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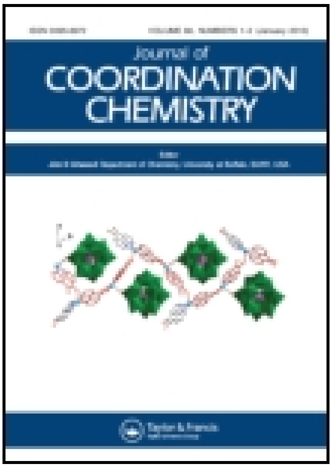

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Tetra-nuclear copper complex having P-N-P ligand to P-O-P ligand - synthesis, structural, and mechanistic studies

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Tetra-nuclear copper complex having P–N–P ligand to P–O–P ligand – synthesis, structural, and mechanistic studies

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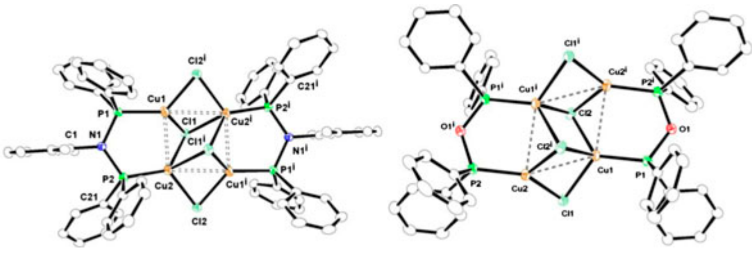

Tetra-nuclear copper(I) complexes, $[Cu_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_2\{\mu_2\text{-}(2,6\text{-}Me_2C_6H_3N(PPh_2)_2)\}_2]$ (**2**), were obtained from $[2,6\text{-}Me_2C_6H_3N(PPh_2)_2]$ (**1**) and copper(I) chloride in the presence of triphenylphosphine. The mixed cobalt(II)/(III) complex $[(CoCl_2)\{\mu_2\text{-}2,6\text{-}Me_2C_6H_3N(PPh_2)_2\}_2][CoCl_3NH_2(2,6\text{-}Me_2Ph)]$ (**3**) was obtained by the analogous reaction of **1** and $CoCl_2$ in methanol.

We report the synthesis and structures of three copper(I) complexes, $[Cu_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_2\{\mu_2\text{-}(2,6\text{-}Me_2C_6H_3N(PPh_2)_2)\}_2]$ (**2**), $[Cu_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_2\{\mu_2\text{-}(Ph_2POPPh_2)\}_2]$ (**4**), and $[Cu_2(\mu_2\text{-}Cl)_2(\mu_2\text{-}PPh_2OPPh_2)(\eta^1\text{-}Ph_2PP(=O)Ph_2)(PPh_3)]$ (**5**), and one cobalt complex, $[(CoCl_2)\{\mu_2\text{-}2,6\text{-}Me_2C_6H_3N(PPh_2)_2\}_2][CoCl_3NH_2(2,6\text{-}Me_2Ph)]$ (**3**). Tetra-nuclear copper complex **2** was prepared in good yield by the reaction of bis(diphenylphosphino)-2,6-dimethylaniline $[2,6\text{-}Me_2C_6H_3N(PPh_2)_2]$ (**1**) with copper(I) chloride along with triphenylphosphine in methanol. Adding a calculated amount of water and dichloromethane mixture (1 : 10) to **2** produced a second tetra-nuclear copper(I) complex, **4**, with a P–O–P backbone, along with a small amount of the unsymmetrical copper(I) complex **5**. The cobalt complex **3** was obtained by reaction of **1** with cobalt(II) chloride. The solid-state structures of **2**–**5** were established by single-crystal X-ray diffraction analysis. In the solid state, both **2** and **4** form a tetra-nuclear copper core. In the $^{31}P\{^1H\}$ NMR study, we observed the conversion of **2**, with P–N–P backbone, to **4**, with P–O–P backbone.

Keywords: Copper(I); tetra-nuclear; P–N–P ligand; P–O–P ligand; P–P bond

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1. Introduction

Copper is essential for all organisms because of its presence as a catalytic and structural element in enzymes and other molecules [1–3]. Copper(I) compounds have many applications as catalysts in homogeneous catalysis [4]. In particular, copper(I) was found to be an efficient catalyst in the 1,3-dipolar cycloaddition of azides and alkynes, with the best "click reaction" to date [5–9]. A number of organometallic compounds with diphosphine ligands containing a P–C–P backbone are used for numerous investigations [10–14]. In contrast, analogous diphosphinoamine ligands have recently proved their potency as versatile catalysts [15, 16], as substituents on both phosphorus and nitrogen can be easily varied with attendant changes in the P–N–P bond angle and conformation around the phosphorus centers [17, 18]. Fairly, small differences in these ligands can cause significant changes in their coordination behavior and structural features in the resulting complexes [19]. Furthermore, diphosphazanes bearing heterofunctionalities (namely P,O–, P,S–, or P,N–) at one or both phosphorus centers can be readily obtained from their precursors; however, these ligand systems have low thermal stability [20–23]. Thus, the choice of substituents on nitrogen favors bidendate ligation over monodentate chelation of $RN(PX_2)_2$, by suitable orientation of the lone pairs of phosphorus [22, 23]. The coplanar geometry of nitrogen in diphosphazanes allows facile incorporation of the ligand as chelates or bridges toward transition metal complexes [24]. The coordination and organometallic chemistry of these short bite diphosphazane ligands have been reviewed extensively [25–31]. Interest in these ligands also stems from the formation of multinuclear transition metal complexes where the metals are held in close proximity [32]. A variety of complexes of this class of ligands has been reported with various transition metals [33–61]. Recently, Samuelson *et al.* reported a number of copper (I) and silver(I) complexes with P–N–P ligands [62–66]. They also showed that with hydrogen as a substituent on nitrogen of P–N–P, the ligand forms a bridge, whereas with a methyl, it prefers to form a chelate. Recently, chelating *versus* bridging bonding modes of these ligands have been reported in platinum as well as Co_2Pt clusters [67].

We synthesized a series of phosphineamines $[Ph_2PNHR]$ ($R = 2,6\text{-}Me_2C_6H_3$, $CHPh_2$, CPh_3) and their chalcogen derivatives $[Ph_2P(O)NHR]$, $[Ph_2P(S)NHR]$, and $[Ph_2P(Se)NHR]$ [68–71]. The phosphineamine chalcogenates were introduced in alkali metal and heavier alkaline earth metal chemistry. The synthesis, full characterization, and mechanistic studies of three copper(I) complexes, with molecular formulas $[Cu_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_2\{\mu_2\text{-}(2,6\text{-}Me_2C_6H_3N(PPh_2)_2)\}_2]$ (**2**), $[(Cu_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_2\{\mu_2\text{-}(Ph_2POPPh_2)\}_2]$ (**4**), and $[Cu_2(\mu_2\text{-}Cl)_2(\mu_2\text{-}PPh_2OPPh_2)(\eta^1\text{-}Ph_2PP(=O)Ph_2)(PPh_3)]$ (**5**), and one chelating cobalt(II) complex $[(CoCl_2)\{\mu_2\text{-}2,6\text{-}Me_2C_6H_3N(PPh_2)_2\}_2][CoCl_3NH_2(2,6\text{-}Me_2Ph)]$ (**3**) are reported here.

2. Experimental

2.1. *General information*

All manipulations were performed using standard Schlenk techniques under an atmosphere of nitrogen. Dichloromethane was dried over P_2O_5 and distilled in nitrogen. ^1H NMR (400 MHz), $^{13}C\{^1H\}$ (100 MHz), and $^{31}P\{^1H\}$ NMR (161.9 MHz) spectra were recorded on a BRUKER AVANCE III-400 spectrometer. BRUKER ALPHA FT-IR was used for FT-IR measurement. Elemental analyses were performed on a BRUKER EURO EA at the

Indian Institute of Technology, Hyderabad. Bis(diphenylphosphino)-2,6-dimethylaniline [68] was prepared according to the procedure prescribed in the literature. Copper(I) chloride and anhydrous $CoCl_2$ were purchased from Sigma-Aldrich and used without purification.

2.2. *Preparation of* $[Cu_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_2\{\mu_2\text{-}(2,6\text{-}Me_2C_6H_3N(PPh_2)_2)\}_2]$ *(2)*

In a methanol (15 mL) solution, *N,N*-bis(diphenylphosphino)-2,6-dimethylaniline 200 mg (0.40 mM), triphenylphosphine 104 mg (1.60 mM), and a little excess copper(I) chloride 158.4 mg (1.6 mM, 4 equivalent), were stirred for 12 h at room temperature. A white solid was obtained, which was filtered. The white compound was dissolved in dichloromethane and stored at −4 °C; colorless crystals were obtained from the dichloromethane after one day. Yield 140 mg (50%). ^1H NMR (400 MHz, C_6D_6): δ = 7.56–7.30 (m, 40H, PhH), 7.17–7.10 (m, 2H, ArH), 7.04 (d, 4H, J = 7.48 Hz, ArH), and 1.26 (s, 12H, $-C\underline{H}_3$), ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ = 65.2 ppm. FT-IR (selected frequencies): υ = 2961 (m), 2866(w), 1589(w), 1462(w), 1436(w), 1258(s), 1179(w), 1092(w), 1047(m), 864(w), 792(s), 750(s), 723(s), and 571(m) cm^{-1}. $C_{70}H_{70}Cl_{16}Cu_4N_2P_4$ (1884.56): Calcd: C, 44.61; H, 3.74; N, 1.49; found: C, 44.27; H, 3.19; N, 1.32.

2.3. *Preparation of* $[(CoCl_2)\{\mu_2\text{-}2,6\text{-}Me_2C_6H_3\ N(PPh_2)_2\}_2][CoCl_3NH_2(2,6\text{-}Me_2Ph)]$ *(3)*

In a dry Schlenk tube, 85.7 mg of anhydrous cobalt(II) chloride (0.66 mM) and 646 mg of *N,N*-bis(diphenylphosphino)-2,6-dimethylaniline (1.32 mM) were placed with 5 mL of dry dichloromethane added. After 12 h of stirring at room temperature, the green reaction mixture was filtered through a cannula and the filtrate was concentrated to one-third of its volume. Dark green crystals appeared at −4 °C. Yield 400 mg (54%). IR (selected frequencies): υ = 3084(w), 2959(m), 2922(m), 2853(w), 1589(w), 1462(w), 1436(w), 1259 (s), 1089(m), 1012(s), 865(w), 790(s), 741(w), 689(s), and 574(w) cm^{-1}. $C_{75}H_{75}Cl_{11}Co_2N_3P_4$ (1650.07): Calcd: C, 54.59 H, 4.58; N, 2.55; found: C, 53.89; H, 4.32; N, 2.35.

2.4. *Preparation of* $[(Cu_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_2\{\mu_2\text{-}(Ph_2POPPh_2)\}_2]$ *(4)*

The white solid obtained while preparing **2** (924 mg, 0.56 mM) was dissolved in dichloromethane (5 mL) and then stirred with 0.5 mL of degassed water for 6 h at room temperature. The solution was filtered through a cannula, and the filtrate was concentrated to half of its volume. Colorless crystals appeared after three days of being stored at 15 °C. Yield 340.4 mg (52%). ^1H NMR (400 MHz, C_6D_6): δ = 7.50–7.10 (m, 40H, PhH) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ = 34.6 ppm. IR (selected frequencies): υ = 3049(w), 1478(m), 1433(s), 1183(w), 1094(m), 997(m), 742(s), 690(s), and 572(w) cm^{-1}. $C_{48}H_{40}Cl_4Cu_4O_2P_4$ (1168.68): Calcd: C, 49.33; H, 3.45; found: C, 48.92; H, 3.31.

2.5. *Preparation of* $[Cu_2(\mu_2\text{-}Cl)_2(\mu_2\text{-}PPh_2OPPh_2)(\eta^1\text{-}Ph_2PP(=O)Ph_2)(PPh_3)]$ *(5)*

Compound **4** was separated by usual crystallization method from CH_2Cl_2. From the mother liquor, **5** was obtained as cube-shaped colorless crystals. Yield 210 mg (30%). ^1H NMR (400 MHz, C_6D_6): δ = 7.50–7.10 (m, 40H, PhH) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ = 34.8 (POP) −2.67 (PPh_3), 28.3 (d, P=O), −21.7 (d, PPh_2)

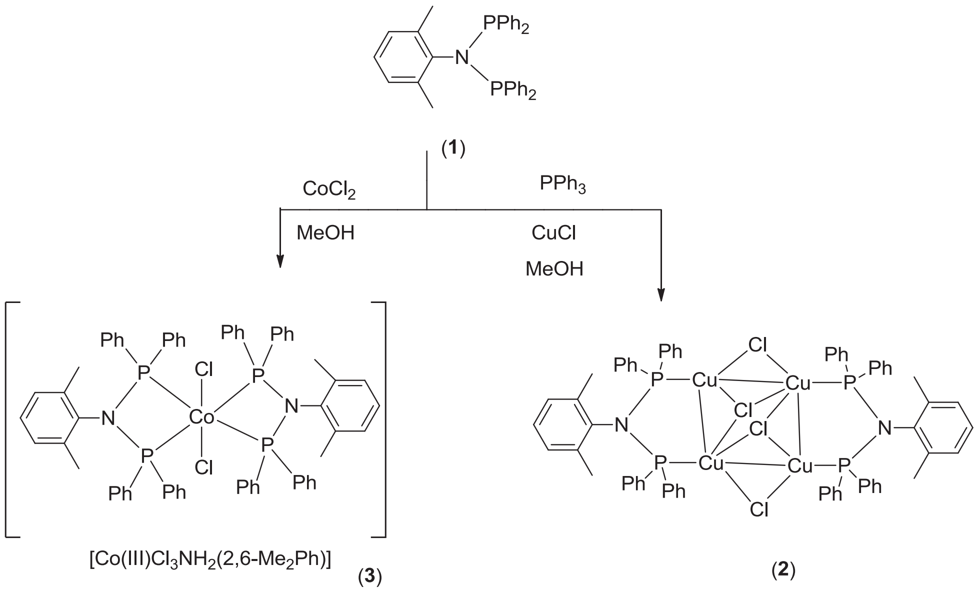
ppm. IR (selected frequencies): υ = 3049(w), 1478(m), 1433(s), 1183(w), 1094(m), 997 (m), 742(s), 690(s), and 572(w) cm^{-1}. $C_{66}H_{55}Cl_2Cu_2O_2P_5$ (1233.1): Calcd: C, 64.29; H, 4.50; found: C, 63.77; H, 4.25.

3. Results and discussion

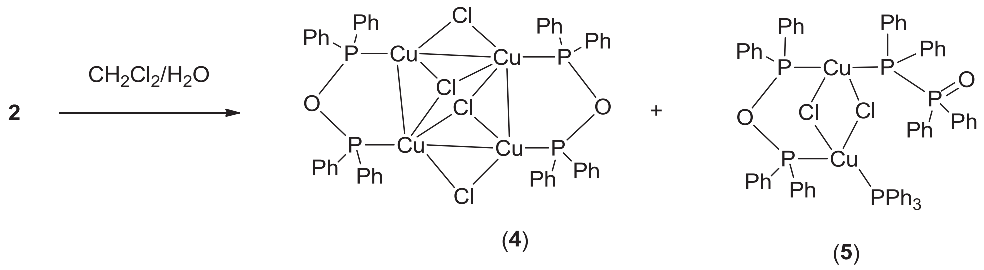
3.1. *Synthesis and characterization of 2–5*

The reaction of bis(diphenylphosphino)-2,6-dimethylaniline (**1**) with copper(I) chloride in a 1 : 2 M ratio in the presence of triphenylphosphine in methanol resulted in the tetrameric copper complex $[Cu_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_2\{\mu_2\text{-}(2,6\text{-}Me_2C_6H_3N(PPh_2)_2)\}_2]$ (**2**) in good yield (scheme 1). The analogous reaction of **1** with anhydrous cobalt(II) chloride afforded a bis-chelated monomeric compound, $[(CoCl_2)\{\mu_2\text{-}2,6\text{-}Me_2C_6H_3N(PPh_2)_2\}_2][CoCl_3NH_2(2,6\text{-}Me_2Ph)]$ (**3**), in good yield (scheme 1). The tetrameric copper complex **2** was dissolved in dichloromethane–water (10 : 1) mixture and stirred for 12 h. After crystallization, the tetrameric **4** with P–O–P as the backbone was isolated, in good yield, as the major product (scheme 2). The unsymmetrical copper compound **5** was also isolated in small quantity from the same reaction mixture after the removal of **4** (scheme 2). The characteristics of **2–5** were analyzed using standard analytical/spectroscopic techniques, and the solid-state structures of **2–5** were established by single-crystal X-ray diffraction analysis.

In the ^{1}H NMR spectra of the diamagnetic tetra-nuclear **2** measured in $CDCl_3$, one singlet is observed at 1.26 ppm for the methyl protons attached to the aromatic rings. The resonance of the phenyl protons is in the expected region. In the $^{31}P\{^1H\}$ NMR spectra, one signal is observed at 65.2 ppm, which is slightly downfield-shifted when compared to that



Scheme 1. Syntheses of copper(I) and cobalt(II) complexes with P–N–P ligand **1**.



Scheme 2. Synthesis of **4** and **5** from **2**.

of **1** (56.8 ppm) upon addition of copper to bis(diphenylphosphino)-2,6-dimethylaniline moiety. Only one signal in the $^{31}P\{^1H\}$ NMR indicates that all the four phosphorus atoms are magnetically equivalent in solution. Complex **3** is NMR-silent due to the paramagnetic nature of the compound. In the ^1H NMR spectra of **5**, the resonance for phenyl protons was observed in the expected regions. In the $^{31}P\{^1H\}$ NMR spectra of **4**, only one signal at 34.6 ppm is observed and this is significantly highfield-shifted when compared to that of **2** (64.6 ppm). This significant shift can be explained by the replacement of nitrogen with the more electronegative oxygen on the phosphorus, which is highly shielded. The one signal in the $^{31}P\{^1H\}$ NMR indicates that all the four phosphorus atoms are magnetically equivalent in the solution. In the $^{31}P\{^1H\}$ NMR spectra of **5**, we observe four distinct signals for four magnetically different phosphorus atoms. The resonance at 34.8 ppm can be assigned to the P–O–P backbone; the signal at −2.7 ppm clearly reveals that the triphenylphosphine is attached to the copper ion [75]. Two doublets are observed at 28.3 and −21.7 ppm, which can be assigned to the $Ph_2P(O)PPh_2$ fragment. These observations are in agreement with the reported values published by Aydemir *et al.* [76].

3.2. *Crystal structures of 2–5*

Single crystals of **2–5** were grown from dichloromethane in an inert atmosphere. Complex **2** crystallizes in the centrosymmetric triclinic space group *P-1*, with one molecule in the unit cell along with six dichloromethane molecules. The details of the structural parameters are given in table 1. The solid-state structure of **2** is given in figure 1. Two bis(diphenylphosphino)-2,6-dimethylaniline moieties are bound to four copper(I) centers in a bridging fashion, and four chloride bridges complete the core structure. In the tetrameric **2**, all four copper ions lie on the same plane to form a four-membered ring along with two μ_3 chloride bridges. The Cu–Cl distance for μ_3 chloride ions ranges from 2.388 to 2.608 Å, and the Cu–Cl distance of 2.940 Å is slightly long to consider a Cu–Cl covalent bond. Complex **2** is isostructural, and the Cu_4 ring in the analogous compound $[Cu_4(dppan)Cl_4]$ (dppan = $C_6H_5N(PPh_2)_2$) was recently reported by Samuelson *et al.* [66]. The PNP angle (119.80°) in **2** is almost in the same range on chelation with the metal compared to that of the free ligand [122.8(2)°], since the formation of the Cu_4 ring provides some extra room for coordination of the phosphorus with the copper ions. The P1, N1, and P2 atoms are almost coplanar, with the plane containing four copper ions, and only have a dihedral angle of 6.16° between the two planes. The Cu–Cu distances in **2** (2.684 and 2.840 Å) are within the range [2.648(2) to 2.784(2)] for $[Cu_4(dppan)Cl_4]$, as reported by Samuelson *et al.* [66].

Table 1. Crystal data for **2**–**5**.

	2	**3**	**4**	**5**
CCDC no.	955707	955708	955705	955709
Empirical formula	$C_{70}H_{70}Cl_{16}Cu_4N_2P_4$	$C_{75}H_{75}Cl_{11}Co_2N_3P_4$	$C_{48}H_{40}Cl_4Cu_4O_2P_4$	$C_{66}H_{55}Cl_2Cu_2O_2P_5$
Formula weight	1884.56	1650.07	1168.64	1232.95
Temperature (K)	150(2)	150(2)	150(2)	150(2)
Wavelength (A)	1.54184	0.71073	1.54184	1.54184
Crystal system, space group	Triclinic, *P-1*	Triclinic, *P-1*	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Unit cell dimensions	$a = 10.1861(12)$ Å, $b = 13.2706(16)$ Å, $c = 15.8952(15)$ Å, $\alpha = 103.669(9)°$, $\beta = 105.845(9)°$, $\gamma = 97.912(10)°$	$a = 14.877$ Å, $b = 17.449$ Å, $c = 17.597$ Å, $\alpha = 112.05°$, $\beta = 96.90°$, $\gamma = 111.46°$	$a = 10.7440(8)$ Å, $b = 16.1776(13)$ Å, $c = 16.5406(16)$ Å, $\alpha = 90°$, $\beta = 125.626(6)°$, $\gamma = 90°$	$a = 20.0869(11)$ Å, $b = 12.9761(4)$ Å, $c = 24.1522(11)$ Å, $\alpha = 90°$, $\beta = 114.332(6)°$, $\gamma = 90°$
Volume (Å^3)	1960.9(4)	3760.8	2336.9(3)	5736.1(4)
Z, Calcd density (Mg/m^3)	1, 1.596	2, 1.457	2, 1.661	4, 1.428
Absorption coefficient (mm^{-1})	7.340	0.962	5.761	3.445
F(0 0 0)	952	1694	1176	2536
Theta range for data collection	3.51°–69.98°	1.41°–25.91°	4.28°–70.83°	3.74°–70.75°
Reflections collected/ unique	14,502/7302 [*R*(int) = 0.0592]	27,620/14,098 [*R* (int) = 0.0833]	9709/4402 [*R*(int) = 0.0494]	24,321/10,831 [*R* (int) = 0.0447]
Completeness to theta	(69.98) 98.3%	(25.91) 96.4%	(70.83) 97.9%	(70.75) 98.1%
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Max. and min. transmission	0.360 and 0.253	1.00000 and 0.50182	1.000 and 0.231	1.000 and 0.411
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	7302/0/435	14,101/0/863	4402/0/280	10,831/0/694
Goodness-of-fit on F^2	1.071	1.031	1.035	1.094
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0805$, $wR_2 = 0.2323$	$R_1 = 0.0848$, $wR_2 = 0.2129$	$R_1 = 0.0538$, $wR_2 = 0.1429$	$R_1 = 0.0538$, $wR_2 = 0.1251$
R indices (all data)	$R_1 = 0.0923$, $wR_2 = 0.2493$	$R_1 = 0.1542$, $wR_2 = 0.2438$	$R_1 = 0.0801$, $wR_2 = 0.1626$	$R_1 = 0.0726$, $wR_2 = 0.1370$
Largest diff. peak and hole (e A^{-3})	1.652 and −0.771	2.031 and −1.156	1.188 and −0.690	0.508 and −0.534

[a] $R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ [72].
[b] $wR_2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^4)]^{1/2}$ [73].

The variation in Cu–Cu distances by the use of different halides is well demonstrated by Knight *et al.* [74]. Furthermore, the P–N–P ligands also affect the Cu–Cu distances [63].

Cobalt complex **3** crystallizes in the triclinic space group *P-1*, with two formula units in the unit cell. In **3**, one symmetrical part $[(CoCl_2)\{2,6\text{-}Me_2C_6H_3N(PPh_2)_2\}_2]$, where cobalt (II) is ligated through both phosphorus atoms of two ligand moieties, is present along with one unsymmetrical part $[CoCl_3NH_2(2,6\text{-}Me_2Ph)]$, where cobalt(III) is coordinated with free 2,6-dimethylaniline. The formation of the cobalt(III) compound is presumably due to oxidation of cobalt(II) in the reaction conditions. The details of the structural parameters are given in table 1. The solid-state structure of **3** is given in figure 2. In the centrosymmetric part, cobalt(II) is bound to two chelating **1** moieties along with two chlorides, resulting in a distorted octahedral geometry around the metal center. The P–N–P angle (103.4°) in **3** is reduced upon chelation with the metal compared with that of the free ligand [122.8(2)°]. A

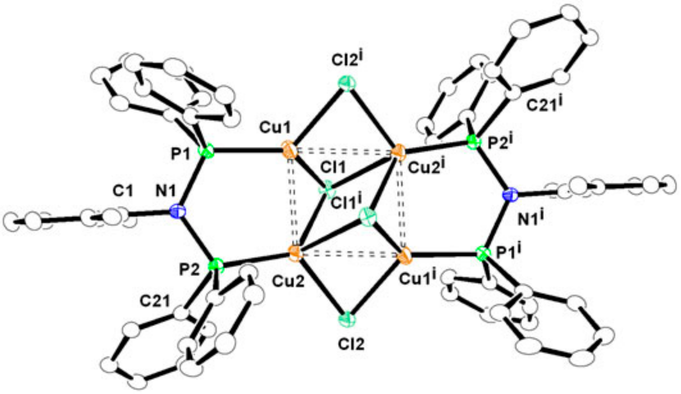


Figure 1. ORTEP diagram of **2** with thermal displacement parameters drawn at the 30% probability level; hydrogens were omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Cu1–Cu2 2.684(3), Cu2–P2 2.195(3), Cu2–Cl2 2.330(3), Cu2–Cl1 2.483(3), Cu2–Cl1^{i} 2.607(3), Cu1–P1 2.185(3), Cu1–Cl2^{i} 2.286(3), Cu1–Cl1 2.388 (3), Cu1–Cu2^{i} 2.840(2), P1–N1 1.723(8), P2–N1 1.727(8), Cl1–Cu2^{i} 2.607(3), Cl2–Cu1^{i} 2.286(3), P2–Cu2–Cl2 122.05(12), P2–Cu2–Cu1 93.20(10), Cu2–Cu1–Cu2^{i} 84.78(7), P2–N1–P1 119.7(5), Cu1–Cu2–Cu1^{i} 95.22(7).

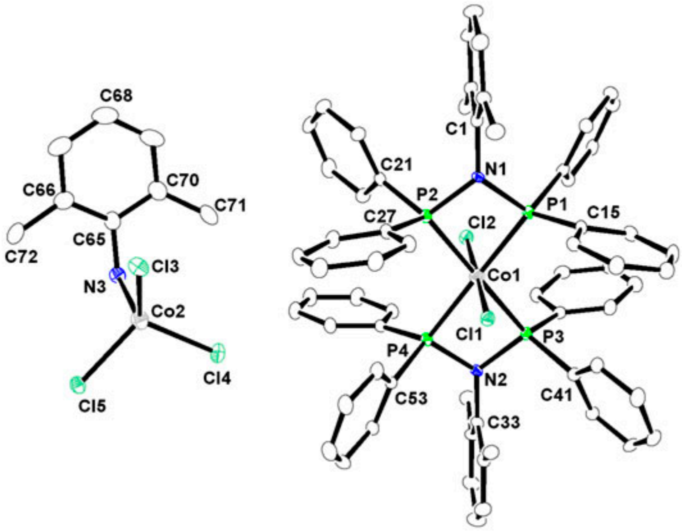


Figure 2. ORTEP diagram of **3** with thermal displacement parameters drawn at the 30% probability level; hydrogens were omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Co1–P1 2.266(2), Co1–P2 2.280(2), Co1–P3 2.274(2), Co1–P4 2.277(2), Co1–Cl1 2.2376(19), P1–N1 1.716(5), P2–N1 1.717(5), P4–N2 1.731(5), P3–N2 1.722(5), Co2–N3 2.102(5), Co2–Cl3 2.237(2), Co2–Cl4 2.258(2), Co2–Cl5 2.262(2), P1–Co1–P2 72.72(7), P1–Co1–P3 106.92(7), P4–Co1–P3 72.69(7), P4–Co1–P2 107.60(8), P1–N1–P2 103.6(3), P3–N2–P4 102.7(3), P1–Co1–Cl1 90.90(7), Cl1–Co1–Cl2 179.54(9), P3–Co1–Cl1 89.68(7), N3–Co2–Cl3 107.81(18), N3–Co2–Cl4 103.94(18), N3-Co2–Cl5 103.76(18), Cl3–Co1–Cl4 117.31(9), Cl4–Co2–Cl5 109.49(9).

similar observation was made with regard to the analogous chelated monomeric copper complex [Cu(dppan)$_2$ClO$_4$], as reported by Samuelson *et al.* [63]. The Co–P distances (ranging from 2.267 to 2.276 Å) are within the reported values.

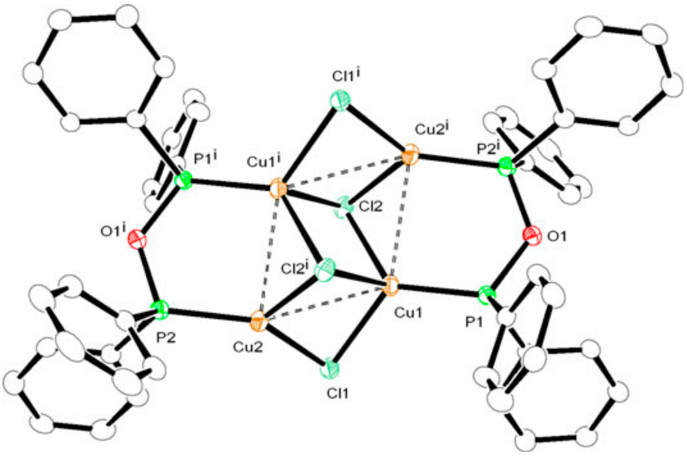


Figure 3. ORTEP diagram of **4** with thermal displacement parameters drawn at the 30% probability level; hydrogens were omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Cu1–P1 2.1750(14), Cu1–Cl2 2.3584 (14), Cu1–Cl1 2.3705(14), Cu1–Cl2^{i} 2.5534(14), Cu1–Cu2^{i} 2.9033(11), Cu1–Cu2 3.0021(11), Cu2–P2 2.1676(14), P1–O1 1.648(3), O1–P2^{i} 1.646(4), Cu2–P2 2.1676(14), Cu2–Cl1 2.2350(14), P2^{i}–O1–P1 124.1(2), Cu2–Cl1–Cu1 81.30(5), Cu1–Cl2–Cu2^{i} 75.74(4), Cu1–Cl2–Cu1^{i} 84.76(5), Cu2^{i}–Cl2–Cu1^{i} 75.02(4), O1–P1–Cu1 118.39(13), P1–Cu1–Cu2 146.76(5), P1–Cu1–Cu2^{i} 85.88(4), Cl1–Cu1–Cl2^{i} 91.28(5), Cl2–Cu1–Cl2^{i} 95.24(5), Cl2^{i}–Cu1–Cu2^{i} 82.13(4), Cl1–Cu1–Cu2^{i} 151.69(4), O1^{i}–P2–Cu2 112.97(13).

The centrosymmetric **4** crystallizes in the monoclinic space group $P2_1/c$, with two molecules in the unit cell. The details of the structural parameters are given in table 1. The solid-state structure of **4** is given in figure 3. Two tetraphenyldiphosphoxane moieties (P–O–P) are bound to four copper(I) centers in a bridging fashion to construct the Cu$_4$ core. Two copper ions are four-coordinate with three chlorides and one phosphorus in a distorted tetrahedral geometry, whereas the other two copper ions are three-coordinate and their geometry can be described as trigonal planar. The P–N–P angle (124.1°) in **4** is slightly greater on chelation with the metal compared with those of **3** and free **1** [120.0° and 122.8 (2)°, respectively]. The Cu–Cu distances (2.903 and 3.002 Å) in **4** are significantly longer than those in **2** (2.684 and 2.839 Å) and the range for [Cu$_4$(dppan)Cl$_4$] is [2.648(2)–2.784 (2)], as reported by Samuelson *et al.* to consider any interaction among them [66]. Thus, when compared with **2**, a slight elongation in Cu–Cu bond in the Cu$_4$ core is observed in **4** due to a ligand exchange reaction. Two chlorides are in μ_3 mode and the other two are in μ_2-bridging mode, constructing a polymetallacyclic zigzag structural motif for Cu$_4$Cl$_4$.

The unsymmetrical **5** crystallizes in the monoclinic space group $P2_1/c$, with four molecules in the unit cell. The details of the structural parameters are given in table 1, and the solid-state structure of **5** is given in figure 4. In **5**, one tetraphenyldiphosphoxane (P–O–P) is bound to two copper(I) centers in a bridging fashion along with two μ_2 chlorides. The chemical environment of the copper is different for both copper ions. One copper is coordinated with two chlorides, one phosphorus from the tetraphenyldiphosphoxane group and one phosphorus of tetraphenyldiphosphine oxide generated by rearrangement of tetraphenyldiphosphoxane moiety. The second copper ion is ligated by two chlorides, one phosphorus from the tetraphenyldiphosphoxane group and one phosphorus from triphenylphosphine. The geometry of both copper ions is distorted tetrahedral. The P–N–P angle (127.81°) in **5** is greater on chelation with the metal compared with that of **4**, **2**, and

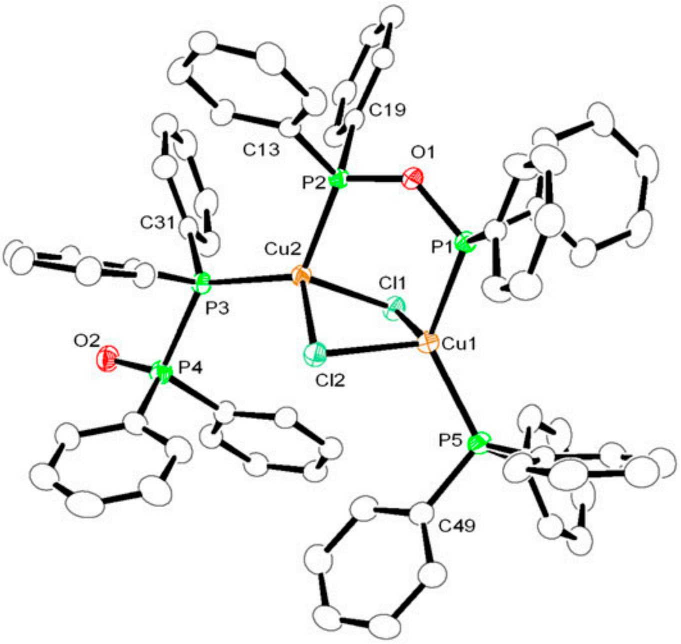
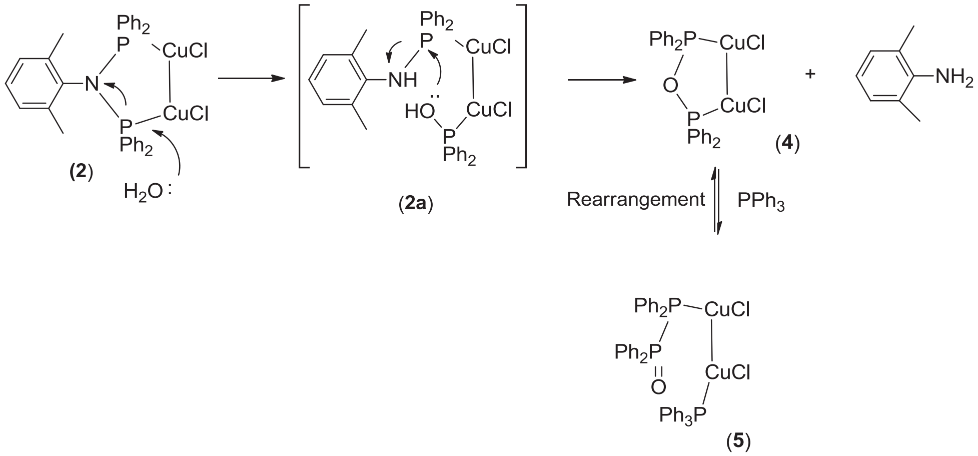


Figure 4. ORTEP diagram of **5** with thermal displacement parameters drawn at the 30% probability level; hydrogens were omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Cu1–P1 2.2363(11), Cu1–P5 2.2619 (12), Cu1–Cl2 2.3864(11), Cu1–Cl1 2.4384(11), Cu1–Cu2 3.0199(8), Cu2–P2 2.2407(11), Cu2–P3 2.2637(11), Cu2–Cl2 2.3832(10), Cu2–Cl1 2.4023(11), P1–O1 1.644(3), P2–O1 1.651(3), P3–P4 2.2555(15), P4–O2 1.487(3), P1–Cu1–P5 128.32(4), P1–Cu1–Cl2 105.55(4), P5–Cu1–Cl2 108.61(4), P1–Cu1–Cl1 98.62(4), P5–Cu1–Cl1 114.81(4), Cl2–Cu1–Cl1 95.95(4), P1–Cu1–Cu2 89.12(3), P5–Cu1–Cu2 142.54(4), Cl2–Cu1–Cu2 50.67(3), Cl1–Cu1–Cu2 50.87(3), P2–Cu2–P3 120.35(4), P(2)–Cu2–Cl2 105.28(4), P3–Cu2–Cl2 111.68(4), P2–Cu2–Cl1 99.33 (4), Cl(2)–Cu(2)–Cl1 97.00(4), P1–O1–P2 127.81(17).

free **1** [124.0°, 120.0°, and 122.8(2)°, respectively]. The Cu–Cu distance is also slightly greater (3.020 Å), indicating no interaction between them. Two six-membered metallacycles P1–O1–P2–Cu2–Cl1–Cu1 and P1–O1–P2–Cu2–Cl2–Cu1 are formed along with one four-membered core Cu_2Cl_2. Both copper ions, Cu1 and Cu2, are coplanar with the plane containing P1, O1, and P2. P1–Cu1 (2.236 Å) and P2–Cu2 (2.241 Å) distances are similar to those observed for **2** [2.185(3)–2.195(3) Å)] and **4** [2.167(4)–2.175(14) Å].

3.3. *Most plausible mechanism for conversion of 4–5*

We have observed that the ligand distribution reaction of **2** yields **4** and **5** where the bis (diphenylphosphino)-2,6-dimethylaniline moieties (PNP) are replaced by tetraphenyldiphosphoxane moieties (Ph_2POPPh_2) and 2-oxo-tetraphenyldiphosphine ($Ph_2P(O)PPh_2$) with the reaction of methylene chloride and water mixture (10 : 1). On the basis of the crystal structures and the ^{31}P signals obtained from **2** to **5**, we could propose the most plausible mechanism for the ligand distribution reaction of **2** as shown in (scheme 3). Initial nucleophilic attack by water molecule led to break in the P–N bond to form an intermediate **2a**, which undergoes further nucleophilic attack at the second phosphorus atom attached to nitrogen to release free 2,6 dimethylaniline and **4**. In the ^{1}H NMR of the reaction mixture, we could



Scheme 3. Most plausible mechanism for ligand distribution reaction of **2**.

also detect the amine proton at 3.84 ppm for free 2,6 dimethylaniline. As in **4**, both phosphorus atoms are in +3 oxidation state, one phosphorus can be oxidized due to adjacent oxygen to lead to unsymmetrical phosphorus atoms which have been isolated as the minor product, **5**. Similar interconversion of ligands is reported for a ruthenium complex by Aydemir *et al.* [29, 76, 77]. Burrows *et al.* also reported the analogous P–N bond cleavage of rhodium(I) complexes *trans*-[RhCl(CO)(PR$_2${NC$_4$H$_3$C(O)Me-2})$_2$] (R = Ph, NC$_4$H$_4$) with water to give diphosphoxane-bridged dimers [Rh$_2$Cl$_2$(CO)$_2$(μ-PR$_2$OPR$_2$)$_2$] [78].

4. Conclusion

We have demonstrated the synthetic and structural features of copper and cobalt complexes with P–N–P ligands. Two P–N–P ligands bind four copper(I) centers in a bridging fashion to form a Cu$_4$ core structure, whereas in the cobalt complex, two P–N–P ligands coordinate with one cobalt in a chelating fashion to give a monomeric complex. We also found that in wet conditions, with methylene chloride, the P–N–P ligand attached to copper undergoes ligand distribution to generate a P–O–P moiety, which eventually forms a second tetranuclear copper complex.

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