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Formation of a Tetranuclear Copper (II) Cluster Assembled by Metal-Assisted Hydrolysis and Desulfurization of Bis(3,5-dimethylpyrazolyl)methylphosphine Sulfide, $MeP(S)(3,5\text{-}Me_2Pz)_2$[#]

V. Chandrasekhar,*,[†] S. Kingsley,[†] A. Vij,[‡] K. C. Lam,[§] and A. L. Rheingold[§]

Department of Chemistry, Indian Institute of Technology, Kanpur-208016, India,
Department of Chemistry, University of Idaho, Moscow, Idaho 83844-3010, and
Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

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The reaction of methylphosphine sulfide, $MeP(S)(3,5\text{-}Me_2Pz)_2$, **1**, with anhydrous $CuCl_2$ affords a tetranuclear copper cluster$[Cu_2Cl_2(3,5\text{-}Me_2Pz)_3(MePO_3)]_2$, **2**, and a dinuclear compound $Cu_2Cl_4(3,5\text{-}Me_2Pz)_4$, **3**. This reaction involves a metal-assisted desulfurization along with concomitant hydrolysis of P−N bonds. The X-ray structures of **1**−**3** have been determined, and the crystal parameters for these are the following. **1**: space group = $C2/c$, a = 15.2552(1) Å, b = 8.7364(2) Å, c = 21.4490(3) Å, β = 93.349(1)°, V = 2853.74(8) Å^3, and Z = 8. **2**: space group = $P2_1/n$, a = 12.5964(4) Å, b = 15.7773(4) Å, c = 13.9781(4) Å, β = 116.6280(10)°, V = 2483.32(12) Å^3, and Z = 2. **3**: space group = $P2_1/c$, a = 8.7137(8) Å, b = 13.5493(14) Å, c = 11.8847(12) Å, β = 106.179(2)°, V = 1347.6(2) Å^3, and Z = 2. The structure of **2** shows that it comprises two dinuclear copper cores bridged together by two tripodal methylphosphinate, $MePO_3$, ligands. **2** is weakly antiferromagnetically coupled, as revealed by variable temperature magnetic susceptibility measurements.

Introduction

Copper (II) complexes are of great interest from both structural and functional points of view.[1] The coordination sphere around the Cu(II) ion can be modulated relatively easily, and this structural flexibility has led to the isolation of a number of mono- and multinuclear copper (II) complexes.[1a,1c] Many of the multinuclear complexes are of interest because of their relevance as active site structures of biomolecules[1b,3] and also because of the interesting magnetic properties that they display.[2] Recently, there has also been interest in the use of copper (II) complexes as artificial metallopeptidases.[4]

We have been studying the interaction of metal ions in general and that of Cu(II) in particular with a number of inorganic heterocyclic ligands based on pyrazolyl-substituted cyclophosphazenes and have observed an interesting N_3 coordination mode from the ligand involving two exocyclic pyrazolyl nitrogen atoms and one cyclophosphazene ring nitrogen atom to the copper (II) ion.[5] To extend this study to the acyclic pyrazolyl-substituted phosphorus (V) derivatives we have prepared bis(3,5-dimethylpyrazolyl)methylphosphine sulfide, $MeP(S)(3,5\text{-}Me_2Pz)_2$, **1**, and studied its reaction with copper (II) chloride. We report the isolation of an unusual tetranuclear copper (II) cluster in this reaction, which is formed as a result of a metal-assisted hydrolysis of P−N bonds with a concomitant desulfurization involving the cleavage of the P═S bond.

Experimental Section

Reagents and General Procedures. The solvents were purified and dried according to standard procedures.[6] Anhydrous copper (II) chloride and methylphosphonic acid were acquired from Fluka, Switzerland and used as such. Triethylamine (Qualigens, India) was dried over KOH and freshly distilled before use. 3,5-Dimethylpyrazole was prepared according to literature procedure.[6]

Instrumentation. Infrared spectra were recorded as KBr pellets using a Bruker Vector 22 FTIR spectrophotometer. ^1H and ^{31}P NMR spectra were recorded on a JEOL spectrometer operating at 400 and 135 MHz, respectively. EPR spectra were recorded on a Varian spectrometer at X-band frequency, and the magnetic field was calibrated with DPPH. Optical absorption spectra were obtained by using 1 cm quartz cells in a Shimadzu UV-160 spectrophotometer. Mass spectra were recorded on a JEOL Sx 102/DA 6000 mass spectrometer using xenon (6 kV, 10 mA) as the FAB gas. C, H, and N analyses were carried out at the Central Drug Research Institute's (Lucknow, India) regional instrumentation facility. Variable temperature magnetic susceptibility data were obtained for polycrystalline samples of **2** using a Lewis coil-

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[#] Dedicated to 65th birthday of Prof. P. T. Manoharan.

[†] Indian Institute of Technology.

[‡] University of Idaho.

[§] University of Delaware.

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force (George Associate, Inc.) magnetometer system equipped with a closed-cycle cryostat (Air Products) working in the temperature range 300−10 K and a Cahn balance. Hg[Co(NCS)$_4$] was used as the calibrant.

Synthesis of Bis(3,5-dimethyl pyrazolyl)methylphosphine Sulfide, MeP(S)(3,5-Me$_2$Pz)$_2$, 1. To a solution of MeP(S)Cl$_2$ (1.49 g 10.0 mmol) in benzene (50 cm^3) was added a mixture of 3,5-dimethylpyrazole (1.92 g, 20.0 mmol) and triethylamine (2.23 g, 22.0 mmol), also dissolved in benzene (50 cm^3). The addition was dropwise over a period of 30 min at room temperature. The reaction mixture was heated under reflux for 24 h. The amine hydrochloride formed in the reaction mixture was filtered and the solvent was removed from the filtrate in vacuo, affording a solid. It was recrystallized from a mixture of anhydrous dichloromethane and *n*-hexane at 5 °C (2.15 g, 80.2%); mp 70 °C. ^{1}H NMR (CDCl$_3$, ppm): δ 5.90(s, 2H), 2.69(d, 3H, ^2J(P−H),15.7 Hz), 2.24(s, 6H), 2.18(s, 6H). ^{31}P NMR (CDCl$_3$,ppm): δ 65.8(s). FAB MS: 268 (parent ion). Anal. Calcd for $C_{11}H_{17}N_4PS$: C, 49.24; H, 6.39; N, 20.88. Found: C, 49.11; H, 6.42; N, 20.52.

Reaction of MeP(S)(3,5-Me$_2$Pz)$_2$, 1, with CuCl$_2$ and Isolation of [Cu$_2$Cl$_2$(3,5-Me$_2$Pz)$_3$(MePO$_3$)]$_2$, 2, and Cu$_2$Cl$_4$(3,5-Me$_2$Pz)$_4$, 3. Ligand **1** (0.27 g, 1.0 mmol) was dissolved in anhydrous dichloromethane (50 cm^3) and to it was added anhydrous copper (II) chloride (0.13 g, 1.0 mmol). A clear yellowish-brown solution was obtained, which was further stirred at room temperature for 10 h. Removal of solvent afforded a solid. Crystallization from *n*-hexane and dichloromethane afforded a green microcrystalline solid that was recrystallized by a slow diffusion of *n*-hexane into a solution of the green solid in dichloromethane at room temperature to afford **2**, mp 174 °C (0.12 g), and **3**, mp 149 °C (0.05 g).

Reaction of MeP(O)(OH)$_2$ with CuCl$_2$ and 3,5-Dimethylpyrazole. To a stirred suspension of 0.26 g (2.0 mmol) of anhydrous copper (II) chloride in 20 cm^3 of dichloromethane was added a mixture of methylphosphonic acid (0.10 g 1.0 mmol) and 3,5-dimethylpyrazole (0.43 g, 4.5 mmol) in dichloromethane (30 cm^3). The resulting green solution was stirred at room temperature for 10 h. Removal of solvent from the reaction mixture afforded a green solid that was purified by crystallization from dichloromethane/hexane (1:1) to afford **3** (0.39 g). No other pure products could be isolated. Repeating the experiment in the presence of 2 equiv of triethylamine also essentially gave the same result as above.

Characterization Data for 2. Anal. Calcd for $C_{32}H_{48}N_{12}O_6P_2Cl_4Cu_4$: C, 33.28; H, 4.19; N, 14.56. Found: C, 33.45; H, 5.16; N, 14.82. IR (cm^{-1}, KBr pellet): 3266(vs), 2922(s), 1746(s), 1615(s), 1571(s), 1472(m), 1416(s), 1314(m), 1276(m), 1170(vs), 1046(s), 1013(s), 947(m), 879(m), 795(m), 688(m). UV−visible {CH$_2$Cl$_2$, [λ_{max}/nm (ϵ_{max}/M^{-1} cm^{-1})]}: 850 (31), 405 (274), 289 (903), 236 (1446). EPR (CH$_2$Cl$_2$/toluene, 1:1, 300 K): broad isotropic signal with half line width of 125 G and g_{iso} of 2.145. EPR (CH$_2$Cl$_2$/toluene, 1:1, 77 K): $g_\|$ 2.28, $A_\|$ 150 G; $g_\perp$ 2.04 (half line width 90 G).

Characterization Data for 3. Anal. Calcd for $C_{20}H_{32}N_8Cl_4Cu_2$: C, 36.76; H, 4.94; N, 17.15. Found: C, 36.72; H, 5.12; N, 16.93. IR (cm^{-1}, KBr pellet): 3267(vs), 2922(m), 1570(vs), 1472(m), 1447(m), 1384(m), 1331(s), 1276(m), 1244(s), 1223(s), 1172(m), 1146(m), 1044(m), 984(vs), 818(s), 794(m), 745(vs), 687(m), 661(s), 614(s), 477(vs), 430(vs). UV−visible {CH$_2$Cl$_2$, [λ_{max}/nm (ϵ_{max}/M^{-1} cm^{-1})]}: 875 (121), 414 (1048), 295 (2757), 234 (3255). EPR (CH$_2$Cl$_2$/toluene, 1:1, 77 K): broad isotropic signal, half line width, 150 G, g_{iso} 2.21.

X-ray Crystallography. The crystal data, data collection methodology, and refinement parameters for **1**−**3** are given in Table 1. The X-ray diffraction data for **1** and **2** were collected on a Siemens SMART3 circle diffractometer equipped with a CCD detector. The structure was solved by direct methods using the SHELX-904 program and refined by the least-squares method on F^2 using SHELXTL, version 5.03.5. The X-ray diffraction data for **3** were collected on a Bruker SMART diffractometer equipped with a CCD area detector. The structure was solved by direct methods using SHELXS-97 (Sheldrick-1990) program and refined by the least-squares method on F^2 using SHELXL-97 (Sheldrick-97).

Table 1. X-ray Crystallographic Data for Compounds **1**−**3**

	compound		
	1	**2**	**3**
emprical formula	$C_{11}H_{14}N_4PS$	$C_{32}H_{48}Cl_4Cu_4N_{12}O_6P_2$	$C_{20}H_{32}Cl_4Cu_2N_8$
fw	265.29	1154.72	653.42
space group	$C2/c$	$P2_1/n$	$P2_1/c$
a (Å)	15.2552(1)	12.5964(4)	8.7137(8)
b (Å)	8.7364(2)	15.7773(4)	13.5493(14)
c (Å)	21.4490(3)	13.9781(4)	11.8847(12)
α (deg)	90	90	90
β (deg)	93.349(1)	116.6280(10)	106.179(2)
γ (deg)	90	90	90
V (Å^3)	2853.74(8)	2483.32(12)	1347.6(2)
ρ_{calcd} (mg m^{-3})	1.235	1.544	1.610
Z	8	2	2
μ (mm^{-1})	0.324	1.010	2.000
λ (Å)	0.710 73	0.710 73	0.710 73
temp (K)	213(2)	213(2)	173(2)
total reflns	7879	29792	6096
independent reflns	2876	5872	2985
R_{int}	0.0284	0.1237	0.0238
R1^a [$I > 2\sigma(I)$]	0.0379	0.0721	0.0455
wR2^a [$I > 2\sigma(I)$]	0.0884	0.1820	0.1235

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

Results and Discussion

Synthetic Aspects. Ligand **1** was prepared in high yield by the reaction of MeP(S)Cl$_2$ with 2 equiv of 3,5-dimethylpyrazole in the presence of triethylamine as the hydrogen chloride scavenger. The ^{31}P NMR spectrum of **1** shows a single peak at +65.8 ppm. In the proton NMR of **1** the methyl groups attached to the pyrazolyl moiety appear as two singlets at 2.24 and 2.18 ppm, while the methyl attached to the phosphorus appears as a doublet at 2.68 ppm. To test the hydrolytic sensitivity of **1**, an NMR tube experiment was carried out by adding H$_2$O (1μL) to a solution of **1** in CDCl$_3$. No change in the phosphorus chemical shift was observed even after a week.

Reaction of **1** with anhydrous CuCl$_2$ in a 1:1 stoichiometry afforded a green solid that was identified as a mixture of **2** and **3**. Recrystallization of this solid from a mixture of dichloromethane and hexane (1:1) afforded a separation of the green and teal crystals with the former being identified as [Cu$_2$Cl$_2$(3,5-Me$_2$Pz)$_3$(MePO$_3$)]$_2$, **2**, and the latter as [CuCl$_2$(3,5-Me$_2$Pz)$_2$]$_2$, **3**. The formation of these products involves a complete desulfurization of ligand **1** along with the hydrolysis of P−N bonds. A plausible mechanism for this process is depicted in Scheme 1. We propose that in the initially formed Cu(II) complex (**1**·CuCl$_2$) the phosphorus center is rendered electrophilic because of the involvement of the pyrazolyl nitrogens and the sulfur atom in coordination to the Cu(II) ion. Such simultaneous coordination of the sulfide and the nitrogen centers has been recently reported in the metal complexes obtained from the phosphorus dihyrazide, PhP(S)[N(Me)NH$_2$]$_2$.[7] The activated phosphorus center in **1**·CuCl$_2$ is extremely susceptible to nucleophilic attack by adventitious amounts of water present in the solvent medium. This leads to the formation of a five-coordinate phosphorus having a geminal P(OH)(SH) moiety as shown in structure **1a** of Scheme 1. Expulsion of H$_2$S is readily anticipated from such a structural entity, and indeed, H$_2$S has been detected during the formation of **2** and **3**. The relative hydrolytic insensitivity of the uncomplexed ligand (vide supra)

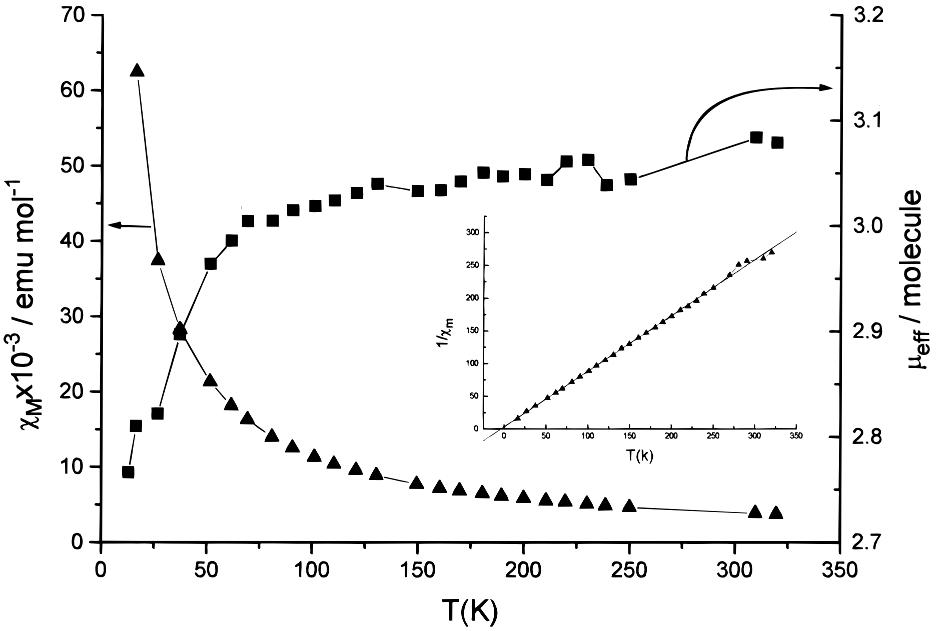
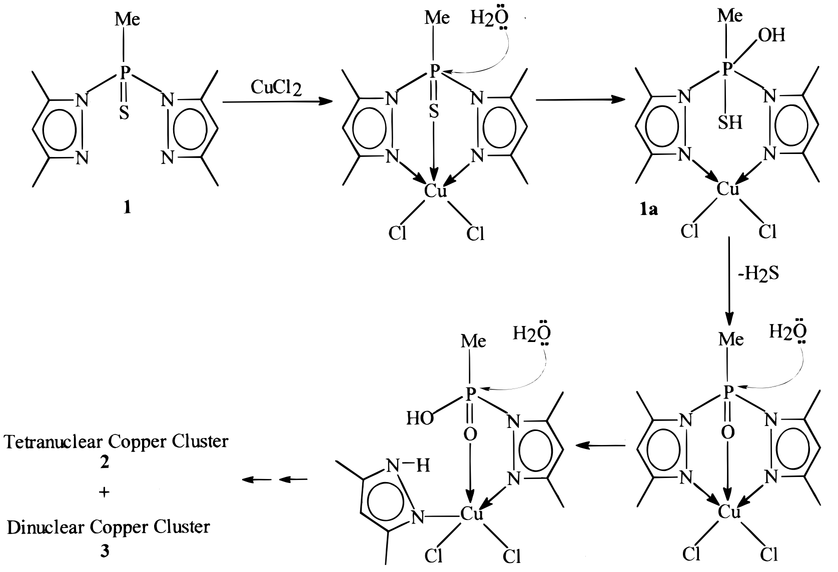


Figure 1. χ_m vs *T* (K) and μ_{eff} vs *T* (K) plot for **2**. Inset shows a plot of 1/χ_m vs *T* (K) for **2**.

Scheme 1



points out the critical role of Cu(II) in promoting the hydrolysis reaction. Although previously the sensitivity of P−N bonds in the presence of metal ions has been noted,[8] this is the first example of a simultaneous desulfurization and hydrolysis of P−N bonds at ambient temperature. Previous examples of cleavage of sulfur from the P═S moiety involved the reaction of $RP(S)Cl_2$ with $Na_2Fe(CO)_4$.[9] To prepare **2** by a *direct process*, we have reacted methylphosphonic acid with $CuCl_2$ in the presence of 3,5-dimethylpyrazole. However, while **3** has been formed in this reaction as a major product, there was no evidence for the formation of **2**.

Variable temperature magnetic susceptibility measurements on **2** show that it is weakly antiferromagnetically coupled (Figure 1). The μ_{eff} per molecule at 309 K is 3.08 μ_B, while at 12 K it is 2.77 μ_B. In accordance with the magnetic data observed, the EPR spectrum of **2** recorded at room temperature in dichloromethane solution is seen as a broad isotropic signal with a half line width of 125 G and a g_{iso} value of 2.145. The EPR spectrum of **2** recorded as a glass (toluene/dichloromethane, 1:1) at 77 K is slightly better resolved with the appearance of four parellel lines ($g_{\parallel}$ = 2.28; $A_{\parallel}$ = 150.0 G) and a broad perpendicular line ($g_{\perp}$ = 2.04) with a half line width of 90 G.

X-ray Crystal Structures of 1−3. The X-ray crystal structures of **1**−**3** have been determined. The structure of **1** is unexceptional and shows a near-tetrahedral arrangement of the substituents around phosphorus.

Figure 2 shows the ORTEP diagram of the tetranuclear copper (II) cluster **2**. The most common structural type among tetracopper (II) clusters comprises a Cu_4O core where the copper (II) ions are arranged at the vertexes of a tetrahedron around the oxygen.[10] The six edges are bridged by different kinds of ligands. Other types of tetranuclear copper (II) clusters include

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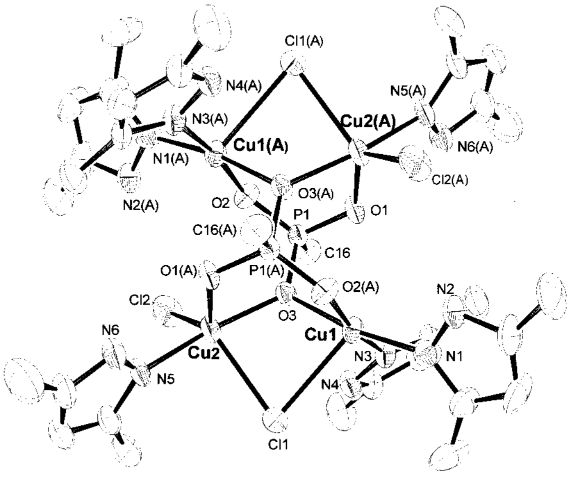
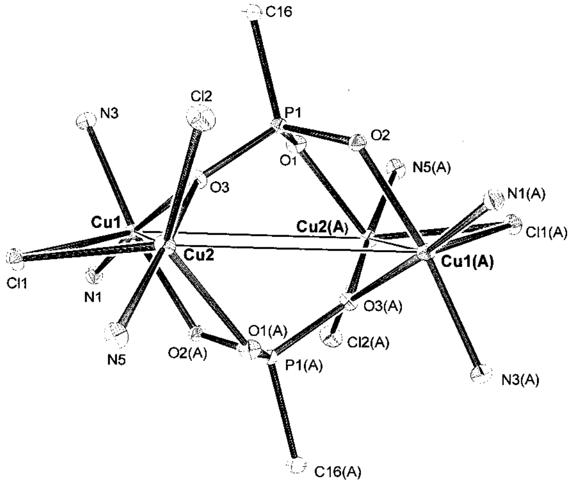


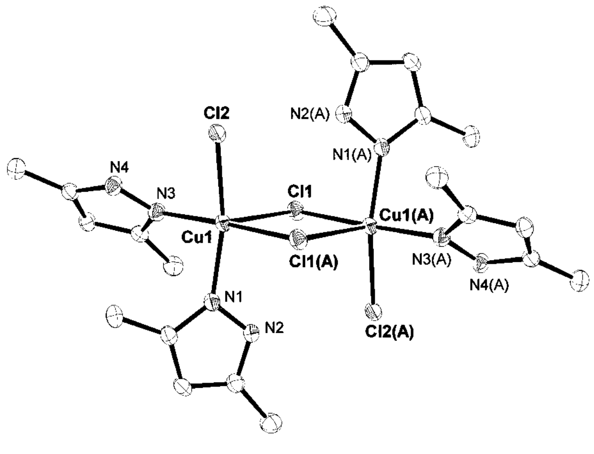
2

Figure 2. Structure of the tetranuclear copper cluster **2** showing the atomic labeling scheme (30% probability thermal ellipsoids). Hydrogen atoms have been omitted for clarity.



2

Figure 3. Structure of **2** showing the bicapped $MePO_3$ coordination to a planar Cu_4 assembly. Only the atoms directly attached to copper and phosphorus are shown. The relevant distances (Å) and angles (deg) are the following: Cu(1)−Cu(2) 3.229(3), Cu(1)−Cu(2A) 3.975(3), Cu(1)−Cu(1A) 5.228(2), Cu(1)−Cu(2)−Cu(1A) 87.54(3), Cu(2)−Cu(1)−Cu(2A) 92.46(4).



3

Figure 4. Structure of **3** showing the atom labeling scheme (30% probability thermal ellipsoids). Hydrogen atoms have been omitted for clarity. Important bond lengths (Å) and bond angles (deg) are the following: Cu(1)−N(1) 2.003(3), Cu(1)−N(3) 2.018(3), Cu(1)−Cl(2) 2.3045(10), Cu(1)−Cl(1A) 2.3285(10), Cu(1)−Cl(1) 2.6822(11), Cl(1)−Cu(1A) 2.3285(10), N(1)−Cu(1)−N(3) 88.61(14), N(1)−Cu(1)−Cl(2) 162.68(10), N(3)−Cu(1)−Cl(2) 89.06(10), N(1)−Cu(1)−Cl(1A) 89.39(10), N(3)−Cu(1)−Cl(1A) 174.58(10), Cl(2)−Cu(1)−Cl(1A) 91.36(4), N(1)−Cu(1)−Cl(1) 98.68(10), N(3)−Cu(1)−Cl(1) 100.51(10), Cl(2)−Cu(1)−Cl(1) 98.62(4), Cl(1A)−Cu(1)−Cl(1) 84.77(4), Cu(1A)−Cl(1)−Cu(1) 95.23(4).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound **2**

	Cu(1)		
Cu(1)−Cl(1)	2.660(2)	Cu(1)−O(2A)	1.936(4)
Cu(1)−N(1)	1.979(6)	Cu(1)−O(3)	2.010(4)
Cu(1)−N(3)	1.988(6)		
Cl(1)−Cu(1)−N(1)	110.5(2)	Cl(1)−Cu(1)−N(3)	90.7(2)
Cl(1)−Cu(1)−O(2A)	98.5(2)	Cl(1)−Cu(1)−O(3)	78.72(13)
N(1)−Cu(1)−N(3)	93.5(2)	N(1)−Cu(1)−O(2A)	86.5(2)
N(1)−Cu(1)−O(3)	170.6(2)	N(3)−Cu(1)−O(2A)	170.3(2)
N(3)−Cu(1)−O(3)	87.8(2)	O(2A)−Cu(1)−O(3)	90.6(2)
	Cu(2)		
Cu(2)−Cl(1)	2.528(2)	Cu(2)−O(1A)	2.070(5)
Cu(2)−Cl(2)	2.309(2)	Cu(2)−O(3)	1.970(4)
Cu(2)−N(5)	1.979(6)		
Cl(1)−Cu(2)−Cl(2)	123.16(8)	Cl(1)−Cu(2)−O(1A)	109.38(14)
Cl(1)−Cu(2)−N(5)	89.8(2)	Cl(1)−Cu(2)−O(3)	82.81(14)
Cl(2)−Cu(2)−O(1A)	127.4(2)	Cl(2)−Cu(2)−N(5)	94.2(2)
Cl(2)−Cu(2)−O(3)	95.2(2)	O(1A)−Cu(2)−N(5)	86.9(2)
O(1A)−Cu(2)−O(3)	89.5(2)	N(5)−Cu(2)−O(3)	170.2(2)
	P(1)		
P(1)−O(1)	1.525(5)		
P(1)−O(2)	1.515(5)		
P(1)−O(3)	1.558(5)		
Cu(1)−O(3)−P(1)	118.0(3)	C(16)−P(1)−O(2)	107.9(3)
Cu(2)−O(3)−P(1)	129.8(3)	C(16)−P(1)−O(3)	107.7(3)
Cu(1A)−O(2)−P(1)	127.8(3)	O(1)−P(1)−O(2)	114.5(3)
Cu(2A)−O(1)−P(1)	121.5(3)	O(1)−P(1)−O(3)	108.1(3)
C(16)−P(1)−O(1)	107.6(3)	O(2)−P(1)−O(3)	110.8(3)

gridlike structures,[11] cube[1a] and open-cube forms,[12] and structures involving dimetallic cores with two monometallic auxiliaries.[13] In this regard the structural type observed in **2** is unusual and contains two dimeric copper (II) cores $[\{CuClO\}_2]_2$ linked to each other in a centrosymmetric manner by the *tripodal* methylphosphinate, $MePO_3$, unit. All three oxygens of $MePO_3$ participate in coordination. One of the oxygen atoms functions as a μ^2-bridging ligand (for Cu1 and Cu2) and forms part of the four-membered [Cu(1)−Cl(1)−Cu(2)−O(3)] core. The other two oxygen atoms of $MePO_3$ are utilized as monodentate ligands to link the two copper (II) ions of the other dimeric copper (II) unit. All four copper (II) ions lie in a perfect rectangular plane with the shortest Cu−Cu distance being 3.229(3) Å [Cu(1)−Cu(2)] and the other distances being 3.975(3) Å [Cu(1)−Cu(2A)] and 5.228(2) Å [Cu((1)−Cu(1A)] (Figure 3). The PO_3

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units function as “bicapping” motifs being present on the top and bottom of the rectangular plane (Figure 3). Another interesting aspect of the structure of **2** is that the two copper ions Cu(1) and Cu(2) do not have a symmetrical disposition of ligands and have different geometries. Thus, Cu(1) has a near-square-pyramidal geometry with the apical position being taken up by Cl(1) and positions of the square plane being occupied by two nitrogen and two oxygen atoms. In contrast, Cu(2) has an approximate trigonal bipyramidal geometry with the equatorial positions being spanned by the chlorine atoms Cl(1) and Cl(2) and the oxygen atom O(1A). The axial positions are taken up by the nitrogen N(5) and the μ^2-bridging oxygen atom O(3). The Addison and Reedijk geometric parameter τ for Cu(1) is nearly zero as expected for a square pyramidal arrangement.[14] On the other hand while the expected τ value for a regular trigonal bipyramidal geometry is 1.0, the value observed for Cu(2) is 0.78, indicating that it has a distorted trigonal bipyamidal geometry around it. Some of the important metric parameters of **2** are summarized in Table 2.

Figure 4 shows the X-ray crystal structure of **3**. A dinuclear copper complex bridged by two chloride bridges forms the core of this complex. The terminal ligands on each copper are one chloride and two pyrazole units, respectively. The important metric parameters for this compound are summarized in Figure 4.

In conclusion we have observed an unusual desulfurization and simultaneous hydrolysis of the P—N bonds in MeP(S)(3,5-$\mathrm{Me_2Pz)_2}$ upon interaction with a Cu(II) ion. This leads to the assembly of a novel tetracopper cluster. We are investigating the general applicability of this synthetic route for assembling other metal clusters.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of MeP(S)(3,5-$\mathrm{Me_2Pz)_2}$, **1**, $\mathrm{[Cu_2Cl_2(3,5\text{-}Me_2Pz)_3(MePO_3)]_2}$, **2**, and $\mathrm{Cu_2Cl_4(3,5\text{-}Me_2Pz)_4}$, **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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