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# Mitigating repulsions in close quarters: Copper tells us how!

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#### Abstract

Four copper(I) complexes of short bite ligands, bis(diphenylphosphino)amine (dppa) and bis(diphenylphosphino)isopropylamine (dppipa) were synthesized from appropriate precursors. All complexes were characterized by single crystal X-ray crystallography and spectroscopic techniques. In each of these complexes, two filled shell cations are forced into close proximity ( $\approx 2.7-2.8$  Å). With no strong  $\pi$  acid ligands to siphon electron density from the filled d shell, the unavoidable repulsive  $d^{10}-d^{10}$  interaction is mitigated when an unsymmetrical coordination environment around the copper atoms exists. The coordinatively saturated copper ion functions as a donor to the coordinatively unsaturated copper. A Cambridge Structural Database (CSD) search reveals the greater propensity of clusters with short contacts to adopt unsymmetrical coordination.

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#### 1. Introduction

Closed shell interactions in inorganic chemistry have been a challenge to experimental and theoretical chemists alike [1,2]. Group 11 monocations have been the subject of innumerable studies for they form many polynuclear complexes and extended lattices with short contacts in the solid state despite the formally closed shell  $(d^{10})$  electronic configuration of the metals involved. The nature of this closed shell interaction has been an area of considerable debate. In the case of gold, the attractive nature of this interaction has been particularly well documented and accepted. The term "aurophilicity" is used to collectively describe Au-Au interactions [3-6]. Some of these interactions are unsupported by exogenous ligands. This attractive interaction has found its theoretical justification in the ligand-induced [7] and relativistically-supported [8] stabilization, which leads to favorable mixing of the empty 6s with 5d states to effectively reduce the population of the 5d

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valence shell. Whereas in the lighter congeners, the existence of analogous cuprophilicity and argentophilicity [1,4,5,9] have not been substantiated by many ligandunsupported M(I)-M(I) (M = Cu, Ag) contacts in coordination compounds. Very short distances, for example 2.42 Å between two copper centers has been observed by White et al. [10] in a complex with a short bite ligand 2-((6-methyl)pyridyl)trimethylsilylamine. Another example of an unusually short Cu(I)–Cu(I) distance (2.35 Å) [11] is found in [Cu(tolyl-NNNN-tolyl)]<sub>3</sub>. This complex has been analyzed at different levels of theory and the Cu-Cu interaction has been shown to be attractive as a result of  $s + p_z + d_{z^2}$  mixing [12]. In the few unsupported short contacts, strong electrostatic interactions between the subunits cloud the analysis. This has resulted in a controversy about the degree of stabilization, if any, offered by metalmetal contacts in ligand supported cases.

We have examined in this study, four complexes of a diphosphinoamines of the type  $Ph_2PN(R)PPh_2$  (dppa; R = H, dppipa;  $R = {}^{i}Pr$ ). These ligands are well known for their short bite [13], which force short metal-metal contacts. There would be considerable difficulty in accommodating

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the short-bite of the ligand with the closed shell repulsion of Cu(I). Yet copper(I) adopts another route for relieving the repulsive interactions in these examples. Unsymmetrical coordination makes one copper electron rich relative to the other by the presence of an extra ligand. This makes one copper a donor and the other an acceptor and masks the otherwise repulsive interaction. The generality of this phenomenon in complexes with a short contact was brought out by analysis of data readily available in the Cambridge Structural Database (CSD) [14].

## 2. Results and discussion

## 2.1. X-ray crystal structure determinations

Complex 1 consists of a cationic dppa bridged dimer with an unsymmetrical coordination. The perspective view is represented in Fig. 1. Although Cu1 and Cu2 have 3 and 4 coordinating atoms around them respectively, including the distant copper in the coordination sphere makes the description easy to follow. Cu1 has a distorted tetrahedral geometry with P1, P3, N3 and Cu2 around it. Cu1 is merely 0.2336(1) Å from the plane formed by two P atoms (P1 and P3) and the N3 of acetonitrile. The sum of the three angles in this trigonal plane is approximately equal to 360° (see Table 1). The tetrahedral coordination is provided by the second copper atom (Cu2). Cu2 is found to adopt a severely distorted trigonal bipyramidal geometry. It has two P atoms P2, P4 and an oxygen atom of the perchlorate anion in the equatorial plane. Cu2 deviates from this plane by 0.227(1) Å. The axial ligands around Cu2 are the oxygen atom of the water (Ow1) and Cu1 subtending an angle of 166.3(2)° along this axis. Cu1 and Cu2 deviate by -2.6182(1) Å and -0.010(1) Å from the P2, P4, and O5a plane respectively, while Cu2 has a deviation of



Fig. 1. Cationic fragment of complex 1  $[Cu_2(dppa)_2(CH_3CN)(H_2O)-(OClO_3)]ClO_4$  with a Cu–Cu distance of 2.7483(9) Å (phenyl rings on phosphorus and hydrogen atoms removed for clarity).

Table 1								
Selected bond	distances	(Å) and	i bond	angles	(°)	for	complex	x 1

Bond distances			
Cu1–Cu2	2.7483(9)	Cu2–Ow1	2.189(5)
Cu1–P1	2.235(1)	Cu2–O5a	2.172(19)
Cu1–P3	2.2213(12)	P1-N1	1.676(3)
Cu1-N3	1.965(4)	P2-N1	1.676(3)
Cu2–P2	2.2645(12)	P3–N2a	1.673(3)
Cu2–P4	2.2632(13)	P4–N2a	1.688(3)
Bond angles			
P1-Cu1-P3	131.95(5)	P2-Cu2-P4	139.46(5)
P1-Cu1-N3	107.56(13)	P2-Cu2-Ow1	101.50(15)
P3-Cu1-N3	116.87(13)	P4-Cu2-Ow1	98.80(14)
P1-Cu1-Cu2	95.87(4)	O5a-Cu2-Ow1	58.4(5)
P3-Cu1-Cu2	98.69(4)	O5a-Cu2-Cu1	108.4(5)
N3–Cu1–Cu2	93.49(14)	Ow1-Cu2-Cu1	166.31(17)
P2–Cu2–O5a	111.1(5)	P1-N1-P2	122.2(2)
P2-Cu2-Cu1	81.65(3)	P3–N2a–P4	121.8(2)
P4–Cu2–O5a	109.4(5)		

2.9766(1) Å from the P1 P3 N3 plane. The two trigonal planes P1, P3, N3 and P2, P4, O5a, have a dihedral angle of 14.82(6) Å. The eight membered ring formed by the two PNP bridges adopts a twist boat conformation. Nitrogen atoms of the ligand are almost planar with the angles not very different from those of the free ligand. There is no significant change in the metrical parameters of the ligand on complexation (P–N bond length in the free ligand is 1.692 Å with a PNP angle of  $118.9^{\circ}$ ).

The second  $\text{ClO}_4^-$  is found outside the coordination sphere. The counter anion  $\text{ClO}_4^-$  shows weak intermolecular hydrogen bonding interactions with the aromatic protons, H of the acetonitrile and the NH protons. The bound water is found to have a short contact with a phenylic proton as well. Some of the short contacts are listed in the Supplementary information (Table S1).

The ORTEP plot of the dication of complex **2** is given in Fig. 2 and shows that complexes **1** and **2** are similar. Cu1 is



Fig. 2. Cationic fragment of complex  $2 [Cu_2(dppa)_2(CH_3CN)_3](BF_4)_2$  with a Cu–Cu distance of 2.8215(8) Å (phenyl rings on phosphorus and hydrogen atoms removed for clarity).

found in a severely distorted tetrahedral geometry. Cul deviates by -0.2237(5) Å from the P1, P3, N3 plane and Cu2 forms the fourth coordination site of the tetrahedron. The second metal atom Cu2 adopts an irregular trigonal bipyramidal geometry with Cu2 being -0.352(1) Å away from the P2, P4, N5 plane. The axial sites are occupied by Cu1 and N4 (CH<sub>3</sub>CN) subtending an angle of 166.92(9)° at Cu2 (Table 2). The two counter anions lie far from the metal center.

Cu1 and Cu2 deviate by 2.4525(5) Å and -0.352(1) Å from the P2, P4, N5 plane respectively, -0.2237(5) Å and -3.043(1) Å from the P1, P3, N3 plane respectively. The two planes P1, P3, N3 and P2, P4, N5 have a dihedral angle of 6.92(7) Å. The short contacts formed by BF<sub>4</sub><sup>-</sup> with phenylic protons and NH protons do not appear to affect the structure significantly and are listed in the Supplementary information (Table S2).

The movement of the two Cu atoms in complex 1 towards one other is quite striking. Complex 1 is also remarkable for it is the first example of a Cu(I) complex having a water molecule and a phosphine in the coordination sphere. Surprisingly, in spite of very similar synthetic conditions, they have different ancillary donors and Cu-Cu distances. Recently, an analogous complex with  $PF_6^-$  was characterized in both symmetrical (Cu–Cu distance = 3.341(2) Å) and unsymmetrical environments (Cu-Cu distance = 2.869(4) Å) [15]. Significantly, the shorter distance is associated with the unsymmetrical structure. While the unsymmetrical structure has donors similar to 2, an entirely different orientation of the ligand leads to shorter Cu-Cu distance (2.8215(8) Å) in 2. In 1 and 2, the complex is coordinatively unsaturated in one of the metal centers although excess acetonitrile is present during the synthesis.

In a related study with the ligand dppipa, we isolated complexes 3 and 4. The ORTEP plot of the dppipa complexes 3 and 4 are shown in Figs. 3 and 4 respectively. The two halide (chloride and bromide) dimers have highly unsymmetrical structures. There are two dppipa units, out of which one is found in a chelating and the other one in a

Table 2 Selected bond dis	tances (Å) and hor	nd angles (°) for comp	lav <b>7</b>
Science bolid dis	tances (A) and bor	id angles ( ) for comp	
Bond distances			
Cu1–Cu2	2.8215(8)	Cu2–N4	2.073(3)
Cu1–P1	2.2725(10)	Cu2–N5	2.046(3)
Cu1–P3	2.2316(11)	P1-N1	1.687(3)
Cu1–N3	2.023(3)	P2-N1	1.677(3)
Cu2–P2	2.273(1)	P3–N2a	1.680(3)
Cu2–P4	2.2723(11)	P4–N2a	1.693(3)
Bond angles			
P1–Cu1–P3	129.87(4)	P4-Cu2-N5	103.33(9)
P1-Cu1-N3	96.07(9)	P2-Cu2-N4	95.71(9)
P3-Cu1-N3	130.71(8)	P4-Cu2-N4	105.55(9)
P1–Cu1–Cu2	97.93(3)	N4–Cu2–N5	96.15(12)
P3–Cu1–Cu2	93.66(3)	N4-Cu2-Cu1	166.92(9)
N3–Cu1–Cu2	96.87(8)	P1-N1-P2	123.31(15)
P2-Cu2-P4	130.68(4)	P3–N2a–P4	124.92(16)
P2–Cu2–N5	118.21(9)		



Fig. 3. Complex 3  $[Cu_2(dppipa)_2(Cl)_2]$  with a Cu–Cu distance of 2.7664(14) Å (phenyl rings on phosphorus and hydrogen atoms removed for clarity).



Fig. 4. Complex 4  $[Cu_2(dppipa)_2(Br)_2]$  with a Cu–Cu distance of 2.7675(8) Å (phenyl rings on phosphorus and hydrogen atoms removed for clarity).

bridging mode. Important bond lengths and bond angles for complex **3** and **4** are given in Tables 3 and 4 respectively. Both complexes have Cu–Cu distances within the sum of the Van der Waal's radii. The chloride complex **3** has two copper centers at a distance of 2.7664(14) Å and the bromide complex **4** has a Cu–Cu distance of 2.7675(8) Å.

In complex **3**, Cu1 has three of its coordination sites occupied by P1, P4 and Cl1 (bridged). The fourth coordination site is held by P3 at a comparatively longer distance of 2.263(1) Å. The other copper, Cu2 is trigonal planar with Cl1, Cl2 and P2 in its coordination sphere with sum of the three angles close to  $360^{\circ}$ . The two trigonal planes P2, Cl1, Cl2 and P1, P4, Cl1 are hinged by a chloride bridge, Cl1 and the dihedral angle is  $69.59(2)^{\circ}$ . The deviations of Cu1 and Cu2 from P1, P4, Cl1 planes are -0.358(1) Å and 2.115(1) Å respectively. On the other hand, Cu1 and Cu2 deviate by 2.161(1) Å and 0.1883(6) Å from P2, Cl1, Cl2 plane respectively. This indicates that Cu2 moves towards Cu1 in a cuprophilic fashion.

Table 3 Selected bond distances (Å) and bond angles (°) for complex  ${\bf 3}$ 

Bond distances			
Cu1–Cu2	2.7664(14)	Cu2–Cl1	$2.363(1)^{c}$
Cu1–P1	$2.2604(12)^{a}$	Cu2–Cl2	$2.1824(12)^{d}$
Cu1–P3	$2.339(1)^{b}$	P1-N1	1.708(3)
Cu1–P4	$2.301(1)^{b}$	P2-N1	1.720(3)
Cu1–Cl1	$2.320(1)^{c}$	P3-N2	1.709(3)
Cu2–P2	$2.186(1)^{a}$	P4–N2	1.721(3)
Bond angles			
P1–Cu1–P3	111.60(4)	P2-Cu2-Cl1	108.49(4)
P1–Cu1–P4	126.51(4)	P2-Cu2-Cl2	134.33(4)
P3–Cu1–P4	71.95(4)	Cl1-Cu2-Cl2	114.97(4)
P1–Cu1–Cl1	108.72(4)	P1-N1-P2	115.10(13)
P3-Cu1-Cl1	115.10(4)	P3-N2-P4	105.27(14)
P4–Cu1–Cl1	117.47(4)		

<sup>a</sup> Bridging dppipa.

<sup>b</sup> Chelating dppipa.

<sup>c</sup> Bridging Cl<sup>-</sup>.

Table 4

<sup>d</sup> Terminal Cl<sup>-</sup>.

Selected bond	distances (Å) and bond angles (°) for complex 4	

Bond distances			
Cu1–Cu2	2.7675(8)	Cu2-Br1	2.4437(8) <sup>c</sup>
Cu1–P1	2.3404(12) <sup>a</sup>	Cu2–Br2	$2.3094(8)^{d}$
Cu1–P2	2.2956(13) <sup>a</sup>	P1-N1	1.706(4)
Cu1–P3	2.263(1) <sup>b</sup>	P2-N1	1.722(4)
Cu1–Br1	2.4496(7) <sup>c</sup>	P3-N2	1.703(3)
Cu2–P4	2.1853(13) <sup>b</sup>	P4-N2	1.715(3)
Bond angles			
P1–Cu1–P3	112.11(4)	P4-Cu2-Br1	109.24(4)
P1–Cu1–P2	72.23(4)	P4-Cu2-Br2	132.91(4)
P2–Cu1–P3	126.21(5)	Br1-Cu2-Br2	114.64(3)
P1–Cu1–Br1	114.18(4)	P1-N1-P2	105.7(2)
P3–Cu1–Br1	108.49(4)	P3-N2-P4	115.47(19)
P2–Cu1–Br1	118.10(4)		

<sup>a</sup> Bridging dppipa.

<sup>b</sup> Chelating dppipa.

<sup>c</sup> Terminal Br<sup>-</sup>.

<sup>d</sup> Bridging Br<sup>-</sup>.

Similarly in case of complex 4, there are two trigonal planes Br1, Br2, P4 and P2, P3, Br1 (common vertex at Br1) at a dihedral angle of  $67.66(2)^{\circ}$ . Cu1 is four coordinate with three coordination sites, Br1, Br2 and P3 almost in a plane with a weak interaction at a distance of 2.3404(12) Å with P1. Cu1 and Cu2 deivate by 0.3613(4) Å and -2.1246(6) Å from P2, P3, Br1 plane respectively. The three coordinate Cu2 deviates by 0.2346(6) Å from Br1, Br2, P4 plane with Cu1 deviating by 2.2484(4) Å from the same plane. In this case also, one can find Cu2 moving towards Cu1.

One would expect the Cu–Cu distance in the case of the bromide bridged dimer to be longer than in the case of analogous chloride complex due to larger size of the bridging bromide ion. Surprisingly the two Cu–Cu distances are not very different. This behavior is reminiscent of the behavior of copper in trimeric complexes [16]. The greater  $\pi$ -donation of bridging chloride ligands leads to larger Cu–Cu distances.

## 2.2. Solution behavior

One expects that complex 1 would exhibit conductivity corresponding to a 1:1 electrolyte and complex 2 would show conductivity corresponding to that of a 1:2 electrolyte [17]. Indeed complex 2 showed a conductivity value of 220.64 S cm<sup>-1</sup> mol<sup>-1</sup> (10<sup>-3</sup> M in acetone), which shows that it is a 1:2 electrolyte. On the other hand complex 1 gave a value of 203.64 S cm<sup>-1</sup> mol<sup>-1</sup> (10<sup>-3</sup> M in acetone), which was considerably higher than that of a 1:1 electrolyte suggesting significant dissociation in solution. This observation clearly indicates that the perchlorate anion, which is  $\eta^1$ -bound to the metal center, dissociates in solution and a 1:2 electrolyte is formed. The dissociation of the perchlorate in solution suggests that the structure in solution could be symmetrical even though the solid state structure is unsymmetrical.

#### 2.3. Cambridge Structural Database analysis

To probe the frequency of unsymmetrical coordination, we explored the CSD and found 1227 instances where Cu-Cu distances were below 2.8 Å. Out of these, 829 fragments were obtained when the search was limited to "symmetrical" dimers with coordination numbers 2,2; 3,3 and 4,4, etc. Among these symmetrically coordinated fragments, 530 of them have coordination numbers up to 4,4. The remaining have higher coordination numbers. Fragments with coordination number of four each (221) were analyzed in detail. Although the CSD lists them as having the same coordination number, and it was found that about 76% (163) have an unsymmetrical coordination by virtue of different coordinating atoms or very different bond distances around the metal centers. In addition, these apparently "symmetrically bridged" compounds several (143 out of 221) have single atom bridges with acute angles in structures that lead to 3c-2e<sup>-</sup> bonds and so promote attractive Cu-Cu interactions.

On the contrary, unsymmetrical coordination occurred in 398 cases, which accounts for about one-third of the total number. Of these, 305 fragments have coordination number less than or equal to 4. There are 142 hits for coordination number 3 and 4, 119 hits with coordination numbers 2 and 3 and the remaining 44 have 2 and 4 coordinate Cu<sup>I</sup> ions. Fig. 5 represents the distribution of M-M distances in complexes with coordination numbers 3/4 and 2/3 respectively. The histograms clearly reflect a welldefined interaction between the metal ions around 2.6-2.7 Å. This is below the sum of the van der Waal's radii for two  $Cu^{I}$  ions (2.8 Å) suggesting the presence of an attractive interaction between the two copper(I) centers. A similar analysis of structures having Cu-Cu distances above 2.8 Å shows that the probability of encountering unsymmetrical coordination is less (1/4th).



Fig. 5. Histograms of Cu–Cu distances in (a)  $CuL_3$  and  $CuL_4$  and (b)  $CuL_2$  and  $CuL_3$  complexes.

Among the complexes short listed from the CSD search, two complexes closely related to 3 and 4 were encountered with CCDC refcodes CAGBIW [18] and ODODAM [19] (Fig. 6(a) and (b)). These two structures have very similar coordination environments to those observed in the present study. The former has one copper having a coordination number of four with one bromide, two nitrogen atoms and one phosphorus bound to it. The three coordinate copper has two bromides (one terminal and one bridging) and one nitrogen in its coordination sphere. Similarly the latter structure has the three coordinate copper with two chlorides, one nitrogen and the four coordinate copper with one chloride, two nitrogen atoms and one phosphorus. The Cu-Cu distances are 2.658 and 2.665 Å respectively. These two examples again augment the fact that complexes that have Cu-Cu distances within the sum of the Van der Waal's radii of two copper centers tend to be unsymmetrically coordinated. A survey of short metal-metal contacts in systems with incomplete d shells, invariably reflected lesser preference for forming unsymmetrical dimers in comparison with the formation of symmetrical structures.



Fig. 6. Two unsymmetrical copper(I) dimers in wireframe style with refcodes: (a) CAGBIW and (b) ODODAM.

#### 3. Conclusions

As expected for the short bite dppa as well as dppipa ligands, dinuclear copper(I) complexes formed have two copper(I) centers close to each other. In the absence of significant  $\pi$ -acceptor character in the ligand, such a short Cu-Cu distance is clearly repulsive and is forced by the ligand. Due to the plasticity of the coordination sphere in monovalent group 11 complexes, a change in the coordination number is energetically accessible. Hence, the coordination environment around only one of the copper(I) ions is altered to give a 4 coordinate-3 coordinate system. The four coordinate copper(I) can act as an electron donor and pump some electron density into a coordinatively unsaturated three coordinate copper. Computational work to justify this statement is underway. A CSD analysis reveals more frequent occurrence of unsymmetrical coordination in complexes with short contacts. Four complexes investigated in the present study along with two of the closely related copper(I) dimers with ((dimethylaminomethyl)phenyl)phosphine-N, N', N'', P ligand and analogous

hexafluorophosphate copper(I) dppa dimers reinforce the importance of unsymmetrical coordination in relieving the repulsion between two closed shells. In spite of closed shell repulsions, a close contact results because the resourceful copper(I) adopts unsymmetrical coordination!

## 4. Experimental

#### 4.1. General remarks

Dichloromethane, diethyl ether, acetonitrile, petroleum ether (b.p. 60–80 °C) and benzene (Caution: benzene is carcinogenic and should be handled with extreme caution!) were purified and dried under nitrogen atmosphere by conventional methods [20]. Bis(diphenylphosphino)amine [21] and bis(diphenylphosphino)isopropylamine [22] were synthesized using existing procedures and were further purified using column chromatography. [Cu(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub> [23], [Cu(CH<sub>3</sub>CN)<sub>4</sub>]BF<sub>4</sub> [24], CuCl [25] and CuBr [26] were prepared by reported methods. All manipulations were carried out under an atmosphere of purified N<sub>2</sub> using a standard double manifold and Schlenk ware.

### 4.2. Physical measurements

<sup>1</sup>H NMR spectra were recorded either on a Bruker ACF 200 MHz or AMX 400 MHz spectrometer with tetramethylsilane (TMS) as the internal reference. <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded either on a Bruker AMX 400 MHz spectrometer operating at 162.2 MHz or a Bruker ACF 200 MHz operating at 81.1 MHz with H<sub>3</sub>PO<sub>4</sub> (85%) as the external reference. IR spectra were recorded in the solid state as KBr pellets on an Equinox 55 Bruker spectrometer. Elemental Analyzer model 1106 and HRESMS on Micromass Q-Tof micro. The conductivity measurements were carried out with a Control Dynamics Conductivity Meter with KCl (10<sup>-3</sup> M) used as a standard solution.

### 4.3. Synthesis of complexes

Complex 1: dppa (0.19 g, 0.5 mmol) was added to 15 ml CH<sub>2</sub>Cl<sub>2</sub> containing [Cu(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub> (0.16 g, 0.5 mmol) and stirred for 1 h at room temperature. Subsequently the solution was concentrated to about 7 and 15 ml of diethyl ether was allowed to diffuse through the solution to obtain colorless crystals (yield: 86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta = 1.98$  (s, 3H, CH<sub>3</sub>CN), 4.13 (s, 2H, NH), 7.12–7.43 (m, 40H, Ph); <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta = 46.3$  (s); IR (KBr, cm<sup>-1</sup>): 2303 (w), 2270 (w) (CH<sub>3</sub>CN); 1099 (vs, br) 1064 (br) (ClO<sub>4</sub><sup>-</sup>). Elemental *Anal.* Calc. for Cu<sub>2</sub>C<sub>50</sub>H<sub>45</sub>N<sub>3</sub>P<sub>4</sub>. Cl<sub>2</sub>O<sub>8</sub> · H<sub>2</sub>O · CH<sub>2</sub>Cl<sub>2</sub>: C, 49.15; H, 3.74; N, 3.16. Found: C, 49.3; H, 3.95; N, 3.38%.

Complex 2: A similar procedure was adopted except that  $[Cu(CH_3CN)_4]BF_4$  (0.15 g, 0.5 mmol) was used for the reaction which afforded colorless crystals (yield: 88%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta = 1.98$  (s, 9H, CH<sub>3</sub>CN), 4.63 (s, 2H, NH),

7.12–7.45 (m, 40H, Ph).  ${}^{31}P{}^{1}H{}$  NMR (CDCl<sub>3</sub>):  $\delta = 47.8$  (s). IR (KBr, cm<sup>-1</sup>): 2303 (w), 2264 (w) (CH<sub>3</sub>CN); 1102, 1052 (vs, br) (BF<sub>4</sub><sup>-</sup>). HRESMS: [M–(CH<sub>3</sub>CN)<sub>3</sub>]<sup>2+</sup> obsd. m/z 448.0487, calc. for C<sub>48</sub>H<sub>42</sub>N<sub>2</sub>P<sub>4</sub> 448.0445.

Complex 3: To 15 ml of CH<sub>2</sub>Cl<sub>2</sub> was added dppipa (0.22 g, 0.50 mmol) followed by the addition of CuCl (0.025 g, 0.25 mmol). The reaction was stirred at room temperature for half an hour. Subsequently the obtained yellow colored solution was concentrated to 2 ml and about 7 ml of petroleum ether was allowed to diffuse through the dichloromethane solution. Bright yellow colored shaped crystal were obtained in about 10–12 h (yield: 91%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta = 0.06$ , 0.50 (d, 6H, Me of <sup>*i*</sup>Pr) (1:1), 3.57 (sep., 2H, br, –CH of <sup>*i*</sup>Pr), 6.98–7.49 (m, 40H, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta = 77.1$  (w), 55.9 (s). Elemental *Anal.* Calc. for Cu<sub>2</sub>C<sub>54</sub>H<sub>54</sub>N<sub>2</sub>P<sub>4</sub>Cl<sub>2</sub> · 0.5CH<sub>2</sub>Cl<sub>2</sub>0.5H<sub>2</sub>O: C, 59.26; H, 5.07; N, 2.54. Found: C, 59.28; H, 5.06; N, 2.53%.

Complex 4: A similar procedure was adopted except that CuBr (0.036 g, 0.25 mmol) was used for the reaction that gave bright yellow single crystals (yield: 91%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C):  $\delta = 0.05$ , 0.44 (d, 6H, Me of <sup>*i*</sup>Pr) (1:1), 3.54 (sep., 2H, br, -CH of <sup>*i*</sup>Pr), 6.97–7.51 (m, 40H, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta = 77.1$  (w), 55.9 (s). Elemental *Anal.* Calc. for Cu<sub>2</sub>C<sub>54</sub>H<sub>54</sub>N<sub>2</sub>P<sub>4</sub>Br<sub>2</sub> · CH<sub>2</sub>Cl<sub>2</sub>: C, 53.84; H, 4.57; N, 2.28. Found: C, 53.78; H, 4.69; N, 2.20%.

#### 4.4. X-ray crystallographic study

Single crystals of complex 1, 3 and 4 were mounted in a Lindemann capillary with paraffin oil and crystal of complex 2 was glued to the tip of a glass fiber along the largest dimension and coated with paraffin oil. Data were collected on a Bruker AXS single crystal diffractometer equipped with SMART APEX CCD detector and a sealed Mo Ka source working at 1.75 kW. Intensity data were collected at room temperature. Crystallographic computations were performed using the WINGX package [27]. The data were corrected for Lorentz and polarization effects. Absorption correction was applied using Psi-Scan [28] for complex 1, 3 and 4 and sADABS [29] for complex 2. The positions of heavy atoms were determined by SHELXS86 [30]. The remaining atoms were located from the difference Fourier map using SHELXL-97 [31]. Hydrogen atoms were geometrically fixed for all four complexes.

Single crystal structure of complex **1** ( $C_{51}H_{49}Cl_4Cu_2-N_3O_9P_4$ ): (0.42 × 0.40 × 0.38 mm<sup>3</sup>); triclinic;  $P\bar{1}$ ; a = 11.0536(16) Å, b = 12.3546(18) Å, c = 22.106(3) Å,  $\alpha = 78.332(3)^\circ$ ,  $\beta = 84.031(2)^\circ$ ,  $\gamma = 68.189(2)^\circ$ ; V = 2743.5(7) Å<sup>3</sup>; Z = 2;  $\rho_{calc.} = 1.502$  Mg/m<sup>3</sup>;  $\mu_{calc.} = 1.143$  mm<sup>-1</sup>; R = 0.0594 for 10753 independent reflections with  $(I > 2\sigma(I))$ .

Complex 2:  $C_{54}H_{51}B_2Cu_2F_8N_5P_4$ :  $(0.36 \times 0.32 \times 0.20 \text{ mm}^3)$ ; triclinic;  $P\bar{1}$ ; a = 11.169(3) Å, b = 12.349(4) Å, c = 22.083(7) Å,  $\alpha = 94.374(5)^\circ$ ,  $\beta = 95.555(5)^\circ$ ,  $\gamma = 106.850(4)^\circ$ ; Z = 2;  $\rho_{calc.} = 1.376 \text{ Mg/m}^3$ ;  $\mu_{calc.} = 0.914 \text{ mm}^{-1}$ ; R = 0.0519 for 13298 independent reflections  $(I \ge 2\sigma(I))$ .

Complex 3:  $C_{55}H_{56}Cl_4Cu_2N_2P_4$ :  $(0.45 \times 0.4 \times 0.38 \text{ mm}^3)$ ; monoclinic; P21/c; a = 21.042(10) Å, b = 13.733(7) Å, c = 20.649(10) Å,  $\alpha = 90^\circ$ ,  $\beta = 114.365(8)^\circ$ ,  $\gamma = 90^\circ$ ; V = 5435(5) Å<sup>3</sup>; Z = 4;  $\rho_{calc.} = 1.390$  Mg/m<sup>3</sup>;  $\mu_{calc.} = 1.135$  mm<sup>-1</sup>; R = 0.0502 for 12748 independent reflections with  $(I \ge 2\sigma(I))$ .

Complex 4:  $C_{55}H_{56}Br_2Cl_2Cu_2N_2P_4$ :  $(0.24 \times 0.22 \times 0.21 \text{ mm}^3)$ ; monoclinic; P21/c; a = 21.287(3) Å, b = 13.678(2) Å, c = 20.660(3) Å,  $\alpha = 90^\circ$ ,  $\beta = 114.071$  (2)°,  $\gamma = 90^\circ$ ; V = 5492.5(15) Å<sup>3</sup>; Z = 4;  $\rho_{calc.} = 1.483$  Mg/m<sup>3</sup>;  $\mu_{calc.} = 2.481$  mm<sup>-1</sup>; R = 0.0545 for 13015 independent reflections with  $(I > 2\sigma(I))$ .

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#### Appendix A. Supplementary material

CCDC-200619, CCDC-200620, CCDC-191476, CCDC-247449 contain the supplementary crystallographic data for **1**, **2**, **3** and **4**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk).

Weak hydrogen bonding interactions of  $\text{ClO}_4^-$  and  $\text{BF}_4^$ ions in complex 1 and 2, list of "refcodes" having Cu–Cu distances (<2.8 Å) with unsymmetrical coordination, histogram of short contacts in CuL<sub>2</sub> and CuL<sub>4</sub>, and references dealing with apparent "cuprophilic" interactions. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.08.004.

#### References

- [1] P. Pyykkö, Chem. Rev. 97 (1997) 597.
- [2] M. Jansen, Angew. Chem. 99 (1987) 1136.

- [3] H. Schmidbaur, Gold Bull. 23 (1990) 11.
- [4] P. Pyykkö, Y.-F. Zhao, Angew. Chem., Int. Ed. Engl. 30 (1991) 604.
- [5] P. Pyykkö, J. Li, Chem. Phys. Lett. 197 (1992) 586.
- [6] P. Pyykkö, J. Li, Inorg. Chem. 32 (1993) 2630.
- [7] O.D. Häberlen, H. Schmidbaur, N. Rosch, J. Am. Chem. Soc. 116 (1994) 8241.
- [8] P. Pyykkö, Chem. Rev. 88 (1988) 563.
- [9] M.A. Omary, R.R. Webb, Z. Assefa, G.E. Shankle, H.H. Patterson, Inorg. Chem. 37 (1998) 1380.
- [10] L.M. Engelhardt, G.E. Jacobsen, W.C. Patalinghug, B.W. Skelton, C.L. Raston, A.H. White, J. Chem. Soc., Dalton Trans. (1991) 2859.
- [11] J. Beck, J. Strähle, Angew. Chem., Int. Ed. Engl. 24 (1985) 409.
- [12] K.M. Merz Jr., R. Hoffmann, Inorg. Chem. 27 (1988) 2120.
- [13] J.T. Mague, J. Cluster Sci. 6 (1995) 217.
- [14] F.H. Allen, O. Kennard, Chem. Des. Autom. News. 8 (1993) 31.
- [15] H. Liu, M.J. Calhorda, M.G.B. Drew, V. Félix, J. Novosad, L.F. Verios, F.F. de Biani, P. Zanello, J. Chem. Soc., Dalton Trans. (2002) 4365.
- [16] J.K. Bera, M. Nethaji, A.G. Samuelson, Inorg. Chem. 38 (1999) 218.
- [17] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.
- [18] H. Lang, M. Leschke, H.A. Mayer, M. Melter, C. Weber, G. Rheinwald, O. Walter, G. Huttner, Inorg. Chim. Acta 324 (2001) 266.
- [19] M. Leschke, H. Lang, M. Melter, G. Rheinwald, C. Weber, H.A. Mayer, H. Pritzkow, L. Zsolnai, A. Driess, G. Huttner, Z. Anorg. Allg. Chem. 628 (2002) 349.
- [20] D.D. Perin, W.L.F. Armarego, Purification of Laboratory Reagents, 3rd ed., Pergamon Press, London, 1988.
- [21] V.H. Nöth, L. Meinel, Z. Anorg. Allg. Chem. 5-6 (1967) 225.
- [22] M.S. Balakrishna, T.K. Prakasha, S.S. Krishnamurthy, U. Siriwardane, S.N.J. Hosmane, Organomet. Chem. 390 (1990) 203.
- [23] B.J. Hathaway, D.G. Holah, J.D. Postlethwaite, J. Chem. Soc. (1961) 3215.
- [24] G.J. Kubas, Inorg. Synth. 19 (1979) 90, and references therein.
- [25] R.N. Keller, H.D. Wycoff, Inorg. Synth. 50 (1946) 1.
- [26] R.N. Keller, H.D. Wycoff, Inorg. Synth. 50 (1946) 3.
- [27] L.J. Farrugia, G.X. Win, J. Appl. Crystallogr. 32 (1999) 837.
- [28] A.C.T. North, D.C. Phillips, F.S. Mathews, Acta Crystallogr. Sect. A 24 (1968) 351.
- [29] R.H. Blessing, Acta Crystallogr. Sect. A 51 (1995) 33.
- [30] G.M. Sheldrick, SHELXS-86, Program for Crystal Structure Determination, University of Cambridge, Cambridge, England, 1986.
- [31] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.