

Synthesis, structure and spectroscopic properties of $[\text{Cu}_3(\mu\text{-dnpapy})_3(\text{CH}_3\text{CN})][\text{ClO}_4]_3 \cdot \text{CH}_3\text{CN}$ (dnpapy = 7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine) with a linear copper atom array

Wing-Han Chan,^a Shie-Ming Peng^b and Chi-Ming Che^{*a}

^a Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

^b Department of Chemistry, National Taiwan University, Taipei, Taiwan

The co-ordination chemistry of 7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine (dnpapy) with Cu^{I} has been examined. Reaction of $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{ClO}_4]$ with dnpapy in CH_3CN afforded $[\text{Cu}_3(\mu\text{-dnpapy})_3(\text{CH}_3\text{CN})][\text{ClO}_4]_3 \cdot \text{CH}_3\text{CN}$. The crystal structure of $[\text{Cu}_3(\mu\text{-dnpapy})_3(\text{CH}_3\text{CN})][\text{ClO}_4]_3 \cdot \text{CH}_3\text{CN}$ reveals a linear Cu–Cu–Cu array with both trigonal and tetrahedral co-ordination modes for the copper atoms. The intramolecular Cu–Cu distances of 2.449(2) and 2.721(2) Å suggest that only two of the copper atoms have a bonding interaction. Complex **1** reacts with triphenylphosphine (PPh_3) and 2,2'-bipyridine (bpy) to give $[\text{Cu}(\text{bpy})(\text{dnpapy})_2][\text{ClO}_4]_2 \cdot 2[\text{ClO}_4]$ and $[\text{Cu}_2(\mu\text{-dnpapy})_3][\text{ClO}_4]_2 \cdot 3[\text{ClO}_4]_2$, respectively. Spectroscopic properties of the complexes have been examined.

There has been considerable interest in using polyfunctional ligands for the construction of heterometallic complexes. In this context, rigid pyridylphosphine ligands with short bite distances have attracted our attention since they can support linear chains or more complex arrays of metal atoms.¹ The ligand dnpapy (7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine), reported by Lo Schiavo,^{2a} has a short bite distance and the combined structural features of the binucleating 1,8-naphthyridine (napy) and 2-(diphenylphosphino)pyridine (dppy) ligands. The possible co-ordination modes of dnpapy are shown in Scheme 1. Lo Schiavo and co-workers have studied the reactions of dnpapy with Ir^{I} , Rh^{I} , Pt^{II} and Pd^{II} and the co-ordination modes I–V (Scheme 1) were found.² However, no trinuclear metal complex with dnpapy (VI) has been reported. Herein is described the co-ordination chemistry of dnpapy with Cu^{I} , showing the formation of a linear Cu–Cu–Cu array supported by this ligand.

Experimental

Materials

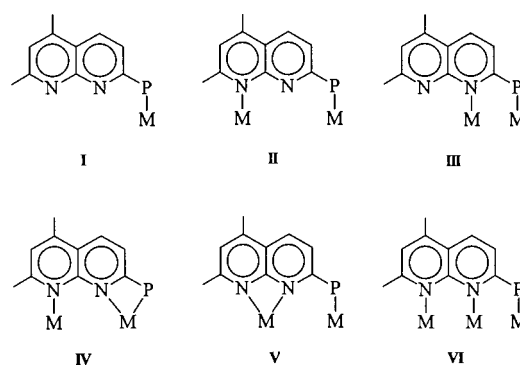
The salt $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{ClO}_4]$ and dnpapy were prepared according to literature methods.^{2a,3} 2,2'-Bipyridine (bpy) and triphenylphosphine were purchased from Aldrich. All reactions were performed under a nitrogen atmosphere unless otherwise stated. Solvents for emission measurements were of spectroscopic grade and solutions for photochemical experiments were degassed by at least four freeze–pump–thaw cycles.

Instrumentation

Proton, ^{13}C and ^{31}P NMR spectra were recorded on a DPX-500 Bruker spectrometer and SiMe_4 was added as internal standard; FAB and ESI mass spectra were collected on a Finnigan MAT 95 high-resolution mass spectrometer. Elemental analyses were performed by Butterworth Laboratories Ltd. Cyclic voltammetry was performed on a Princeton Applied Research (PAR) model 273 potentiostat-galvanostat. Tetrabutylammonium hexafluorophosphate (Aldrich) in acetonitrile was used as supporting electrolyte. The UV/VIS absorption spectra were recorded on a Milton Roy Spectronic 3000 diode-array spectrophotometer. Emission spectra were recorded on a SPEX Fluorolog-2-Model 1680 spectrophotometer.

Preparation of complexes

$[\text{Cu}_3(\mu\text{-dnpapy})_3(\text{CH}_3\text{CN})][\text{ClO}_4]_3 \cdot \text{CH}_3\text{CN}$. The salt $[\text{Cu}$



Scheme 1 Possible co-ordination modes of dnpapy

$(\text{CH}_3\text{CN})_4][\text{ClO}_4]$ (0.33 g, 1.0 mmol) was suspended in acetonitrile (25 ml) and a solution of dnpapy (0.34 g, 1.0 mmol) in dichloromethane (5 ml) was added dropwise. The solution was stirred at room temperature for 1 h. The solvent was removed *in vacuo* leaving an orange solid. Orange crystals of $[\text{Cu}_3(\mu\text{-dnpapy})_3(\text{CH}_3\text{CN})][\text{ClO}_4]_3 \cdot \text{CH}_3\text{CN}$ (1.12 g, 70%) were obtained by diffusion of diethyl ether into an acetonitrile solution (Found: C, 56.6; H, 4.0; N, 7.0. Calc. for $\text{C}_{70}\text{H}_{63}\text{Cl}_3\text{Cu}_3\text{N}_8\text{O}_{12}\text{P}_3$: C, 56.2; H, 4.0; N, 7.0%).

$[\text{Cu}(\text{bpy})(\text{dnpapy})_2][\text{ClO}_4]_2 \cdot 2[\text{ClO}_4]$. A mixture of $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{ClO}_4]$ (1.34 g, 1.0 mmol) and bpy (0.20 g, 1.2 mmol) in dichloromethane (25 ml) was stirred at room temperature for 1 h. The mixture gradually turned from orange to clear yellow. The solvent was removed *in vacuo* leaving an orange solid. Recrystallization of the crude product from an acetonitrile–diethyl ether solution afforded a mixture of red and yellow crystals. The red crystals were identified as $[\text{Cu}(\text{bpy})_2][\text{ClO}_4]$ [0.06 g, 20%, FAB MS: $m/z = 375$ (M^+)] and the yellow crystals as $[\text{Cu}(\text{dnpapy})_2][\text{ClO}_4]$ [0.6 g, 60% (Found: C, 64.3; H, 4.6; N, 8.5. Calc. for $\text{C}_{54}\text{H}_{46}\text{ClCuN}_6\text{O}_4\text{P}_2$: C, 64.6; H, 4.6; N, 8.4%)].

$[\text{Cu}_2(\mu\text{-dnpapy})_3][\text{ClO}_4]_2 \cdot 3[\text{ClO}_4]_2$. A mixture of $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{ClO}_4]$ (1.34 g, 1.0 mmol) and PPh_3 (0.32 g, 1.2 mmol) in dichloromethane (25 ml) was stirred at room temperature for 1 h. The mixture gradually turned from orange to clear yellow. The solvent was concentrated to *ca.* 5 ml. Recrystallization of the crude product from a dichloromethane–diethyl ether solution afforded a mixture of orange and yellow crystals. The orange crystals were identified as $[\text{Cu}(\text{dnpapy})(\text{PPh}_3)_2][\text{ClO}_4]$ [0.32 g, 31%, ESI MS: $m/z = 930$ (M^+) (Found: C, 68.3; H, 4.6; N, 2.5.

Table 1 Crystallographic data for **1**[ClO₄]₃·CH₃CN and **2**[ClO₄]

Complex	1 [ClO ₄] ₃ ·CH ₃ CN	2 [ClO ₄]
Formula	C ₇₀ H ₆₃ Cl ₃ Cu ₃ N ₈ O ₁₂ P ₃	C ₅₄ H ₄₆ ClCuN ₆ O ₄ P ₂
<i>M</i>	1598.2	1003.9
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> <i>c</i>
<i>a</i> /Å	13.804(3)	10.253(2)
<i>b</i> /Å	38.427(3)	10.368(2)
<i>c</i> /Å	14.926(2)	23.487(2)
β/°	116.60(2)	95.23(2)
<i>U</i> /Å ³	7079(2)	2486.3(7)
<i>Z</i>	4	2
<i>D</i> _c /g cm ⁻³	1.500	1.341
μ(Mo-Kα)/cm ⁻¹	11.34	5.55
Crystal size/mm	0.13 × 0.25 × 0.45	0.20 × 0.40 × 0.50
<i>F</i> (000)	3279	1042
2θ _{max} /°	45	50
No. of unique reflections	9227	4382
No. of observed reflections (<i>N</i> _o)	4542 [<i>I</i> > 2σ(<i>I</i>)]	3120 [<i>I</i> > 2σ(<i>I</i>)]
No. of variables (<i>N</i> _v)	892	613
<i>R</i>	0.049	0.042
<i>R</i> _w	0.046	0.039
Goodness of fit	1.55	1.58
Residual electron density/e Å ⁻³	+0.56, -0.35	+0.38, -0.35

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, R_w = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|]^2}{\sum w |F_o|^2}, S = \frac{[\sum w(|F_o| - |F_c|)^2 / N_o - N_v]^2}{\sum w |F_o|^2}, w = [\sigma^2(F) + 0.0001F^2]^{-1}.$$

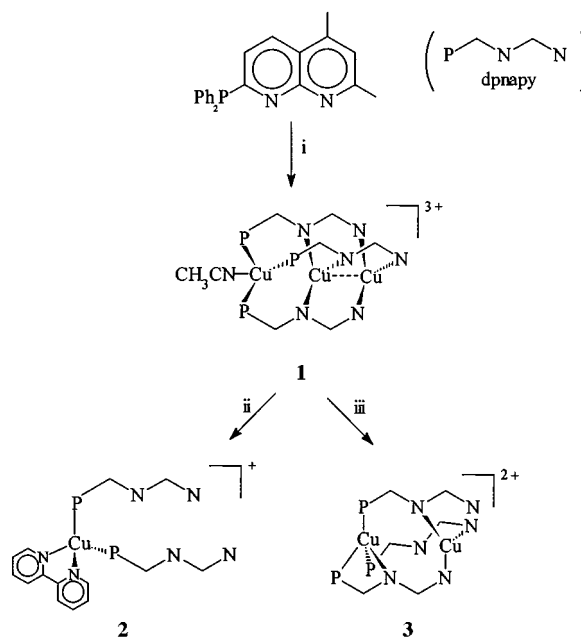
Calc. for C₅₈H₄₉ClCuN₂O₄P₃: C, 67.7; H, 4.8; N, 2.7%) and the yellow crystals as **3**[ClO₄]₂·2H₂O·3CH₃OH [0.86 g, 58% (Found: C, 54.3; H, 4.6; N, 5.5. Calc. for C₆₉H₇₃Cl₂Cu₂N₆O₁₃P₃: C, 55.8; H, 5.0; N, 5.7%)].

X-Ray data collection and refinement

Information concerning the conditions for crystallographic data collection and structure refinement is summarized in Table 1.

Diffraction data for **1**[ClO₄]₃·CH₃CN and **2**[ClO₄] were collected on an Enraf-Nonius diffractometer with monochromatic Mo-Kα radiation (λ = 0.7107 Å).⁴ Intensity data were collected at 298 K using the ω-2θ scan technique. Three standard reflections monitored every hour showed an intensity variation < 2%. The structures were solved by the Patterson method and refined by full-matrix least-squares refinement using the NRCVAX program.⁵ Complex **1** has a long axis and three perchlorates in an asymmetric unit, which leads to fewer observed reflections (50% observed). Complex **2** has a space group *Pc* based on the facts that (1) the intensity distribution indicates that the molecule is non-centrosymmetric, and (2) after successful resolution of the structure the complex cation exhibits a non-crystallographic two-fold axis [passing through the midpoint of N(1)N(2), Cu and the mid-point of P(1)P(2)]. The two-fold axis does not parallel the *b* axis and is impossible as a crystallographic two-fold axis. The ratios of data to parameters for complexes **1** and **2** are low (≈5:1), but both structure analyses are sound on the basis of low *R* values, reasonable thermal parameters and low electron residues.

Diffraction data of **3**[ClO₄]₂·2H₂O·3CH₃OH were collected on a Rigaku RAXIS IIC diffractometer at 293 K using ω-2θ scans technique. Absorption collection was based on ABCOR.⁶ The structure was solved by direct methods and refined by full-matrix least squares using SHELXTL 93.⁷ Crystal data for C₆₉H₇₃Cl₂Cu₂N₆O₁₃P₃, *M* = 1485.2, orthorhombic, space group *P*_{bcn} (no. 6), *a* = 27.709(6), *b* = 16.578(3), *c* = 30.500(6) Å, *U* = 14 010(5) Å³, *Z* = 8, *D*_c = 1.408 g cm⁻³, μ(Mo-Kα) = 8.18 cm⁻¹, crystal dimension = 0.20 × 0.16 × 0.14 mm, *F*(000) = 6160, index range 0 ≤ *h* ≤ 33, 0 ≤ *k* ≤ 20, 0 ≤ *l* ≤ 37, 2θ_{max} = 52°, unique reflections = 11 460, reflections with *F* > 2.0σ(*F*) = 3656, variables = 792, *R* = 0.094, *R*_w = 0.301, goodness of fit = 0.951, residual electron density = 0.51, -0.38



Scheme 2 Preparation of complexes **1**–**3**: i [Cu(CH₃CN)₄][ClO₄], acetonitrile; ii bpy, dichloromethane; iii PPh₃, dichloromethane at room temperature

e Å⁻³. Though the *R* and *R*_w values are high (due to large number of co-crystallized solvents), the bond distances and angles appear to be reasonable.

CCDC reference number 186/1072.

Results and Discussion

Procedures for the preparation of complexes **1**–**3** are depicted in Scheme 2. Complex **1** is readily obtained by the reaction of [Cu(CH₃CN)₄][ClO₄] with a stoichiometric amount of dpnapy in acetonitrile. It is one of the few trinuclear Cu^I complexes with a linear copper atom array.^{8–11} Two notable literature examples are [Cu₃(bpd)₂]⁻ [bpd = *N,N'*-bis(*p*-tolylsulfonyl)pyridine-2,6-diaminato] and [Cu₃(tolN₅tol)₃] (HN₅ = 1,4-pentaazadiene, tol = *p*-tolyl),^{10,11} both of which have short bite bridging

Table 2 Selected ^1H , ^{13}C -{H} and ^{31}P -{H} NMR spectroscopic data for complexes **1–3** at room temperature

Complex	^1H NMR		^{13}C -{H} NMR		^{31}P -{H} NMR δ
	$\delta_{2\text{-Me}}$	$\delta_{4\text{-Me}}$	$\delta_{2\text{-Me}}$	$\delta_{4\text{-Me}}$	
1 ^a	2.80	2.67	27.8	18.6	2.5, 5.3
2 ^a	2.71	2.55	25.9	18.1	3.8
3 ^b	2.75, 2.80, 2.82	2.60, 2.69, 2.71	25.4, 27.4, 28.5	18.2, 18.3, 18.4	2.0, 3.2, 4.1
dpnapy ^b	2.73	2.62	25.6	18.0	-1.1

^a In CD_3CN . ^b In CD_2Cl_2 .

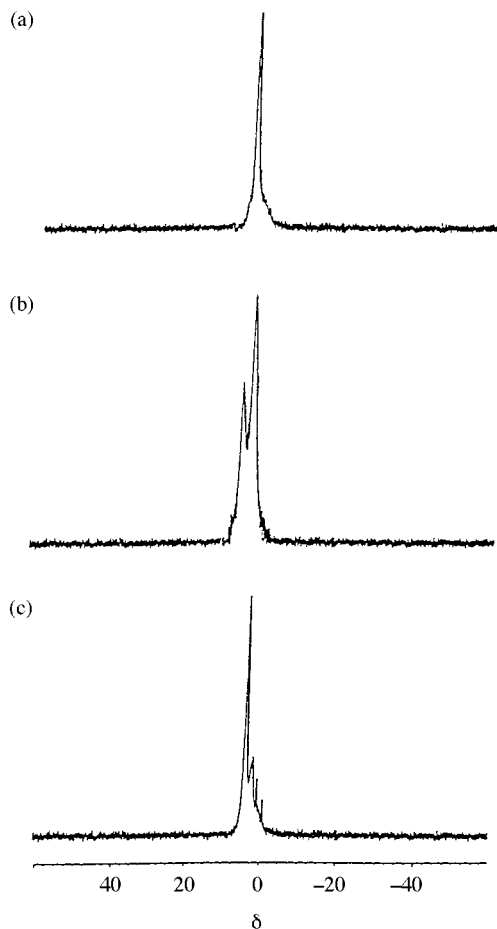
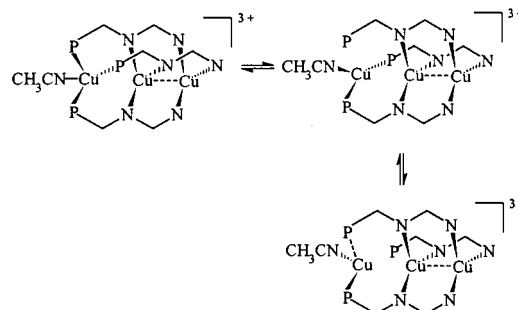


Fig. 1 The ^{31}P -{H} NMR spectra of $\mathbf{1}[\text{ClO}_4]_3$ in CD_3CN at (a) 60, (b) 25 and (c) -60°C

ligands. We conceive that besides the stereochemistry of the bridging ligands, the weakly attractive $\text{Cu}^I\text{--Cu}^I$ interaction is a driving force for the formation of a linear $\text{Cu}\text{--Cu}\text{--Cu}$ array with short intramolecular metal–metal distances. This would be the case in **1** since a considerable coulombic repulsion has to be overcome in bridging the three Cu^I ions at short separations. Indeed, results of molecular orbital calculation also revealed the existence of weakly attractive forces between d^{10} metal ions.^{12,13}

We envisaged that the co-ordinated acetonitrile in **1** would be labile and easily undergo substitution reaction. Treatment of **1** with bpy and PPh_3 resulted in disintegration of the copper atom array with subsequent rearrangement to form **2** and **3**. These reactions were accompanied by the formation of side products such as $[\text{Cu}(\text{bpy})_2][\text{ClO}_4]$ and $[\text{Cu}(\text{dpnapy})(\text{PPh}_3)_2][\text{ClO}_4]$, respectively. It is likely that the three copper atoms in **1** experience strong coulombic repulsion, and cleavage of the trinuclear structure is facilitated through ligand substitution reactions.

The structures of complex cations **1–3** have been determined



Scheme 3 Dynamic behaviour of $\mathbf{1}[\text{ClO}_4]_3$ in acetonitrile showing an on and off switching of the phosphorus moieties

by X-ray crystal analyses. All compounds are air-stable in the solid state, but slow decomposition has been observed in solutions at room temperature. Selected ^1H , ^{13}C and ^{31}P NMR spectral data of the complexes are listed in Table 2. The 2-Me protons of dpnapy in **2** and in the free ligand have similar chemical shifts ($\delta_{2\text{-Me}}$). However, significant downfield shifts are observed for those in **1** and **3**. This is in accordance with the M–N (naphthyridyl) co-ordination in the latter two complexes. Variable-temperature ^{31}P NMR spectroscopy of **1** (Fig. 1) reveals a fluxional behaviour in CD_3CN . At room temperature, the complex exhibits two broad phosphorus signals at δ 2.5 and 5.3. As the temperature increases, they gradually coalesce at δ 3.55 (60°C). By cooling to -60°C several phosphorus resonances are observed. Addition of a stoichiometric amount of dpnapy has no notable effect on the ^{31}P NMR spectrum. This excludes the possibility of a ligand exchange reaction and the dynamic behaviour may be attributed to a switching-on and -off process of the phosphine moieties (Scheme 3).

The electrochemical properties of complexes **1–3** have been studied by cyclic voltammetry. All complexes exhibit irreversible oxidation waves. The voltammogram of **1** is characterized by two irreversible waves with E_{pa} at 1.25 and 1.65 V (vs. SCE), whereas **2** and **3** exhibit a single peak at 1.0 V (broad) and 1.1 V, respectively.

Spectroscopic properties

The UV/VIS absorption spectra of **1–3** are characterized by absorptions at 320–328 nm [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$) for **1**: 328 (2.39), **2**: 320 (1.33) and **3**: 325 (1.88)]. For complex **1**, a low energy absorption tail at 430–450 nm ($\epsilon = 1.22 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) is observed.

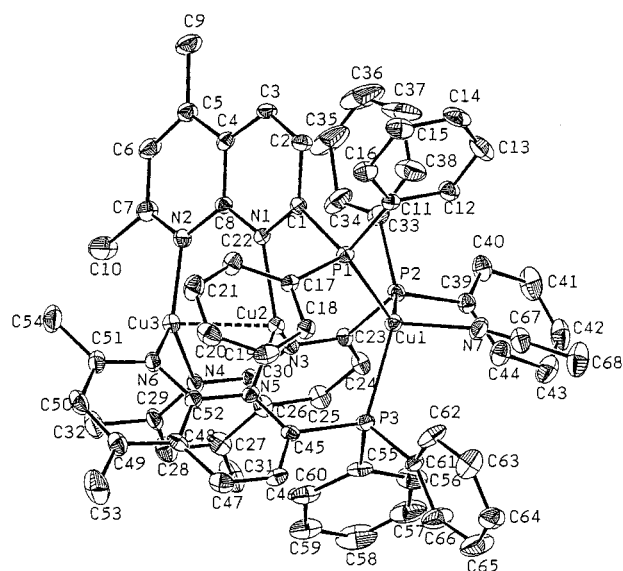
Upon excitation at 350 nm, $\mathbf{1}[\text{ClO}_4]_3$ shows room-temperature emission at ca. 530 nm (lifetime 0.21 μs) in degassed acetonitrile. Cooling the solution to 77 K leads to an increase in emission intensity but no vibrational fine structure is recorded. The emission is assigned to the $d(\text{Cu}) \rightarrow \pi^*(\text{dpnapy})$ MLCT excited state. At room temperature, the solid-state emission of **1** at 634 nm (lifetime 0.44 μs) is considerably red-shifted from the solution emission. We assign the solid-state emission to the excited state of a metal-centred $d\sigma^* \rightarrow p\sigma$ transition, where $d\sigma^*$ refers to the antibonding combination of the $3d_z$ orbitals and $p\sigma$ refers to the bonding combination of the $4s/4p$ orbitals (the $\text{Cu} \cdots \text{Cu} \cdots \text{Cu}$ axis is taken as the z direction).¹⁴

Crystal structures

Perspective drawings of the complex cations **1–3** are depicted in Figs. 2–4. Selected bond lengths and bond angles are listed in Tables 3–5. The three Cu atoms in **1** are held in close proximity and in a nearly linear array [$\text{Cu}(1)\text{--Cu}(2)\text{--Cu}(3)$ angle $177.50(6)^\circ$] by three bridging dpnapy ligands. The dpnapy ligands are in a head-to-head arrangement with the [P(1), P(2), P(3)], [N(1), N(3), N(5)] and [N(2), N(4), N(6)] planes almost parallel to each other. The atom Cu(1) adopts a distorted tetrahedral

Table 3 Selected bond lengths (Å) and bond angles (°) for **1**[ClO₄]₃·CH₃CN

Cu(1)–Cu(2)	2.721(2)	Cu(2)–N(1)	2.033(6)
Cu(2)–Cu(3)	2.449(2)	Cu(2)–N(3)	2.064(6)
Cu(1)–P(1)	2.315(3)	Cu(2)–N(5)	2.029(7)
Cu(1)–P(2)	2.304(3)	Cu(3)–N(2)	1.975(7)
Cu(1)–P(3)	2.327(3)	Cu(3)–N(4)	2.050(7)
Cu(1)–N(7)	2.016(7)	Cu(3)–N(6)	1.977(7)
Cu(2)–P(1)	3.017(3)		
Cu(1)–Cu(2)–Cu(3)	177.50(6)	P(3)–Cu(1)–N(7)	99.8(2)
Cu(2)–Cu(1)–N(7)	174.2(2)	N(1)–Cu(2)–N(3)	111.7(3)
P(1)–Cu(1)–P(2)	113.1(1)	N(1)–Cu(2)–N(5)	127.6(3)
P(1)–Cu(1)–P(3)	116.8(1)	N(3)–Cu(2)–N(5)	116.5(3)
P(1)–Cu(1)–N(7)	107.8(2)	N(2)–Cu(3)–N(4)	113.3(3)
P(2)–Cu(1)–P(3)	111.2(1)	N(2)–Cu(3)–N(6)	132.6(3)
P(2)–Cu(1)–N(7)	106.9(2)	N(4)–Cu(3)–N(6)	113.6(3)

**Fig. 2** A perspective drawing of the complex cation **1** with atomic numbering scheme, H atoms are omitted for clarity

geometry with a co-ordinated acetonitrile molecule. Atoms Cu(2) and Cu(3) are three-co-ordinated and each is bonded to three pyridyl-nitrogen atoms in a distorted trigonal manner. It is noted that the Cu^I–N (acetonitrile) and Cu^I–N (dpnpy) distances are comparable, suggesting that the acetonitrile is weakly co-ordinated to the metal atom. Two distinct Cu–Cu distances are present in the complex, of which the shorter Cu(2)–Cu(3) distance [2.449(2) Å] appears to be comparable to those found in [Cu₂(napy)₂][ClO₄]₂ [2.506(2) Å],¹⁵ [Cu₃(bpd)₂][–] [2.466(1) and 2.468(1) Å]¹⁰ and [Cu₃(tolN₅tol)₃] [2.348(2) and 2.358(2)].¹¹ We believe that there is metal–metal interaction between Cu(2) and Cu(3). The longer Cu(1)–Cu(2) distance of 2.721(2) Å is virtually identical with that observed in [Cu₂(μ-dppy)₃(MeCN)]–[BF₄]₂.¹⁶ This can be indicative of no metal–metal interaction between the copper atoms.

Complex **2** is mononuclear with the Cu atom co-ordinated to two P-monodentate dpnpy ligands and a chelating bipyridyl ring in a distorted tetrahedral geometry. The N–Cu–N angle sustained by bpy is 80.1(2)°. The Cu–P and Cu–N distances are similar to those in [Cu(μ-bpym)(PPh₃)₂][ClO₄]₂ (bpym = bipyrimidine).¹⁷ As shown in Fig. 3, there is a π–π interaction between the naphthyridyl rings of two dpnpy ligands. The dihedral angle between the naphthyridyl planes is 8.37(2)° and the closest inter-planar separation is 3.18(1) Å. This is comparable to the π–π stacking separation found in some organic sandwich compounds.¹⁸

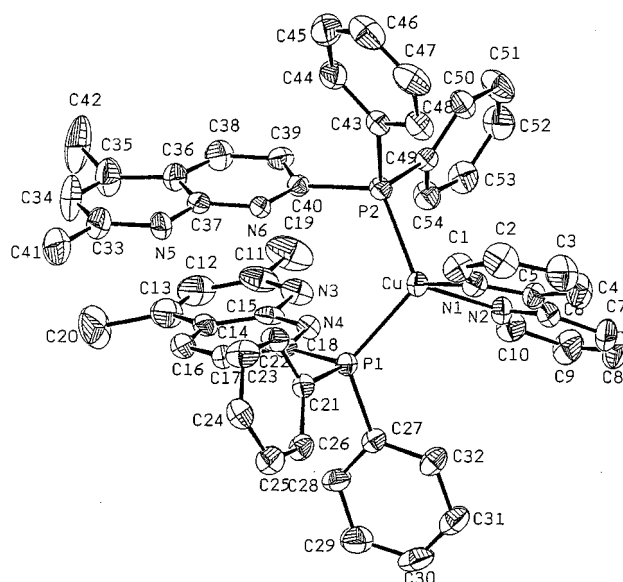
The chemical connectivity of complex **3** has been established

Table 4 Selected bond lengths (Å) and bond angles (°) for **2**[ClO₄]

Cu(1)–P(1)	2.267(2)	Cu(1)–N(1)	2.066(5)
Cu(1)–P(2)	2.247(2)	Cu(1)–N(2)	2.073(5)
P(1)–Cu(1)–P(2)	114.40(6)	N(1)–Cu(1)–N(2)	80.1(2)
P(1)–Cu(1)–N(1)	117.0(2)	Cu(1)–N(1)–C(5)	114.1(4)
P(1)–Cu(1)–N(2)	109.0(2)	Cu(1)–N(2)–C(6)	113.6(4)
P(2)–Cu(1)–N(1)	116.4(2)	N(2)–C(6)–N(5)	115.7(6)
P(2)–Cu(1)–N(2)	115.1(2)	N(1)–C(5)–N(4)	121.3(6)

Table 5 Selected bond lengths (Å) and bond angles (°) for **3**[ClO₄]₂·2H₂O·3CH₃OH

Cu(1)–N(4)	2.106(7)	Cu(2)–N(2)	2.160(7)
Cu(1)–N(5)	2.098(6)	Cu(2)–P(2)	2.253(3)
Cu(1)–P(1)	2.227(3)	Cu(2)–P(3)	2.277(2)
Cu(2)–N(1)	2.239(6)		
N(5)–Cu(1)–N(4)	108.6(2)	N(2)–Cu(2)–N(1)	61.8(2)
N(4)–Cu(1)–P(1)	139.4(2)	N(1)–Cu(2)–P(2)	112.0(2)
N(5)–Cu(1)–P(1)	111.8(2)	N(1)–Cu(2)–P(3)	114.2(2)
N(2)–Cu(2)–P(2)	113.7(2)	P(2)–Cu(2)–P(3)	121.4(2)
N(2)–Cu(2)–P(3)	118.9(2)		

**Fig. 3** A perspective drawing of the complex cation **2** with atomic numbering scheme, H atoms are omitted for clarity

by X-ray crystal analysis but the high *R*_w value of the structure precludes any precise discussion. As shown in Fig. 4, complex cation **3** displays a highly irregular structure. Two kinds of Cu atoms are found in the complex. Atom Cu(1) adopts a trigonal planar co-ordination while Cu(2) is distorted tetrahedral. The dpnpy ligands show three different types of co-ordination geometry, and these are the II, III and V modes (Scheme 1).

Conclusion

The short bite dpnpy ligand reacts with Cu^I to form complexes that display various co-ordination modes. The structure of **1** is interesting as it features one of the few linear trimeric Cu^I complexes. An X-ray crystallographic study revealed that the three Cu atoms are arranged in a nearly linear array and are held in close proximity by the bridging dpnpy ligands. The Cu–Cu distance of 2.449(2) Å is even comparable to the shortest distances of 2.348(2) and 2.358(2) Å observed in [Cu₃(tolN₅tol)₃].¹¹

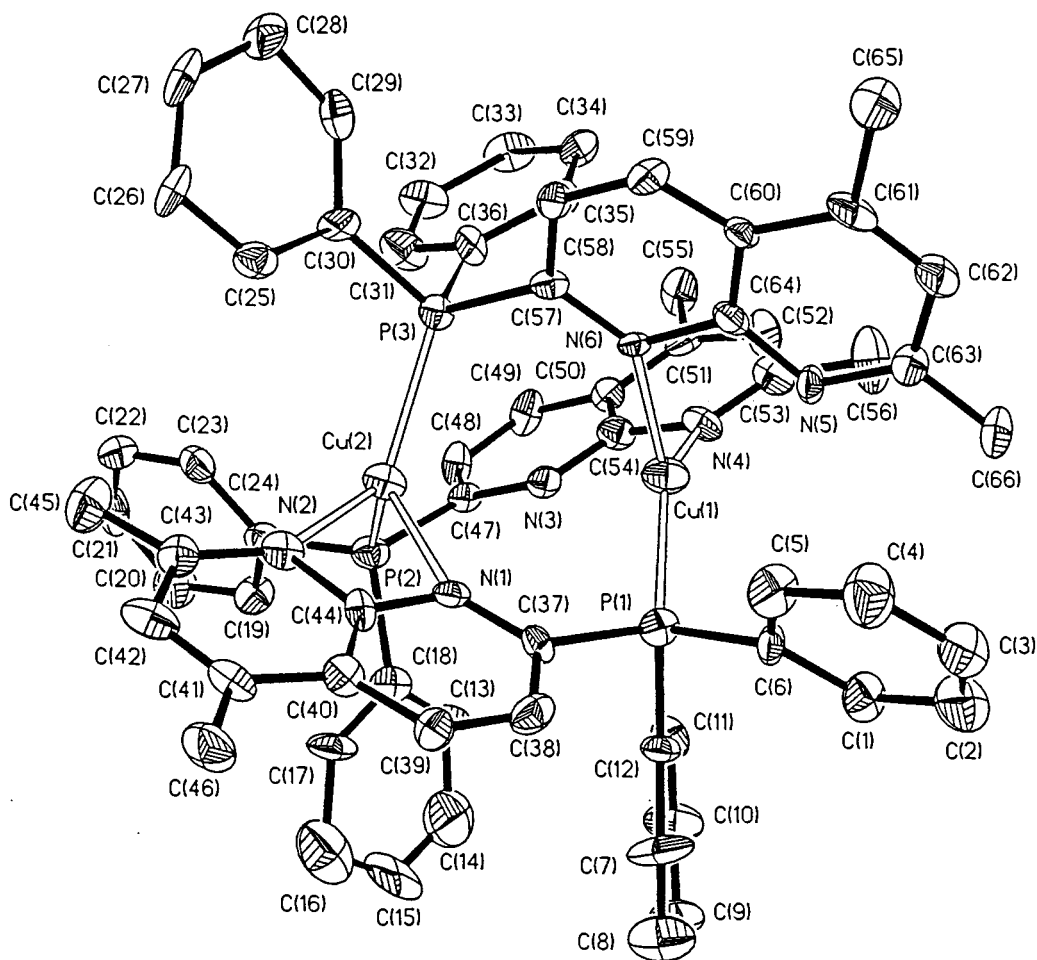


Fig. 4 A perspective drawing of the complex cation 3 with atomic numbering scheme, H atoms are omitted for clarity

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