these studies is that although zinc is most commonly found in these enzymes, an extensive range of metal ions has also been found to promote the cleavage of phosphate esters.[9−12]

Metal complexes incorporating various types of phosphate moieties are being examined in order to explore the metal-binding properties of such ligands and to elucidate the importance of these interactions in biological systems. Mononuclear,[13−15] binuclear,[16−28] trinuclear,[29,30] tetranuclear,[31−34]

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and polymeric[35] complexes have been reported in which the phosphate moieties adopt monodentate, chelating, and bridging dispositions. These examples include heterometallic complexes.[36] Moreover, in addition to phosphate and phosphate ester complexes, complexes incorporating nucleic acid fragments, ATP, polyphosphates, and polyphosphate esters have been structurally characterized.[37−41]

Our recent research has focused on the coordination and bioinorganic chemistry of ligand assemblies derived from 1,4,7-triazacyclononane (tacn).[30,42] We have used a trinucleating ligand, consisting of three tacn moieties linked by 1,3,5-trimethylbenzene, to generate a polymeric Cu(II) complex within which an asymmetric trinuclear constellation consisting of three Cu(II) atoms connected by a single bridging phosphate group can be found.[30] The inequivalent Cu···Cu distances in this complex reproduced a feature common to enzymes with three metals at their active sites such as the trizinc enzymes, phospholipase C (PLC), and P1 nuclease.[1−4] The use of tacn-based ligands in the development of phosphatase mimics[9,43] led us to examine the ability of the complexes of this ligand family to cleave phosphate esters.[44] Our studies are also focusing on the reactions of phosphate and phosphate esters with the metal complexes of tacn and its derivatives since the nature of these interactions will impact on the ability of such complexes to catalyze ester cleavage. We report here metal phosphate ester complexes with three nuclearities, viz., $[Cu_3(Me_3tacn)_3(PhOPO_3)_2](ClO_4)_2\cdot{}^1/_2H_2O$ (**1**), a trinuclear complex in which two phenyl phosphates (Ph−PO$_3$) bridge three Cu(II) centers, $[Zn_2(Me_3tacn)_2(H_2O)_4(PhOPO_3)](ClO_4)_2\cdot H_2O$ (**2**), a binuclear complex in which a single PhOPO$_3$ bridges two Zn(II) centers, and $[Cu(tacn)_2](BNPP)_2$ (**3**), a mononuclear complex in which bis(*p*-nitrophenyl phosphate) (BNPP) is the counteranion to the $[Cu(tacn)_2]^{2+}$ sandwich complex (Me$_3$tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane).

Experimental Section

Materials. Chemicals (reagent grade or better) were obtained from commercial suppliers and used without further purification. The synthesis of tacn·3HCl was based on a well-established method.[45] Me$_3$tacn, a kind donation from Unilever, was distilled prior to use. Solvents were used as received or dried over 4 Å molecular sieves.

Instrumentation. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in D$_2$O on either a Bruker AC200 or a Bruker DPX300 spectrometer. Sodium (2,2,3,3-d_4-3-(trimethylsilyl))propionate (TMSP-D) was used as reference for ^{1}H and ^{13}C spectra and phosphoric acid for the ^{31}P spectrum. Infrared spectra were recorded using KBr disks or Nujol mulls on a Perkin-Elmer 1600 series FTIR spectrophotometer. Electron microprobe analyses were recorded with a JEOL JSM-1 scanning electron microscope through an NEC X-ray detector and pulse-processing system connected to a Packard multichannel analyzer. UV−vis−NIR spectra were measured on a Cary 5G spectrophotometer. Solution spectra were recorded using 1 cm quartz cells and solid state spectra on powdered samples. Microanalyses were performed by CMAS, Melbourne, Australia, or by the University of Otago, Dunedin, New Zealand.

Caution**:** *Although no problems were encountered in this work, metal perchlorate complexes are potentially explosive. They should be prepared in small quantities and handled with care.*

$[Cu_3(Me_3tacn)_3(PhOPO_3)_2](ClO_4)_2\cdot{}^1/_2H_2O$ (1). 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me$_3$tacn) (0.145 g, 0.849 mmol) was dissolved in EtOH (5 mL), and an aqueous solution of disodium phenyl phosphate (Na$_2$PhOPO$_3$) was added (0.104 g, 0.424 mmol in 5 mL of water) followed by $Cu(ClO_4)_2\cdot 6H_2O$ (0.314 g, 0.849 mmol). A precipitate formed immediately which redissolved within ca. 1 min. The resulting dark blue solution was heated gently to reduce the volume before being allowed to slowly evaporate at

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Table 1. Crystal Data for **1**, **2**, and **3**

	1	**2**	**3**
chemical formula	$C_{39}H_{74}Cu_3N_9O_{16.5}Cl_2P_2$	$C_{24}H_{57}Cl_2N_6O_{17}Zn_2P$	$C_{36}H_{46}Cu_{10}O_{16}P_2$
M_r, g mol^{-1}	1188.34	934.38	1000.30
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
T (K)	273	273	123
a, Å	9.8053(2)	13.6248(2)	24.7105(5)
b, Å	12.9068(2)	11.6002(2)	12.8627(3)
c, Å	22.1132(3)	25.9681(4)	14.0079(3)
α, deg	98.636(1)		
β, deg	99.546(1)	102.0072(9)	106.600(1)
γ, deg	101.1733(8)		
V, Å^3	2658.98(8)	4014.5(1)	4266.76(16)
Z	2	4	4
D_c, g cm^{-3}	1.569	1.546	1.557
μ(Mo Kα), cm^{-1}	14.13	14.12	6.71
R^a	0.038	0.039	0.041
R_w	0.040^b	0.041^b	0.077^c

^{a} $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. ^{c} $R_w = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$.

ambient temperature. Dark blue crystals had formed after several days and were suitable for X-ray crystallography. Yield: 0.18 g (51%).

Characterization Data. Anal. Found (%): C, 37.2; H, 5.9; N 10.1. Calcd for $Cu_3C_{39}H_{74}N_9O_{16.5}Cl_2P_2$ (%): C, 37.3; H, 5.9; N, 10.0. UV−vis−NIR spectrum, diffuse reflectance (λ_{max}, nm): 650, 1049. Solution in H_2O (λ_{max}, nm (ϵ, M^{-1}cm^{-1})) 268 (12600), 658 (140), 1140 (85). Major IR bands (KBr, ν, cm^{-1}): 3616 m, 3531 m, 3063 w, 2915 m, 2875 m, 2826 m, 1595 s, 1494 s, 1464 s, 1364 m, 1303 m, 1240 s, 1155 s, 1097 s, 1009 s, 882 s, 767 s, 743 m, 696 m, 623 s, 575 m, 556 m, 530 s. Electron microprobe: Cu, P, and Cl present.

[Zn$_2$(Me$_3$tacn)$_2$(H$_2$O)$_4$(PhOPO$_3$)](ClO$_4$)$_2$·H$_2$O (2). To 20 mL of an ethanol solution of Me$_3$tacn (0.50 g, 2.9 mmol) was added an aqueous solution of $Zn(ClO_4)_2\cdot 6H_2O$ (1.10 g, 2.90 mmol in 10 mL of water), followed by a third molar amount of disodium phenyl phosphate (Na_2PhOPO_3) (0.25 g, 0.97 mmol in 10 mL of water). After slow evaporation, colorless crystals suitable for X-ray crystallography were deposited. These were collected by vacuum filtration and allowed to air-dry. Yield: 0.32 g (34%).

Characterization Data. Anal. Found (%): C, 29.9; H, 6.0; N, 8.7. Calcd for $Zn_2C_{24}H_{61}N_6O_{19}PCl_2$ (%): C, 29.7; H, 6.3; N, 8.7. Major IR bands (KBr; ν, cm^{-1}): 3496 s br, 2870 m, 2825 m, 1654 m, 1639 m, 1594 m, 1490 s, 1467 m, 1426 w, 1366 m, 1303 m, 1235 m, 1090 s br, 1015 s, 994 s, 891 m, 770 m, 746 m, 696 m, 626 s, 554 m. ^{1}H NMR (D_2O): δ 2.54 (s, 9H, CH_3), 2.74 (m, 12H, CH_2 tacn ring), 7.11 (tm, 1H ArCH), 7.21 (dm, 2H, CH_2 tacn ring), 7.36 (t m, 2H, ArCH). ^{13}C NMR (D_2O): δ 45.76 (CH_3), 52.45 (CH_2), 120.16 (ArCH), 122.60 (ArCH), 129.36 (ArCH), 157.73 (quaternary C). ^{31}P NMR (D_2O): δ 1.03 (s, $C_6H_5OPO_3$). Electron microprobe: Zn, Cl, and P present. Electrospray mass spectrum (H_2O/MeOH) (m/z): 817 {[Zn$_2$(Me$_3$tacn)$_2$(PhOPO$_3$)(H$_2$O)$_4$]ClO$_4$}$^+$, 741 {[Zn$_2$(Me$_3$tacn)$_2$(PhOPO$_3$)]ClO$_4$}$^+$.

[Cu(tacn)$_2$](BNPP)$_2$ (3). Method A. A 4 mL solution containing sodium bis(p-nitrophenyl)phosphate (NaBNPP, 5 mM), [Cu(tacn)Cl$_2$] (5 mM), and HEPES (50 mM) at pH 7.4 was maintained at 38 °C for 6 days. A small amount of blue crystals of **3**, suitable for single crystal X-ray analysis, deposited after the solution was cooled to room temperature and allowed to stand overnight.

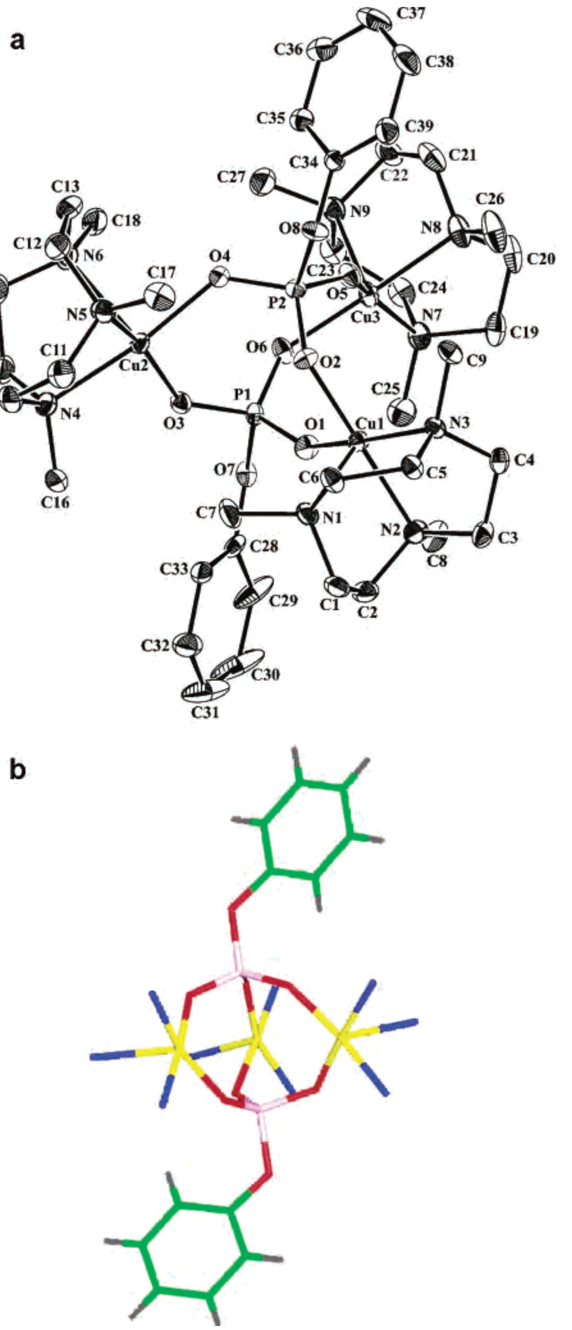

Figure 1. (a) ORTEP plot of [Cu$_3$(Me$_3$tacn)$_3$(PhOPO$_3$)$_2$]$^{2+}$ cations (**1**) with atomic labeling scheme; (b) schematic diagram of **1** with only nitrogens of the Me$_3$tacn units shown for clarity.

Method B. An aqueous solution prepared by dissolving $Cu(ClO_4)_2\cdot 6H_2O$ (0.10 g, 0.27 mmol) in 5 mL of water was added to an aqueous solution of tacn·3HCl (0.13 g, 0.53 mmol dissolved in 10 mL of water). Adjustment of the pH to 5−6 with 1 M NaOH formed a dark blue solution. A solution of NaBNPP (0.09 g, 0.27 mmol) dissolved in a minimum amount of water was then added, producing a small amount of precipitate. More precipitate formed when the pH was increased to ∼7 by adding 1 M NaOH. After standing overnight, the blue product was collected by vacuum filtration, washed three times with water followed by ethanol, and then air-dried. Yield: 0.10 g (80%)

Characterization Data. Found (%): C, 43.1; H, 4.8; N, 14.2. Calcd for $CuC_{36}H_{46}N_{10}O_{16}P_2$ (%): C, 43.2; H, 4.6; N, 14.0. UV−vis−NIR spectrum, diffuse reflectance (λ_{max}, nm): 619, 334. Major IR bands (Nujol, ν, cm^{-1}): 3277 w, 3214 m, 1608 m, 1594 m, 1511s, 1486 m, 1341 s, 1291 m, 1261 s, 1237 s, 1087 s, 910 m, 855 s, 751 m, 737 w, 687 m, 648 w, 612 m, 557 w. Electrospray

Table 2. Selected Bond Distances (Å) and Angles (deg) in **1**

P(1)−O(1)	1.505(2)	P(2)−O(2)	1.514(2)
P(1)−O(3)	1.514(2)	P(2)−O(4)	1.513(2)
P(1)−O(6)	1.511(2)	P(2)−O(5)	1.510(2)
P(1)−O(7)	1.635(2)	P(2)−O(8)	1.633(2)
Cu(1)−N(1)	2.224(2)	Cu(3)−N(7)	2.095(2)
Cu(1)−N(2)	2.073(2)	Cu(3)−N(8)	2.073(2)
Cu(1)−N(3)	2.057(2)	Cu(3)−N(9)	2.238(2)
Cu(1)−O(1)	1.917(2)	Cu(3)−O(5)	1.924(2)
Cu(1)−O(2)	1.932(2)	Cu(3)−O(6)	1.938(2)
Cu(2)−N(4)	2.092(2)	Cu(2)−O(3)	1.959(2)
Cu(2)−N(5)	2.089(2)	Cu(2)−O(4)	1.944(2)
Cu(2)−N(6)	2.248(2)		
O(1)−P(1)−O(3)	115.0(1)	O(2)−P(2)−O(4)	112.38(10)
O(1)−P(1)−O(6)	114.83(10)	O(2)−P(2)−O(5)	114.73(10)
O(1)−P(1)−O(7)	103.85(9)	O(2)−P(2)−O(8)	101.39(10)
O(3)−P(1)−O(6)	113.67(10)	O(4)−P(2)−O(5)	114.58(10)
O(3)−P(1)−O(7)	106.16(9)	O(4)−P(2)−O(8)	107.33(9)
O(6)−P(1)−O(7)	101.41(10)	O(5)−P(2)−O(8)	104.93(10)
N(1)−Cu(1)−N(2)	83.47(8)	N(7)−Cu(3)−N(8)	84.45(9)
N(1)−Cu(1)−N(3)	84.34(8)	N(7)−Cu(3)−N(9)	82.92(8)
N(1)−Cu(1)−O(1)	108.64(8)	N(7)−Cu(3)−O(5)	159.14(7)
N(1)−Cu(1)−O(2)	93.42(7)	N(7)−Cu(3)−O(6)	93.17(8)
N(2)−Cu(1)−N(3)	85.18(8)	N(8)−Cu(3)−N(9)	83.32(9)
N(2)−Cu(1)−O(1)	91.15(8)	N(8)−Cu(3)−O(5)	88.67(8)
N(2)−Cu(1)−O(2)	176.22(8)	N(8)−Cu(3)−O(6)	175.68(8)
N(3)−Cu(1)−O(1)	165.65(8)	N(9)−Cu(3)−O(5)	115.85(8)
N(3)−Cu(1)−O(2)	92.38(7)	N(9)−Cu(3)−O(6)	92.87(7)
O(1)−Cu(1)−O(2)	92.89(7)	O(5)−Cu(3)−O(6)	94.77(7)
N(4)−Cu(2)−N(5)	83.85(8)	Cu(1)−O(1)−P(1)	148.8(1)
N(4)−Cu(2)−N(6)	82.65(8)	Cu(1)−O(2)−P(2)	126.7(1)
N(4)−Cu(2)−O(3)	90.70(7)	Cu(2)−O(3)−P(1)	135.2(1)
N(4)−Cu(2)−O(4)	172.86(7)	Cu(2)−O(4)−P(2)	130.0(1)
N(5)−Cu(2)−N(6)	83.41(9)	Cu(3)−O(5)−P(2)	142.9(1)
N(5)−Cu(2)−O(3)	160.91(8)	Cu(3)−O(6)−P(1)	129.8(1)
N(5)−Cu(2)−O(4)	91.96(8)	N(6)−Cu(2)−O(4)	91.14(7)
N(6)−Cu(2)−O(3)	114.10(8)	O(3)−Cu(2)−O(4)	95.07(7)

Table 3. Comparison of Selected Bond Lengths and Angles for the Copper(II) Centers in **1**

	Cu(1)	Cu(2)	Cu(3)
Cu−N(apical)	2.224(2)	2.248(2)	2.238(2)
Cu−N(basal)	2.073(2)	2.092(2)	2.079(2)
	2.057(2)	2.089(2)	2.095(2)
Cu−O(phosphate)	1.917(2)	1.959(2)	1.924(2)
	1.932(2)	1.944(2)	1.938(2)
N(apical)−Cu−N(basal)	83.47(8)	82.65(8)	82.92(8)
	84.34(8)	83.41(9)	83.32(9)
N(basal)−Cu−N(basal)	85.18(8)	83.65(8)	84.45(9)
N(apical)−Cu−O(phosphate)	108.64(8)	114.10(8)	115.85(8)
	93.72(7)	91.14(7)	92.87(7)
N(basal)−Cu−O(phosphate)	91.15(8)	90.70(7)	88.67(8)
	92.38(7)	91.96(8)	93.17(8)
	165.65(8)	160.91(8)	159.14(7)
	176.22(8)	172.86(7)	175.68(8)
Cu−O−P	148.8(1)	135.2(1)	142.9(1)
	126.7(1)	130.0(1)	129.8(1)

mass spectrum (MeOH) (*m*/*z*): 660 $\{[Cu(tacn)_2](BNPP)\}^+$, 531 $\{[Cu(tacn)](BNPP)\}^+$.

X-ray Structure Determination. Intensity data for dark blue crystals of **1**, colorless crystals of **2**, and blue crystals of **3** were measured on a Nonius Kappa CCD fitted with graphite-monochromated Mo Kα radiation (0.71073 Å). Data were collected to a maximum 2θ value of 59.1°, 55.0°, and 60.0°, respectively, and processed using the Nonius software. The structures of **1** and **2** were solved by direct methods, expanded using Fourier techniques, and refined by full-matrix least-squares on F in the teXsan software package.[46] The structure of **3** was also solved by direct methods but was refined by full-matrix least-squares on F^2 using the SHELXS-97 program suite.[47] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogens were included in calculated positions but not refined. Crystal parameters and details of the data collection, solution, and refinement are summarized in Table 1. ORTEP perspectives of the complexes are presented in Figures 1−3, and selected bond lengths and angles in Tables 1−3.

Results and Discussion

Syntheses. $[Cu_3(Me_3tacn)_3(PhOPO_3)_2](ClO_4)_2 \cdot {}^1/_2H_2O$ (**1**) was initially prepared by mixing an ethanol solution of 1,4,7-trimethyl-1,4,7-triazacyclononane (Me$_3$tacn) with an aqueous solution of disodium phenyl phosphate (Na_2PhOPO_3), and then adding $Cu(ClO_4)_2 \cdot 6H_2O$ (Me$_3$tacn/Cu/PhOPO$_3$ ratio 1:1:0.5). Dark blue crystals of **1** deposited on slow evaporation. A second synthesis, using a Me$_3$tacn/Cu/PhOPO$_3$ ratio (3:3:2) that matched that in the product, afforded a higher yield. In the IR spectrum, strong phosphate stretches at 1240 and 1155 cm^{-1}, and bands at 1595 and 767 cm^{-1} due to C═C vibrations and out of plane bending vibrations of the aromatic ring, respectively, indicated the presence of the phosphate ester. Two sharp ν(OH) stretches at 3616 and 3531 cm^{-1} are due to the water in the crystal lattice. The aqueous solution and solid state (in brackets) electronic spectra of **1** exhibit two weak d → d absorption maxima at 660 (650) and 1140 (1049) nm, which are in the typical range for Cu(II) complexes with distorted square pyramidal geometry commonly formed by tacn-based ligands and are due to the $d_{z^2} \rightarrow d_{x^2-y^2}$ and $d_{yz} \rightarrow d_{x^2-y^2}$ transitions.[42]

$[Zn_2(Me_3tacn)_2(H_2O)_4(PhOPO_3)](ClO_4)_2 \cdot H_2O$ (**2**) was prepared by the method used for **1**. The Me$_3$tacn/Zn/PhOPO$_3$ ratio was 3:3:1. The IR spectrum of **2** also exhibited bands attributable to phenyl phosphate. The presence of Me$_3$tacn and $PhOPO_3^{2-}$ was confirmed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The methylene protons on Me$_3$tacn ligand were observed as multiplets that may be resulting from different orientations of the tacn nitrogens relative to the phosphate ester bridge, i.e., *cis* or *trans*. The methyl groups on Me$_3$tacn, however, give rise to one signal. Elemental analyses of **2** supported the composition established by X-ray crystallography, except that the bulk sample analyzed as a dihydrate. The electrospray mass spectrum shows peaks corresponding to $\{[Zn(Me_3tacn)_2(H_2O)_4(PhOPO_3)](ClO_4)\}^+$ and $\{[Zn(Me_3tacn)_2(PhOPO_3)](ClO_4)\}^+$ at *m*/*z* 817 and 741, respectively.

Blue crystals of $[Cu(tacn)_2](BNPP)_2$ (**3**) formed when an aqueous solution containing $[Cu(tacn)Cl_2]$, BNPP, and HEPES (pH 7.4) buffer was left at 38 °C for 6 days and then allowed to stand at room temperature overnight. Direct reaction using copper(II) perchlorate, tacn·3HCl, and NaBNPP at pH ∼ 7 gave the same product. Bands attributable to the phosphate ester were again evident in the IR spectrum. In particular, strong bands at 1511 and 1341 cm^{-1} confirmed the presence of bis(*p*-nitrophenylate).

Crystal Structure of $[Cu_3(Me_3tacn)_3(PhOPO_3)_2](ClO_4)_2 \cdot {}^1/_2H_2O$ (1). An X-ray structural analysis established that **1**

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[46] *TeXsan: Crystal Structure Analysis Package*; Molecular Structure Corporation: Houston, TX, 1992.

[47] Sheldrick, G. M. *SHELXS-97*; University of Göttingen: Göttingen, Germany, 1997.

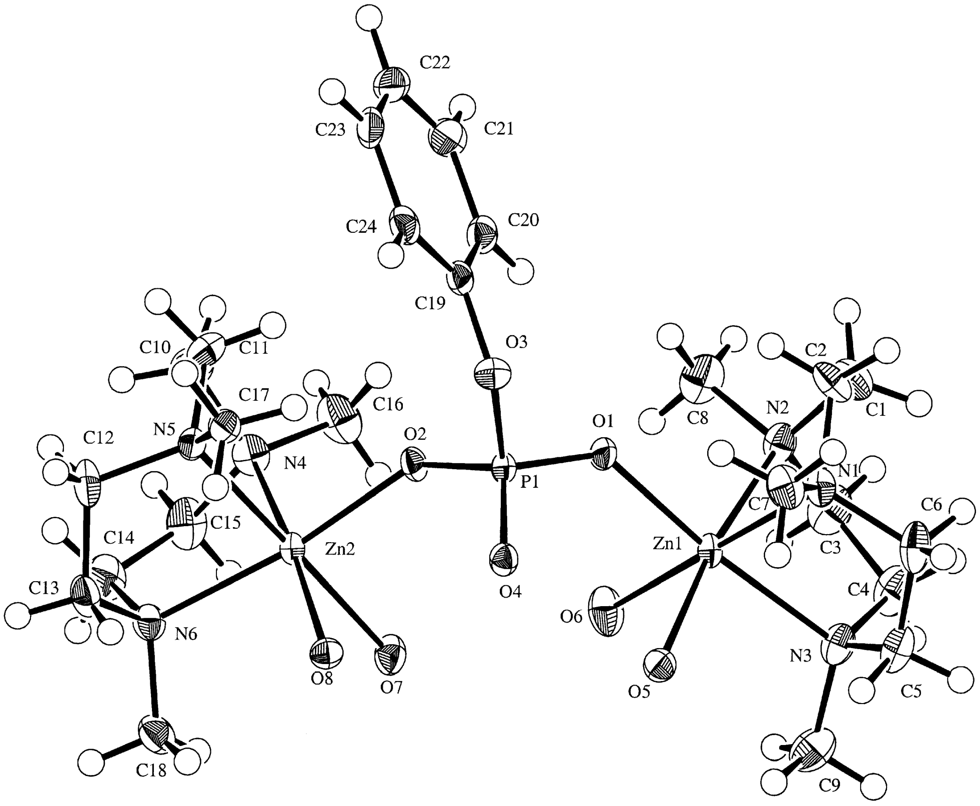

Figure 2. ORTEP plot of $[Zn_2(Me_3tacn)_2(H_2O)_4(PhOPO_3)]^{2+}$ cation (**2**) with atomic labeling scheme.

consists of discrete $[Cu_3(Me_3tacn)_3(PhOPO_3)_2]^{2+}$ cations, perchlorate anions, and water of crystallization. The ORTEP plot (Figure 1a) shows the complex cation to consist of three $[Cu(Me_3tacn)]^{2+}$ moieties linked together by the two phosphate esters via three oxygens, and thus, all three Cu(II) centers are linked to each other by two Cu−O−P−O−Cu bridging units. The two phosphate esters lie above and below the plane defined by the Cu(Me$_3$tacn) units, with the phenoxy groups located perpendicular to the triangular array of copper atoms (Figure 1b). An interesting result of this binding of the two organophosphates is the generation of an empty 11-atom cage defined by the three Cu atoms and two $PhOPO_3^{2-}$ units. Each Cu(II) center is in a distorted square pyramidal (SP) geometry with the Me$_3$tacn macrocycle occupying one face of a distorted square pyramid and phosphate oxygens in the other two coordination sites. The τ values of 0.18, 0.20, and 0.28 for Cu(1), Cu(2), and Cu(3), respectively, calculated using the method of Addison et al.,[48] indicate significant distortion from ideal SP geometry. The Cu−N distances and N−Cu−N angles for the macrocycle donor atoms are typical for tacn complexes.[42] For example, the Cu(1)−N(1) distance to the apical nitrogen (2.224(2) Å) is, as expected, longer than those in the basal plane (viz., Cu(1)−N(2) = 2.073(2) Å and Cu(1)−N(3) = 2.057(2) Å) due to Jahn−Teller distortion in the d^9 Cu center (Table 2). The Cu−O distances (1.917(2) and 1.932(2) Å) are typical for Cu(II) complexes in which the oxygen of either a phosphate or a phosphate monoester is bound in an equatorial position.[19a,23,26,30,32,33] For comparison, the Cu−O distances for apically coordinated phosphate moieties are ca. 0.2 Å longer.[33,49]

Table 4. Selected Bond Distances (Å) and Angles (deg) in **2**

Zn(1)−N(1)	2.173(3)	Zn(2)−N(4)	2.170(3)
Zn(1)−N(2)	2.167(2)	Zn(2)−N(5)	2.188(2)
Zn(1)−N(3)	2.172(2)	Zn(2)−N(6)	2.176(3)
Zn(1)−O(1)	1.997(2)	Zn(2)−O(2)	2.006(2)
Zn(1)−O(5)	2.155(2)	Zn(2)−O(7)	2.232(2)
Zn(1)−O(6)	2.185(2)	Zn(2)−O(8)	2.126(2)
N(1)−Zn(1)−N(2)	82.34(10)	N(4)−Zn(2)−N(5)	82.85(9)
N(1)−Zn(1)−N(3)	82.83(10)	N(4)−Zn(2)−N(6)	82.29(10)
N(1)−Zn(1)−O(1)	91.37(9)	N(4)−Zn(2)−O(2)	93.79(9)
N(1)−Zn(1)−O(5)	93.51(9)	N(4)−Zn(2)−O(7)	95.35(9)
N(1)−Zn(1)−O(6)	175.69(8)	N(4)−Zn(2)−O(8)	173.85(9)
N(2)−Zn(1)−N(3)	82.48(9)	N(5)−Zn(2)−N(6)	82.14(9)
N(2)−Zn(1)−O(1)	94.59(8)	N(5)−Zn(2)−O(2)	91.52(9)
N(2)−Zn(1)−O(5)	172.71(8)	N(5)−Zn(2)−O(7)	177.76(8)
N(2)−Zn(1)−O(6)	93.82(9)	N(5)−Zn(2)−O(8)	100.35(8)
N(3)−Zn(1)−O(1)	173.79(9)	N(6)−Zn(2)−O(2)	172.89(9)
N(3)−Zn(1)−O(5)	91.08(8)	N(6)−Zn(2)−O(7)	96.33(9)
N(3)−Zn(1)−O(6)	94.76(9)	N(6)−Zn(2)−O(8)	92.89(8)
O(1)−Zn(1)−O(5)	91.49(7)	O(2)−Zn(2)−O(7)	89.92(8)
O(1)−Zn(1)−O(6)	90.89(8)	O(2)−Zn(2)−O(8)	91.40(8)
O(5)−Zn(1)−O(6)	90.10(8)	O(7)−Zn(2)−O(8)	81.33(7)

The phosphorus atom in the ester adopts a distorted tetrahedral geometry. The P−O distances (ca. 1.51 Å) for the copper bound oxygens are shorter than the P−O ester bond (ca. 1.63 Å) but are typical of copper-bound phosphate moieties.[19a,26] The O−P−O bond angles for the bridging oxygens are slightly more acute than those in similar structures, viz., ∼114° cf. 118°[19] and 119°.[26] These angles are also more acute than the O−P−O bond angle spanned by the two nonester oxygens in the BNPP anion in **3** (119.72-

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(48) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

(49) Ott, R.; Krämer, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1957.

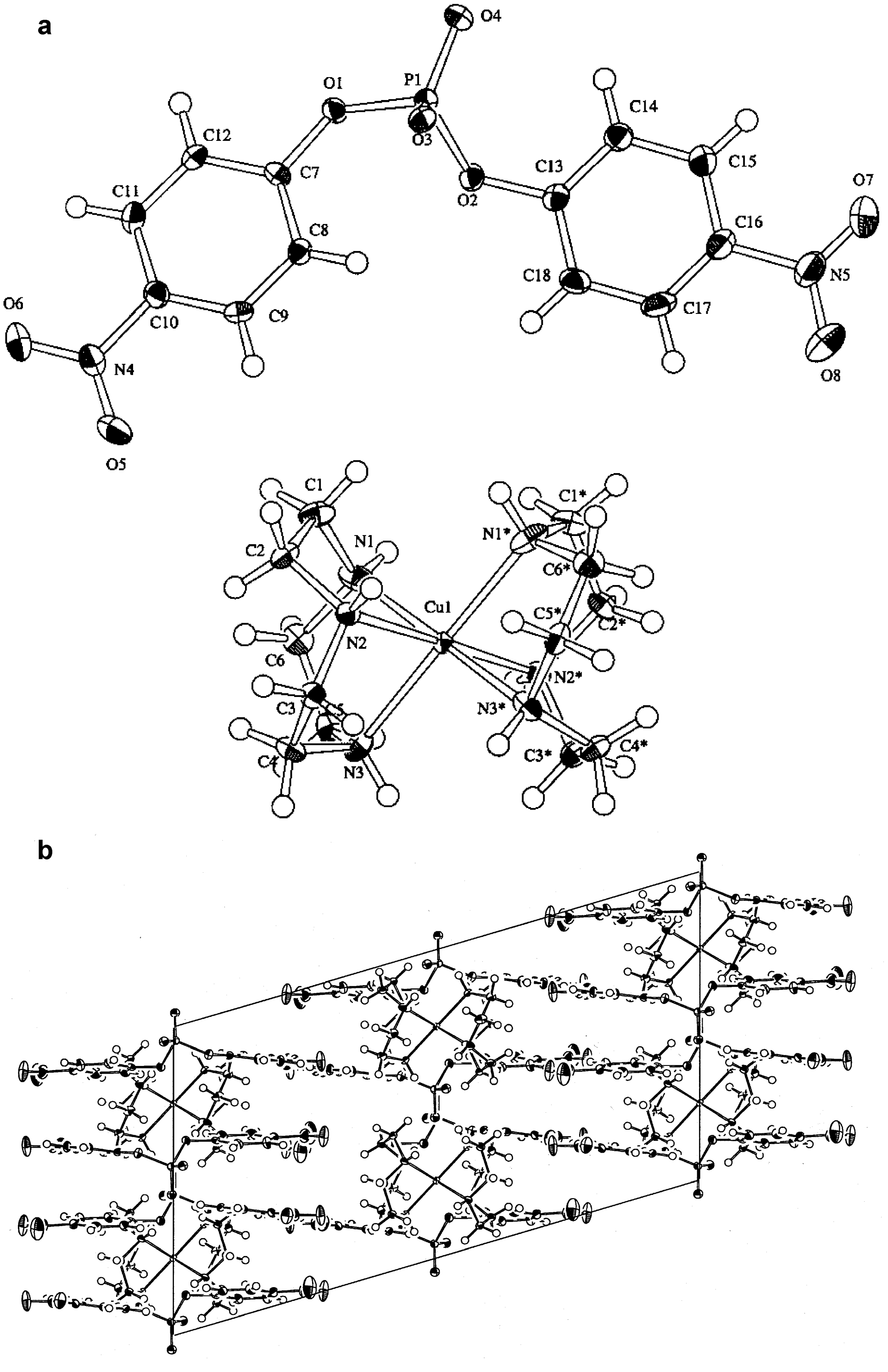

Figure 3. (a) ORTEP plot with atomic labeling scheme and (b) packing diagram of $[Cu(tacn)_2](BNPP)_2$ (**3**).

(7)°) (see Table 2) and in a H-bonded supramolecular complex reported by Gieb et al. (121.2°).[50]

Complex **1** is unique in the way that two organophosphates are bound to three Cu(II) centers. Most other Cu(II) complexes with coordinated phosphate moieties are usually binuclear and, often, have other groups bridging the two Cu(II) centers. An exception is the trinuclear copper array found in the polymeric complex, $\{[Cu_3(T_3mes)(\mu\text{-OH})(\mu_3\text{-HPO}_4)(H_2O)][PF_6]\cdot 3H_2O\}_n$, in which the three Cu(II) centers are linked by an HPO_4^{2-} bridge.[30] This complex, as is the case for most related binuclear complexes, however, has an additional bridge (hydroxo) connecting two of the Cu(II) centers. Other trinuclear non-copper clusters, which, like **1**, have three metal centers bridged by phosphates, include a trinuclear complex which has three [Zn(cyclen)] units (cyclen = 1,4,7,10-tetraazacyclododecane) linked by

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(50) Gieb, S. J.; Hirst, S. C.; Vincent, C.; Hamilton, A. D. *J. Chem. Soc., Chem. Commun.* **1991**, 1283.

the three phosphate oxygens from one nitrophenyl phosphate.[29] In contrast to the example presented here, this Zn(II) complex has a symmetric arrangement of metal centers.

The asymmetry of the trinuclear cluster in **1** is highlighted by the three distinct Cu···Cu distances (Cu(1)···Cu(2) 4.55 Å, Cu(2)···Cu(3) 5.04 Å, and Cu(1)···Cu(3) 4.14 Å). Complementing this asymmetry is the variation in the geometry of each Cu(II) center that is reflected in significant differences in the analogous bond angles and distances around Cu(1), Cu(2), and Cu(3) (Table 3). Shorter M···M distances have been observed in metal complexes with one or more additional single atom bridges between the metal centers. Incorporation of a single atom bridge, in addition to an O−P−O bridge, results in M···M distances of ca. 3.6 Å.[20,24,26] The Cu(1)···Cu(3) distance of 4.14 Å is quite short for two metal centers that are linked by three atom phosphate bridges. These are often greater than 5 Å (e.g., see refs 6, 18, 29, 31, 32, 34). Notably, this Cu(1)···Cu(3) distance is approaching the Zn···Zn separation of 3.94 Å in phosphate modified alkaline phosphatase (AP), where one O−P−O bridges two Zn centers,[51] and is shorter than the distance between similarly bridged Zn centers in phosphate modified PLC (4.5 Å).[52]

Crystal Structure of $[Zn_2(Me_3tacn)_2(H_2O)_4(PhOPO_3)](ClO_4)_2 \cdot H_2O$ (2). The X-ray structure of **2** confirmed the presence of dinuclear $[Zn_2(Me_3tacn)_2(H_2O)_4(PhOPO_3)]^{2+}$ cations (Figure 2) in which one phosphate ester uses two oxygens to bridge two Zn−Me_3tacn moieties. The absence of additional bridging groups results in a relatively large Zn···Zn separation (5.05 Å). The distorted octahedral coordination sphere of each zinc(II) center, indicated by the bond lengths and angles shown in Table 4, is composed of the three macrocycle nitrogens, two water ligands, and an oxygen from the bridging phosphate. The six Zn−N bond lengths are all very similar, av. 2.174 Å, as are the Zn−O(phosphate) distances (1.997(2)−2.006(2) Å). The Zn−O(water) distances on the other hand vary significantly (2.126(2)−2.232(2) Å). Interestingly, the two zinc centers exhibit some differences in the N−Zn−O(water) and the O(water)−Zn−O(water) bond angles. For example, the O(5)−Zn(1)−O(6) angle is close to the ideal octahedral angle (90.10(8)°); however, the equivalent bond angle on Zn(2), O(7)−Zn(2)−O(8), is more acute at 81.33(7)°. The crystal lattice is stabilized by a H-bonding network formed by the bound and free waters and the perchlorate counterions.

In contrast to **1**, complex **2** features two-coordinated water molecules per metal center, which on deprotonation could act as internal nucleophiles in phosphate ester cleavage, as has been proposed for enzymes such as alkaline phosphatase (AP). Other groups have isolated complexes in which two zinc centers are linked by an O−P−O bridge.[16,18,21,29,34] Adams et al.[21] report the structure of two mono-zinc units linked by an *p*-nitrophenylate (NPP) unit in which NPP connects the two Zn(II) centers in the same way as $PhOPO_3^{2-}$ in **2**. The Zn···Zn distance (5.97 Å), however, is longer than that in **2** (5.05 Å). For the NPP complex, use of the tripodal tetradentate ligand tris[(2-pyridyl)methyl]amine (tpa) results in a disordered trigonal bipyramidal zinc(II) geometry that is fully occupied by four tpa nitrogens and one phosphate ester oxygen. Kitajima and co-workers[18] were able to use the tridentate ligand, hydro-tris(3,5-diisopropyl-1-pyrazolyl)-borate, to generate an NPP bridged binuclear complex in which the zinc(II) centers adopt a distorted tetrahedral geometry. More recently, Bazzicalupi et al.[16] reported a binuclear complex of binucleating ligand in which two diphenyl phosphates bridge two Zn(II) centers and a MeOH ligand completes the distorted octahedral metal coordination sphere. The Zn···Zn distances in these complexes are all longer than that found in **2**.

Table 5. Selected Bond Distances (Å) and Angles (deg) in **3**[a]

P(1)−O(1)	1.505(2)	P(2)−O(2)	1.514(2)
P(1)−O(1)	1.6183(12)	P(1)−O(3)	1.4761(13)
P(1)−O(2)	1.6210(12)	P(1)−O(4)	1.4812(12)
Cu(1)−N(1)	2.1817(17)	Cu(1)−N(1)#1	2.1818(17)
Cu(1)−N(2)	2.0916(14)	Cu(1)−N(2)#1	2.0917(14)
Cu(1)−N(3)	2.1691(16)	Cu(1)−N(3)#1	2.1692(16)
O(1)−P(1)−O(2)	97.07(6)	O(2)−P(1)−O(3)	110.08(7)
O(1)−P(1)−O(3)	111.49(7)	O(2)−P(1)−O(4)	110.63(7)
O(1)−P(1)−O(4)	105.42(7)	O(3)−P(1)−O(4)	119.72(7)
N(1)−Cu(1)−N(2)	81.44(5)	N(2)−Cu(1)−N(3)#1	97.72(5)
N(1)−Cu(1)−N(3)	80.88(6)	N(3)−Cu(1)−N(1)#1	179.12(6)
N(1)−Cu(1)−N(1)#1	99.02(8)	N(3)−Cu(1)−N(2)#1	97.72(5)
N(1)−Cu(1)−N(2)#1	99.01(6)	N(3)−Cu(1)−N(3)#1	99.24(8)
N(1)−Cu(1)−N(3)#1	179.13(6)	N(1)#1−Cu(1)−N(2)#1	81.43(5)
N(2)−Cu(1)−N(3)	81.84(5)	N(1)#1−Cu(1)−N(3)#1	80.88(6)
N(2)−Cu(1)−N(1)#1	99.01(6)	N(2)#1−Cu(1)−N(3)#1	81.84(5)
N(2)−Cu(1)−N(2)#1	179.33(8)		

[a] #1 represents the second tacn ring.

The M···M separation for metal centers found at the active sites of phosphatase enzymes is generally shorter than in **2**. For example, in AP isolated with coordinated phosphate, the Zn···Zn distance is 3.94 Å.[51] In the enzyme, the Zn(II) centers are coordinated to the less sterically demanding inorganic phosphate molecule, which may allow closer approach of the two zinc centers. In addition, the synthetic models are not subjected to the constraints imposed by the presetting of the metal-binding cleft in the protein. In phosphate modified PLC, in which phosphate coordinates to all three zinc centers, the distances are the following: Zn(1)···Zn(2) = 5.7 Å; Zn(1)···Zn(3) = 3.5 Å; Zn(2)···Zn(3) = 4.5 Å.[52] In this case, however, the shorter of the Zn···Zn separations is a consequence of a single phosphate oxygen bridge.

Crystal Structure of $[Cu(tacn)_2](BNPP)_2$ (3). The X-ray crystal structure of $[Cu(tacn)_2](BNPP)_2$ confirmed that BNPP is the counteranion to the $[Cu(tacn)_2]^{2+}$ sandwich complex (see Figure 3a). The structure of the tricyanocuprate(II) and perchlorate salts of $[Cu(tacn)_2]^{2+}$ has been reported previously, and the bond angles and lengths in **3** (Table 5) show minor variations from those in these reports.[53,54] An interesting feature of the structure of **3** is the

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(51) Hansen, S.; Hansen, L. K.; Hough, E. *J. Mol. Biol.* **1992**, *255*, 543.

(52) Kim, E. E.; Wyckoff, H. W. *J. Mol. Biol.* **1991**, *218*, 449.

(53) Chaudhuri, P.; Oder, K.; Wieghardt, K.; Weiss, J.; Reedijk, J.; Hinrichs, W.; Wood, J.; Ozarowski, A.; Stratemaier, H.; Reinen, D. *Inorg. Chem.* **1986**, *25*, 2951.

(54) Beveridge, A. D.; Lavery, A. J.; Walkinshaw, M. D.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1987**, 373.

π-stacking of the phenyl rings (see Figure 3b) which results in a short contact distance of 3.348 Å between C(8) and C(18).

The crystallization of the sandwich complex from an aqueous solution containing $[Cu(tacn)(H_2O)_2]^{2+}$ and BNPP indicates that some $[Cu(tacn)_2]^{2+}$ is present in solution. This may have been present in the initial analytically pure sample of $[Cu(tacn)Cl_2]$, but some $[Cu(tacn)_2]^{2+}$ complex could also be formed on dissolution of $[Cu(tacn)Cl_2]$ in water. This is possible because ligand exchange on Cu(II) is very fast, often occurring on the submicrosecond time scale. Previous insightful studies on $[M(tacn)_2]^{2+}$ complexes have found that dissociation occurs in aqueous solution.[53−55] In the case of $[Cu(tacn)_2]^{2+}$, bis(macrocyclic) products, $[Cu(tacn)_2S_n]^{2+}$ (S = solvent), in which one tacn ligand is monodentate and the other bidentate, and monomacrocyclic products, $[Cu(tacn)S_n]^{2+}$, are formed.[55] Conversely, rapid ligand exchange on $[Cu(tacn)(H_2O)_2]^{2+}$ could generate some sandwich complex from which, in the presence of BNPP, $[Cu(tacn)_2](BNPP)_2$ crystallizes.

Conclusions

The isolation of two complexes incorporating bridging phosphate esters provides further insights into the preferred metal binding modes of such moieties that are of relevance to the binding of phosphate esters to the active site of enzymes that catalyze phosphoryl transfer reactions. The information will also be useful in the interpretation of the cleavage of phosphate esters by metal complexes.

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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