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FULL PAPER

Dithiolate clusters of copper(I): utilization of all possible coordination sites of 1-(diethoxyphosphinyl)-1-cyanoethylene-2,2-dithiolate

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Four Cu^I–S clusters, **1**–**4**, containing bridging dppm and 2-(diethoxyphosphinyl)-2-cyanoethylene-1,1-dithiolato ligands were isolated from the reaction of $[Cu_2(\mu\text{-dppm})_2(CH_3CN)_2](PF_6)_2$ and $K_2S_2CC(CN)P(O)(OEt)_2$ in CH_2Cl_2. The cluster nuclearity depends on the coordination pattern of the functionalized 1,1-dithiolates: **1** and **2**, $Cu_4(dppm)_4[S_2CC(CN)P(O)(OEt)_2]_2$ and $Cu_4(dppm)_3(OPPh_2CH_2PPh_2)[S_2CC(CN)P(O)(OEt)_2]_2$, display a tetrametallic tetraconnective (μ-S, μ-S) bridging mode; in **3**, $Cu_5(dppm)_4[S_2CC(CN)P(O)(OEt)_2]_2(PF_6)$, exhibits a novel tetrametallic pentaconnective coordination pattern; in **4**, $Cu_9(dppm)_4[S_2CC(CN)P(O)(OEt)_2]_4(PF_6)$, reveals an unprecedented pentametallic hexaconnective coordination pattern. Pertinent crystallographic data are: **1**, $C_{114}H_{108}Cu_4N_2O_6P_{10}S_4\cdot CH_2Cl_2$, monoclinic, $P2_1/n$, $a = 20.1464(11)$, $b = 23.4222(13)$, $c = 23.7695(14)$ Å, $\beta = 91.837(1)°$, $V = 11210(1)$ Å^3, $Z = 4$; **2**, $C_{114}H_{108}Cu_4N_2O_7P_{10}S_4$, monoclinic, $P2_1/n$, $a = 15.6463(8)$, $b = 52.324(3)$, $c = 15.8286(8)$ Å, $\beta = 118.529(1)°$, $V = 11385(1)$ Å^3, $Z = 4$; **3**, $C_{114}H_{116}Cu_5F_6N_2O_{10}P_{11}S_4$, monoclinic, $C2/c$, $a = 20.4306(11)$, $b = 22.6378(12)$, $c = 26.1927(13)$ Å, $\beta = 90.886(1)°$, $V = 12112.8(11)$ Å^3, $Z = 4$; **4**, $C_{128}H_{128}Cu_9F_6N_4O_{12}P_{13}S_8$, orthorhombic, $Pna2_1$, $a = 38.8644(11)$, $b = 24.3585(8)$, $c = 16.0870(5)$ Å, $V = 15229.2(8)$ Å^3, $Z = 4$.

Introduction

There is a tendency for cluster formation between monovalent Group 11 metals and 1,1- or 1,2-dithio-chelating ligands.[1] Notable examples include $[Au_6(o\text{-}CH_3C_6H_4CS_2)_6]$,[2] $M_8(i\text{-MNT})_6^{4-}$, $M_4(i\text{-MNT})_4^{4-}$ (M = Cu, Ag),[3] $Ag_6(i\text{-MNT})_6^{6-}$,[4] and $Au_2(i\text{-MNT})_2^{2-}$.[5] ($i$-MNT = 1,1-dicyanoethylene-2,2-dithiolate.) Most of the reported structures consist of symmetrically substituted 1,1-dithiolate ligands of the type $S_2CC(X)_2^{2-}$. Seldom has the high-nuclearity metal cluster possessing asymmetrically substituted 1,1-dithiolates, $S_2CC(X)(Y)^{2-}$, been characterized satisfactorily. This is partly due to the difficulty in producing good quality crystals amenable for X-ray diffraction, which result in the presence of several isomeric species in solution caused by the asymmetrical 1,1-dithiolate ligands, and this therefore impedes the subsequent, detailed characterizations for the isolated complexes. On the other hand the isomeric problem may be overcome if the lone pair electrons of the substituents can be activated then become potential donor sites to increase the cluster nuclearity. Lately high-nuclearity copper–thiolato clusters have been used as model compounds for both yeast- and mammalian-copper metallothioneins.[6] Thus it adds more interest to explore the coordination chemistry of Cu^I–S clusters.

With this in mind we focus on the 1-(diethoxyphosphinyl)-1-cyanoethylene-2,2-dithiolates, $[S_2CC(CN)P(O)(OEt)_2]^{2-}$ (abbreviated as cpdt), for a couple of reasons. First, there are two more potential binding sites besides the soft sulfur donors; namely the nitrogen atom of the CN group and the oxygen atom of the phosphinyl group. Secondly, complexes containing this ligand are extremely scarce. Apart from two clusters of Ag(I) recently reported by us,[7] only two with Pt(II) have been synthesized.[8] Thirdly, due to the existence of the phosphinyl group, the ^{31}P NMR may provide a useful screening tool for the isolated products before the detailed single crystal X-ray diffraction study.

Recent work in this laboratory has shown that the cpdt can coordinate to metals by using not only its two sulfur atoms but also the oxygen atom of the phosphinyl group (Chart 1). This affords a new coordination mode of η^3(μ-S-μ$_3$-S′-O) (**E**) for cpdt ligands and observes in the pentanuclear silver complex of $Ag_5(\mu\text{-dppm})_4[S_2CC(CN)P(O)(OEt)_2]_2(PF_6)$.[7] As an extension of this study, we perform a similar cluster synthesis incorporating copper and uncover that, besides the oxygen atom of the P=O group, the nitrogen atom of the cyano group in the cpdt can also be utilized to bind to other metal. Thus an unprecedented pentametallic hexaconnective coordination pattern, η^4(μ-S-μ-S′-O-N) (**G**), found in the novel nonanuclear

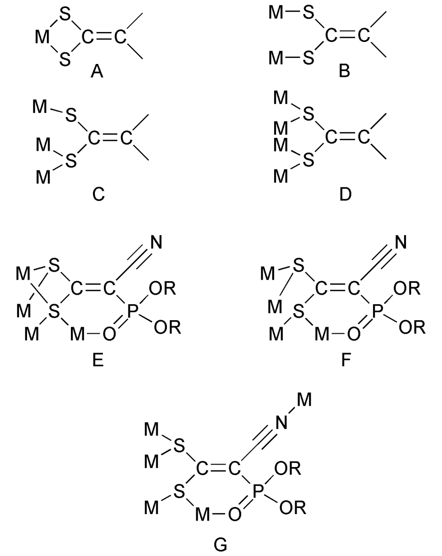

Chart 1

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copper cluster of $Cu_9(\mu\text{-dppm})_4[S_2CC(CN)P(O)(OEt)_2]_4(PF_6)$ is produced. To our knowledge this is one of the rare examples simultaneously exhibiting the connectivities between transitional metals and all potential binding sites of any 1,1-dithiolate ligands. Herein we report the synthetic details of cpdt–Cu(I) complexes where the cluster nuclearities are in the range of four, five, and nine.

Experimental

Apparatus

All infrared spectra were recorded on a Bio-Rad spectrometer at 25 °C using KBr plates. NMR spectra were recorded on a Bruker AC-F200 Fourier transform spectrometer. The $^{31}P\{^1H\}$ NMR are referenced externally against 85% H_3PO_4. Elemental analyses (C, H, N, S) were obtained with a Perkin-Elmer 2400 analyzer. Positive FAB mass spectra were performed on a VG 70-250S mass spectrometer with nitrobenzyl alcohol as the matrix. Absorption spectra were obtained by a Shimadzu UV-2101PC spectrophotometer.

Reagents

$[Cu_2(\mu\text{-dppm})_2(CH_3CN)_2](PF_6)_2$[9] and $K_2S_2CC(CN)(P(O)(OEt)_2)$[10] were prepared according to the literature reports. All reactions were performed in oven-dried Schlenk glassware by using standard inert-atmosphere techniques.

Commercial CH_2Cl_2 and CH_3OH were distilled from P_4O_{10} and Mg, respectively, before use. Hexanes were distilled from Na/K.

Reaction of $[Cu_2(\mu\text{-dppm})_2(CH_3CN)_2](PF_6)_2$ and $K_2S_2CC(CN)P(O)(OEt)_2$

Dichloromethane (50 mL) was added to $[Cu_2(dppm)_2(CH_3CN)_2](PF_6)_2$ (500 mg, 3.9 mmol) and $K_2S_2CC(CN)P(O)(OEt)_2$ (156 mg, 4.7 mmol) in a Schlenk bottle (100 mL) and stirred for 24 h at ambient temperature. The solution underwent color changes from pale yellow to orange during the reaction. It was then evaporated to dryness to give an orange residue. The residue was re-dissolved in CH_3OH (30 mL) from which orange–yellow material of **1** was precipitated out in a few minutes (30 mg, 9% yield). The yellow methanol filtrate was evaporated, then re-dissolved in CH_3CN (20 mL) from which a yellow precipitate of **2** (155 mg, 47% yield) was obtained. Diffusion of diethyl ether to the CH_3CN filtrate afforded crystalline material of **3** and **4** in 12% (54.2 mg) and 11% (118 mg) yield, respectively.

1: UV–Vis (CH_2Cl_2) λ, nm (ε_{max}, dm^3 mol^{-1} cm^{-1}): 245 (33,100), 302 (27,400), 334 (23,700), 365 (15,300). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ 17.1 [s; 2P, *P*(O)], −10.2 (br; 8P). ^1H NMR ($CDCl_3$), δ 1.22 (t; 12H, CH_2CH_3), 3.1 (br; 8H), 4.09 (m; 8H, CH_2CH_3); 6.6–7.4 (m, 80H). IR in KBr, cm^{-1}: ν(CN), 2175. Positive FAB–MS (*m*/*z*): 1910.5 (M^+ − dppm), 1526.3 (M^+ − 2dppm). Anal. Calcd for $C_{114}H_{108}Cu_4O_6N_2P_{10}S_4$: C, 59.68; H, 4.74; N, 1.22; S, 5.59. Found: C, 58.75; H, 5.10; N, 1.35; S, 5.79. Mp: 189 °C.

2: UV–Vis (CH_2Cl_2) λ, nm (ε_{max}, dm^3 mol^{-1} cm^{-1}): 245 (25,700), 294 (23,100), 339 (20,100), 366 (24,100). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ 36.6 [d, ^2J(P, P) = 16 Hz; $P(O)Ph_2$], 24.3 [d, ^2J(P, P) = 16 Hz; $PPh_2P(O)$], 14.9 [s; 2P, *P*(O)], −14.0 (br; 6P). ^1H NMR ($CDCl_3$), δ 1.39 (t; 12H, CH_2CH_3), 3.30 (br; 8H), 4.20 (m; 8H, CH_2CH_3); 6.81–7.70 (m, 80H). IR in KBr, cm^{-1}: ν(CN), 2176. Anal. Calcd for $C_{114}H_{108}Cu_4O_7N_2P_{10}S_4$: C, 59.27; H, 4.71; N, 1.21; S, 5.55. Found: C, 58.78; H, 5.12; N, 1.29; S, 4.99. Mp: 186 °C.

3: UV–Vis (CH_2Cl_2) λ, nm (ε_{max}, dm^3 mol^{-1} cm^{-1}): 241 (44,100), 304 (32,300), 340 (19,700), 370 (21,000). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ 18.1 [s; 2P, *P*(O)], −13.4 (br; 8P). ^1H NMR ($CDCl_3$), δ 1.25 (t; 12H, CH_2CH_3), 3.27 (br; 8H), 4.11 (m; 8H, CH_2CH_3); 6.63–7.24 (m, 80H). IR in KBr, cm^{-1}: ν(CN), 2179. Positive FAB–MS: *m*/*z* (m/z_{calcd}) 2360.0 (2357.7) (M^+), 1971.5 (1973.3) (M^+ − dppm), 1589.0 (1588.9) (M^+ − 2dppm). Anal. Calcd for $C_{114}H_{108}Cu_5F_6O_6N_2P_{11}S_4\cdot4H_2O$: C, 53.18; H, 4.54; N, 1.09; S, 4.98. Found: C, 52.63; H, 4.18; N, 1.25; S, 5.27. Mp: 191 °C.

4: UV–Vis (CH_2Cl_2) λ, nm (ε_{max}, dm^3 mol^{-1} cm^{-1}): 241 (51,000), 308 (44,200), 342 (36,200), 388 (28,100). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ 18.8 [s; 4P, *P*(O)], −13.7 (br; 8P). ^1H NMR ($CDCl_3$), δ 1.04, 1.21 (t; 7 Hz, 24H, CH_2CH_3), 2.77 (br; 8H), 3.93, 4.10 (m; 16H, CH_2CH_3), 6.5–7.7 (m, 80H). IR in KBr, cm^{-1}: ν(CN), 2187. Positive FAB–MS (*m*/*z*): 3114.4 (M^+), 2730.7 (M^+ − dppm), 2346.4 (M^+ − 2dppm). Anal. Calcd for $C_{128}H_{128}Cu_9F_6O_{12}N_4P_{13}S_8$: C, 47.17; H, 3.96; N, 1.72; S, 7.87. Found: C, 47.19; H, 3.90; N, 2.13; S, 7.88. Mp: 192 °C.

X-Ray structure determination

Crystals were mounted on the tip of glass fibers with epoxy resin. Data were collected at 298 K on a Siemens SMART CCD (charged coupled device) diffractometer. For all crystals, data were measured with omega scans of 0.3° per frame for 90 s. Cell parameters were retrieved with SMART software[11] and refined with SAINT software[12] on all observed reflections ($I > 10\sigma(I)$). Data reduction was performed with SAINT, which corrects for Lorentz and polarization. An empirical absorption correction was applied. The structure was solved by the use of direct methods and refinement was performed by the least-squares methods on F^2 with the SHELXL-97 package,[13] incorporated in SHELXTL/PC V5.10.[14] Pertinent crystallographic data for compounds **1**–**4** are listed in Table 1.

$1\cdot CH_2Cl_2$. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 layered with hexanes. A yellow crystal (0.22 × 0.24 × 0.42 mm) was mounted in the manner described above, and data were collected. A total of 39476 reflections were collected, of which 14221 were unique (R_{int} = 0.0894) and 9481 were observed with $I > 2\sigma(I)$. Crystals of **1** diffracted very weakly during the data collection. Two ethyl groups and a solvent molecule, CH_2Cl_2, were disordered. While two positions with equal occupancy were used to refine each disordered ethyl group, a riding mode was used for the solvent molecule of which one of the chloride atoms was divided into two positions having 0.35 and 0.65 site occupancy factor. The final cycle of the full-matrix least-squares refinement was based on 9481 observed reflections, 792 parameters, and converged with unweighted and weighted agreement factors of R_1 = 0.1270, and wR_2 = 0.2967, respectively. The largest residual peak and hole are 1.449 e Å^{-3} and −0.780 e Å^{-3}, respectively. The high *R* value may be attributed to the poor crystal quality.

2. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 layered with hexanes. A yellow crystal (0.26 × 0.3 × 0.44 mm) was mounted in the manner described above, and data were collected. A total of 40133 reflections were collected, of which 19735 were unique (R_{int} = 0.0276) and 17492 were observed with $I > 2\sigma(I)$. Two carbon atoms, C06 and C07, were found disordered. While two positions with equal occupancy were used to model the C06, three positions having site occupancy factor of 50%, 25%, and 25%, respectively, were treated for the C07. The final cycle of the full-matrix least-squares refinement was based on 17492 observed reflections, 1270 parameters, and converged with unweighted and weighted agreement factors of R_2 = 0.0518, and wR_2 = 0.1140, respectively. The largest residual peak and hole are 0.575 e Å^{-3} and −0.385 e Å^{-3}, respectively.

$3\cdot4H_2O$. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 layered with hexanes. A yellow crystal (0.3 ×

Table 1 Crystallographic data for $Cu_4(dppm)_4[S_2CC(CN)P(O)(OEt)_2]_2$ (**1**), $Cu_4(dppm)_3(OPPh_2CH_2PPh_2)[S_2CC(CN)P(O)(OEt)_2]_2$ (**2**), $Cu_5(dppm)_4[S_2CC(CN)P(O)(OEt)_2]_2(PF_6)$ (**3**), and $Cu_9(dppm)_4[S_2CC(CN)P(O)(OEt)_2]_4(PF_6)$ (**4**)

	1	**2**	**3**	**4**
Chemical formula	$C_{115}H_{110}Cl_2Cu_4O_6N_2P_{10}S_4$	$C_{114}H_{108}Cu_4O_7N_2P_{10}S_4$	$C_{114}H_{116}Cu_5F_6O_{10}N_2P_{11}S_4$	$C_{128}H_{128}Cu_9F_6O_{12}N_4P_{13}S_8$
M	2379.05	2310.12	2574.70	3259.29
a/Å	20.1461(11)	15.6463(8)	20.4306(11)	38.8644(11)
b/Å	23.4222(13)	52.324(3)	22.6378(12)	24.3585(8)
c/Å	23.7695(14)	15.8286(8)	26.1927(13)	16.0870(5)
α/°	90	90	90	90
β/°	91.837(1)	118.5290(10)	90.8860(10)	90
γ/°	90	90	90	90
V/Å^3	11210.3(11)	11385.0(10)	12112.8(11)	15229.2(8)
Space group	$P2_1/n$	$P2_1/n$	$C2/c$	$Pna2_1$
Z	4	4	4	4
ρ_{calcd}/Mg m^{-3}	1.410	1.348	1.412	1.422
λ/Å	0.71073	0.71073	0.71073	0.71073
μ/mm^{-1}	1.068	1.005	1.142	1.537
T/K	298(2)	298(2)	298(2)	298(2)
$R_1\ (F_o)^a$	0.1270	0.0518	0.0539	0.0846
$wR_2\ (F_o^2)^b$	0.2967	0.1140	0.1623	0.1636

[a] $R_1\ (F_o) = \Sigma||(F_o)| - |(F_c)||/\Sigma|F_0|$ for $F_o^2 > 2\sigma(F_o^2)$. [b] $wR_2\ (F_o^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.03\ F_o^2)^2$ for $F_o^2 > 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 0$.

0.35 × 0.6 mm) was mounted in the manner described above, and data were collected. A total of 28998 reflections were collected, of which 10461 were unique (R_{int} = 0.0333) and 9167 were observed with $I > 2\sigma(I)$. One of the H_2O molecules in the asymmetric unit was found disordered and two positions with occupancies of 60% and 40% were refined. Four carbon atoms were found disordered: C5, C6, C7, and C8. A model with fixed C–C (1.550 Å) distance was introduced. All but disordered C atoms and H_2O molecules were refined anisotropically. The final cycle of the full-matrix least-squares refinement was based on 9167 observed reflections, 666 parameters, and 2 constraints and converged with unweighted and weighted agreement factors of R_1 = 0.0539, and wR_2 = 0.1623, respectively. The largest residual peak and hole are 1.207 e Å^{-3} and −0.720 e Å^{-3}, respectively.

4. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 layered with hexanes. A yellow crystal (0.4 × 0.4 × 0.4 mm) was mounted in the manner described and data were collected. A total of 25441 reflections were collected, of which 12398 were unique (R_{int} = 0.0603) and 10276 were observed with $I > 2\sigma(I)$. Parts of oxygen and carbon atoms of the ethoxyl groups were found disordered. Bond distances were constrained for disordered atoms and atoms connected to the disordered atoms during the structure refinements. The constraint is O–C = 1.500 Å. All phenyl rings are fixed as a regular hexagon. The final cycle of the full-matrix least-squares refinement was based on 10276 observed reflections, 848 parameters, and 5 constraints and converged with unweighted and weighted agreement factors of R_1 = 0.0846, and wR_2 = 0.1636, respectively. The largest residual peak and hole are 0.772 e Å^{-3} and −0.524 e Å^{-3}, respectively.

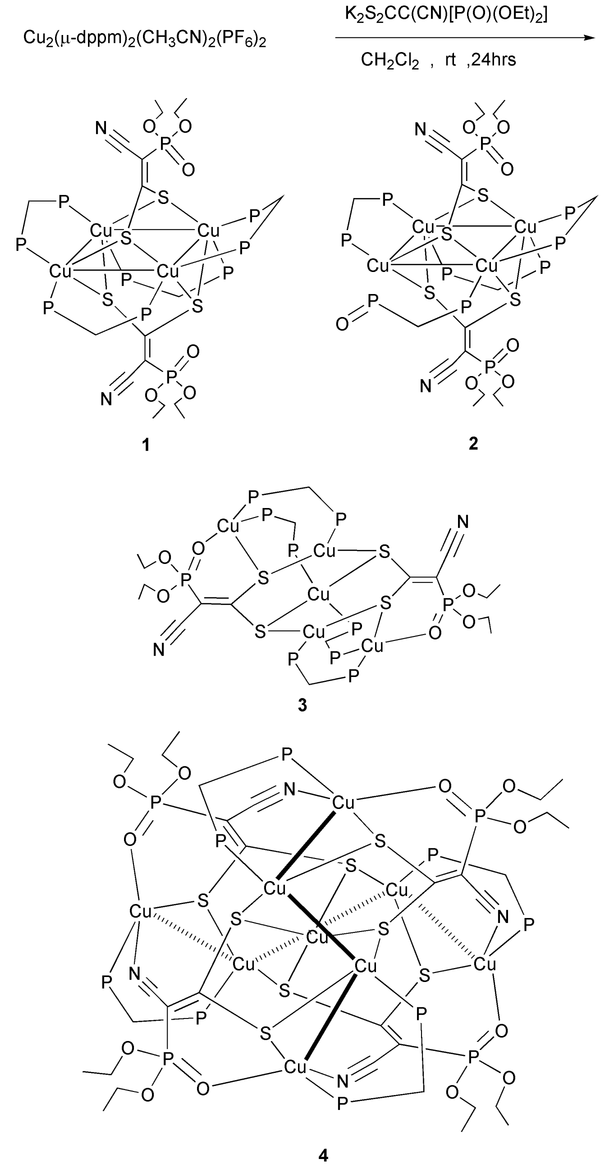
CCDC reference numbers 173563–173566.

See http://www.rsc.org/suppdata/dt/b1/b110028a/ for crystallographic data in CIF or other electronic format.

Results and discussion

Syntheses

Complexes **1**–**4**, formulated as $Cu_4(\mu\text{-dppm})_4[S_2CC(CN)P(O)(OEt)_2]_2$, $Cu_4(\mu\text{-dppm})_3(OPPh_2CH_2PPh_2)[S_2CC(CN)P(O)(OEt)_2]_2$, $Cu_5(\mu\text{-dppm})_4[S_2CC(CN)P(O)(OEt)_2]_2(PF_6)$ and $Cu_9(\mu\text{-dppm})_4[S_2CC(CN)P(O)(OEt)_2]_4(PF_6)$ were isolated in 9%, 47%, 12% and 11% yield respectively starting from the reaction of $[Cu_2(\mu\text{-dppm})_2(CH_3CN)_2](PF_6)_2$ and $K_2S_2CC(CN)P(O)(OEt)_2$ in CH_2Cl_2 (Scheme 1). They can be separated by using solvents with different polarities of which **1** is the only one that does not dissolve in methanol. The cationic clusters, **3** and **4**, were largely separated by re-crystallization in which **4**



Scheme 1

come out first. All complexes are air stable, and as crystalline solids show no appreciable sensitivity to light.

The formation of **2** remains unclear, but it is possible that the presence of trace amount of O_2 coupled with the Cu^I catalytically oxidized the phosphine into phosphine oxide as copper-containing oxygenases[15] do.

Crystal structure analyses

$Cu_4(\mu\text{-dppm})_4[S_2CC(CN)P(O)(OEt)_2]_2$ (1). The compound **1** (Fig. 1) structurally characterized as $[Cu_4(\mu\text{-dppm})_4(S_2CC(CN)P(O)(OEt)_2)_2]$, which is similar in coordination to $Ag_4(\mu\text{-dppm})_4[S_2CC(CN)P(O)(OEt)_2]_2$,[7] has a distorted Cu_4 planar-like geometry. Each copper atom is tetrahedrally coordinated by two sulfur atoms and two phosphorus atoms. Two kinds of bridging ligands surround the Cu_4 unit: while two 1,1-dithiolate ligands exhibiting a "tetrametallic tetraconnective" $\eta^2(\mu\text{-S-}\mu\text{-S}')$ (**D**) coordination pattern are bonded from both sides of the Cu_4 plane and are perpendicular to each other, the four dppm ligands bridge the edges having two-up and two-down conformation. The geometry of Cu_4 is so distorted that the torsion angle of Cu1–Cu2–Cu3–Cu4 is 15.2(1)° and the Cu–Cu distances range from 3.186 to 3.595 Å and show no significant $Cu^I \cdots Cu^I$ interactions. The averaged sulfur–sulfur bite distance of 1,1-dithiolates is 3.074(2) Å and the Cu–S bond distances fall in the range of 2.340(4)–2.392(4) Å. The core geometry of **1** is also similar to that found in $Cu_4(\mu\text{-dppm})_2(CS_3)_2$,[16] and $[Cu_4(\mu\text{-dppm})_2(\mu_4\text{-E})]^{2+}$ (E = S, Se, PPh).[17] The selected bond distances and angles are listed in Table 2.

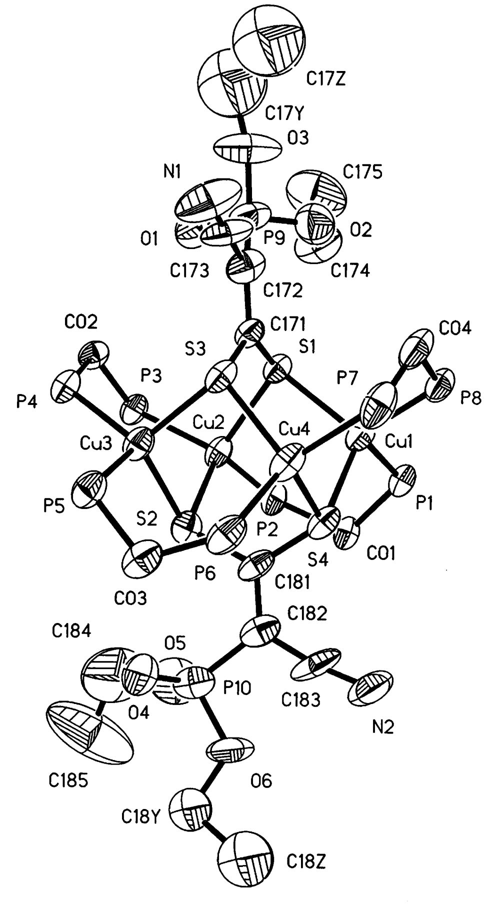


Fig. 1 The thermal ellipsoid drawing (50% probability) of **1** with phenyl rings omitted for clarity.

Table 2 Selected bond lengths [Å] and angles [°] for **1**

Cu(1)–P(1)	2.297(4)	Cu(3)–P(4)	2.295(4)
Cu(1)–P(8)	2.304(4)	Cu(3)–P(5)	2.298(4)
Cu(1)–S(4)	2.345(4)	Cu(3)–S(3)	2.340(4)
Cu(1)–S(1)	2.354(3)	Cu(3)–S(2)	2.392(4)
Cu(2)–P(2)	2.303(4)	Cu(4)–P(6)	2.296(5)
Cu(2)–P(3)	2.304(4)	Cu(4)–P(7)	2.312(5)
Cu(2)–S(2)	2.353(4)	Cu(4)–S(4)	2.353(4)
Cu(2)–S(1)	2.383(4)	Cu(4)–S(3)	2.371(4)
P(1)–Cu(1)–P(8)	110.83(15)	P(4)–Cu(3)–P(5)	110.86(15)
P(1)–Cu(1)–S(4)	104.85(14)	P(4)–Cu(3)–S(3)	110.62(15)
P(8)–Cu(1)–S(4)	106.15(15)	P(5)–Cu(3)–S(3)	103.53(15)
P(1)–Cu(1)–S(1)	112.41(13)	P(4)–Cu(3)–S(2)	113.18(14)
P(8)–Cu(1)–S(1)	111.26(14)	P(5)–Cu(3)–S(2)	108.58(15)
S(4)–Cu(1)–S(1)	110.99(13)	S(3)–Cu(3)–S(2)	109.62(13)
P(2)–Cu(2)–P(3)	109.11(13)	P(6)–Cu(4)–P(7)	116.40(18)
P(2)–Cu(2)–S(2)	109.42(14)	P(6)–Cu(4)–S(4)	108.71(16)
P(3)–Cu(2)–S(2)	109.33(14)	P(7)–Cu(4)–S(4)	109.91(16)
P(2)–Cu(2)–S(1)	109.41(14)	P(6)–Cu(4)–S(3)	111.72(15)
P(3)–Cu(2)–S(1)	105.43(13)	P(7)–Cu(4)–S(3)	102.35(16)
S(2)–Cu(2)–S(1)	114.00(13)	S(4)–Cu(4)–S(3)	107.31(13)

$Cu_4(\mu\text{-dppm})_3(\eta^1\text{-}P\text{-dppmO})[S_2CC(CN)P(O)(OEt)_2]_2$ (2). Fig. 2 shows the thermal ellipsoid drawing of **2** which consists of a Cu_4 unit capped on both sides by two perpendicular cpdt ligands. Unlike compound **1** in which each edge of the Cu_4 plane is bridged by a dppm ligand, only three of the four edges are bridged in **2**. Therefore a dangling dppm ligand having a phosphine oxide at the end is revealed. Consequently the Cu3 is trigonally coordinated to two sulfur atoms and one phosphorus atom, whereas the rest of the copper atoms are each coordinated by two sulfur atoms and two phosphorus atoms.

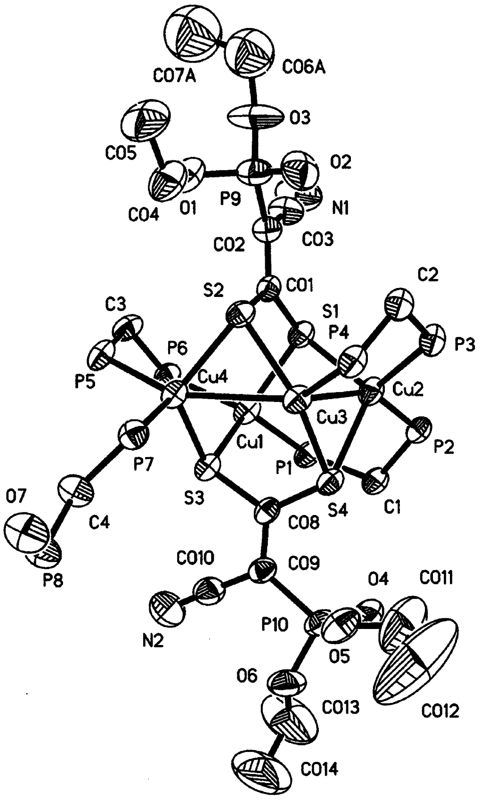


Fig. 2 The thermal ellipsoid drawing (50% probability) of **2** with phenyl rings removed for clarity.

The Cu_4 trapezoidal plane is so distorted that two long and two short Cu–Cu distances are observed. While the longer set (Cu1–Cu2, 3.466(3) Å and Cu1–Cu4, 3.583(3) Å) is comparable to those in **1**, the other two (Cu2–Cu3, 2.7033(7)Å and Cu3–Cu4, 2.8548(7) Å) are significantly shorter. Especially noted is the bond length of Cu2–Cu3 which is even shorter then the sum of the van der Waals radii for copper (2.80 Å).[18] This can be attributed to either the strong d^{10}–d^{10} interactions between the copper centers[19] or the ligand-imposed cluster geometry.[20] The

Table 3 Selected bond lengths [Å] and angles [°] for **2**

Cu(1)–P(6)	2.2734(11)	Cu(4)–S(2)	2.3509(11)
Cu(1)–P(1)	2.2853(10)	S(1)–C(01)	1.749(4)
Cu(1)–S(3)	2.3385(11)	S(2)–C(01)	1.747(4)
Cu(1)–S(1)	2.3501(11)	S(3)–C(08)	1.745(3)
Cu(2)–P(2)	2.2801(10)	S(4)–C(08)	1.742(4)
Cu(2)–P(3)	2.3000(12)	P(8)–O(7)	1.464(3)
Cu(2)–S(1)	2.3295(10)	P(9)–O(2)	1.481(4)
Cu(2)–S(4)	2.4879(11)	P(9)–O(1)	1.555(4)
Cu(2)–Cu(3)	2.7033(7)	P(9)–O(3)	1.560(4)
Cu(3)–S(4)	2.2590(10)	P(10)–O(4)	1.458(3)
Cu(3)–P(4)	2.2592(11)	P(10)–O(5)	1.575(4)
Cu(3)–S(2)	2.3184(10)	P(10)–O(6)	1.577(4)
Cu(3)–Cu(4)	2.8548(7)	N(1)–C(03)	1.143(6)
Cu(4)–P(7)	2.3018(11)	N(2)–C(010)	1.141(6)
Cu(4)–S(3)	2.3247(10)	C(01)–C(02)	1.381(5)
Cu(4)–P(5)	2.3273(11)	C(08)–C(09)	1.384(5)
P(6)–Cu(1)–P(1)	117.40(4)	Cu(2)–Cu(3)–Cu(4)	111.58(2)
P(6)–Cu(1)–S(3)	100.31(4)	P(7)–Cu(4)–S(3)	111.60(4)
P(1)–Cu(1)–S(3)	116.31(4)	P(7)–Cu(4)–P(5)	111.41(4)
P(6)–Cu(1)–S(1)	108.29(4)	S(3)–Cu(4)–P(5)	98.98(4)
P(1)–Cu(1)–S(1)	103.65(4)	P(7)–Cu(4)–S(2)	111.94(4)
S(3)–Cu(1)–S(1)	110.86(4)	S(3)–Cu(4)–S(2)	117.13(4)
P(2)–Cu(2)–P(3)	114.03(4)	P(5)–Cu(4)–S(2)	104.73(4)
P(2)–Cu(2)–S(1)	102.92(4)	P(7)–Cu(4)–Cu(3)	93.71(3)
P(3)–Cu(2)–S(1)	114.17(4)	S(3)–Cu(4)–Cu(3)	82.55(3)
P(2)–Cu(2)–S(4)	101.00(4)	P(5)–Cu(4)–Cu(3)	151.82(4)
P(3)–Cu(2)–S(4)	109.95(4)	S(2)–Cu(4)–Cu(3)	51.80(3)
S(1)–Cu(2)–S(4)	113.92(4)	O(2)–P(9)–O(1)	114.1(2)
P(2)–Cu(2)–Cu(3)	152.25(4)	O(2)–P(9)–O(3)	114.6(3)
P(3)–Cu(2)–Cu(3)	82.61(3)	O(1)–P(9)–O(3)	103.2(3)
S(1)–Cu(2)–Cu(3)	88.72(3)	O(2)–P(9)–C(02)	113.8(2)
S(4)–Cu(2)–Cu(3)	51.38(3)	O(1)–P(9)–C(02)	108.8(2)
S(4)–Cu(3)–P(4)	119.42(4)	O(3)–P(9)–C(02)	101.0(2)
S(4)–Cu(3)–S(2)	138.88(4)	O(4)–P(10)–O(5)	114.4(2)
P(4)–Cu(3)–S(2)	98.22(4)	O(4)–P(10)–O(6)	114.3(2)
S(4)–Cu(3)–Cu(2)	59.38(3)	O(5)–P(10)–O(6)	101.0(2)
P(4)–Cu(3)–Cu(2)	105.36(3)	O(4)–P(10)–C(09)	115.58(19)
S(2)–Cu(3)–Cu(2)	97.02(3)	O(5)–P(10)–C(09)	106.75(19)
S(4)–Cu(3)–Cu(4)	101.86(3)	O(6)–P(10)–C(09)	103.2(2)
P(4)–Cu(3)–Cu(4)	134.70(3)	N(1)–C(03)–C(02)	176.5(6)
S(2)–Cu(3)–Cu(4)	52.83(3)	N(2)–C(010)–C(09)	177.5(5)

sulfur–sulfur bite distances of the cpdt ligands are 3.060 Å and 3.046 Å, respectively. The Cu–S bond distances fall in the range of 2.2590(10)–2.4879(11) Å. The averaged C=C (1.382(5) Å) and C≡N (1.142(6) Å) bond distances of the cpdt in **2** are not unusual and comparable with the normal C=C and C≡N bond distances. The P–O distances (1.458(3) Å and 1.481(4) Å) of the phosphinyl group are slightly shorter than the rest of P–O bond lengths which are in the range of 1.555(4)–1.577(4) Å. Thus a P=O double bond character is revealed and comparable with the P=O bond distance, 1.464(3) Å, of the phosphine oxide in the dangling dppm group.

Clusters or cage molecules consisting of a dangling dppm ligand where the uncoordinated, trivalent P atom has been oxidized to become a phosphine oxide are not uncommon. One of the examples is $[Hg_2(NO_3)_2(dppcb)(\eta^1\text{-}P\text{-}dppmO)_2](NO_3)_2$,[21] where the dppcb is *cis*,*trans*,*cis*-1,2,3,4-tetrakis(diphenylphosphino)cyclobutane. Two mercury atoms are bridged by dppcb and each Hg^{II} is terminally bonded to the oxygen atom of the nitrate group and the phosphorus atom of the dangling dppm ligand. Although there are several examples having such a coordination motif,[22] this has never been structurally characterized in any copper clusters. The selected bond distances and angles are presented in Table 3.

$Cu_5(\mu\text{-dppm})_4[S_2CC(CN)P(O)(OEt)_2]_2(PF_6)$ (3). A crystallographic analysis reveals that complex **3** is a pentanuclear cationic species where the cluster is stabilized by the four bridging dppm and two 1,1-dithiolate ligands. As shown in Fig. 3, there is a C_2 axis through the Cu(3) and the center of the "zig-zag" chain formed by the four copper atoms. Three kinds of copper environments are present: the Cu(3) atom through which the two-fold rotational axis passes is surrounded by two sulfur atoms and two phosphorus atoms forming a tetrahedral arrangement; the Cu(2) and Cu(2A) atoms are each trigonally surrounded by two sulfur atoms and one phosphorus atom; the remaining two are tetragonally coordinated by two phosphorus atoms and one sulfur atom with the oxygen atom from P=O group of the dithiolate ligand occupying the fourth coordination site.

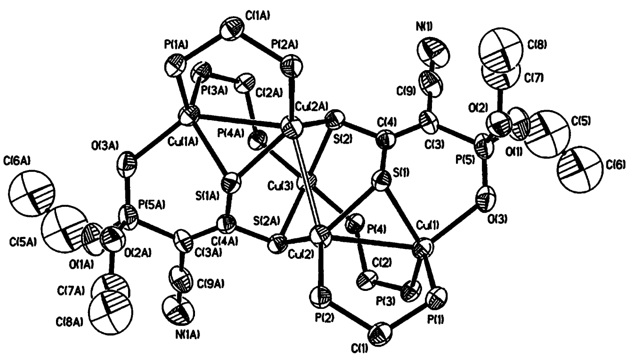


Fig. 3 The thermal ellipsoid drawing (50% probability) of the cluster cation **3** with phenyl rings removed for clarity.

Surprisingly the P(5)–O(3) distance of the phosphinyl moiety, 1.472(4) Å, does not display significant differences by comparison with the phosphinyl groups in compounds **1** and **2** even though the lone electron pair of the oxygen atom has been used to coordinate to other copper atoms. The Cu(1)–Cu(2) distance of 2.9603(8) Å is the shortest copper–copper distance found in this complex. Each sulfur atom of the dithiolates bridges two copper atoms and the Cu–S bond distances fall in the range of 2.2603(11)–2.3597(11) Å. This kind of bridging mode, μ; μ, in conjunction with the oxygen atom of the phosphinyl group makes the 1,1-dithiolate in **3** a rare example of tetrametallic pentaconnective coordination mode, η^3(μ-S-μ-S′-O) (**F**). The dppm ligands act as normal bridging ligands, each connecting two copper atoms. The Cu–P bond distances are in the range 2.2572(12)–2.3130(11) Å. The selected bond distances and angles are listed in the Table 4.

Basically compound **3** is isostructural with its silver analog, $Ag_5(\mu\text{-dppm})_4[S_2CC(CN)P(O)(OEt)_2]_2(PF_6)$.[7] The difference lies in the coordination number of the central metal atoms of the zig-zag chain. Whereas the copper atoms are three-coordinated, the silver ones are four-coordinated.

$Cu_9(\mu\text{-dppm})_4[S_2CC(CN)P(O)(OEt)_2]_4(PF_6)$ (4). A crystallographic analysis reveals that the complex **4** is a nonanuclear cationic species in which the nine copper atoms are arranged in such a way that the Cu(1) atom is sandwiched between two zig-zag chains of which each is composed of four copper atoms and related to each other by the pseudo S_4 axis. In each zig-zag chain, there exist two bridging dppm and cpdt ligands, respectively. As shown in Fig. 4, three kinds of copper environments are present if the Cu–Cu interactions are not taken into consideration: the Cu(1) atom by which the four-fold improper axis passes is surrounded by four sulfur atoms of the four different cpdt ligands forming a tetrahedral arrangement; the terminal copper atoms of the zig-zag chain are each tetragonally surrounded by the sulfur and phosphorus atoms with the oxygen atom from the P=O group and nitrogen atom from the CN group of the cpdt ligand occupying the third and the fourth coordination sites; the central copper atoms within the chain are trigonally coordinated by two sulfur atoms and one phosphorus atom. The Cu–Cu bond lengths within the chain are in the range of 2.873(3)–2.955(3) Å. The torsion angle of the zig-zag chains is averaged to 142.4°. The sulfur atoms of the dithiolates are each bridged to two copper atoms and the Cu–S bond distances fall in the range 2.259(5)–2.403(6) Å. The coordination of oxygen to copper results in the formation of

Table 4 Selected bond lengths [Å] and angles [°] for **3**

Cu(1)–O(3)	2.237(3)	Cu(1)–P(3)	2.2882(12)
Cu(1)–P(1)	2.2881(12)	Cu(1)–S(1)	2.3540(11)
Cu(1)–Cu(2)	2.9603(8)	Cu(2)–P(2)	2.2572(12)
Cu(2)–S(1)	2.2603(11)	Cu(2)–S(2)#1	2.3295(12)
Cu(3)–P(4)#1	2.3130(11)	Cu(3)–P(4)	2.3130(11)
Cu(3)–S(2)	2.3597(11)	Cu(3)–S(2)#1	2.3597(11)
P(5)–O(3)	1.472(4)	P(5)–O(1)	1.549(5)
P(5)–O(2)	1.568(4)	P(5)–C(3)	1.781(5)
S(1)–C(4)	1.754(4)	S(2)–C(4)	1.737(4)
S(2)–Cu(2)#1	2.3295(12)	N(1)–C(9)	1.154(7)
C(3)–C(4)	1.384(6)	C(3)–C(9)	1.421(7)
O(3)–Cu(1)–P(3)	110.58(10)	O(3)–Cu(1)–P(1)	108.58(10)
O(3)–Cu(1)–S(1)	86.66(9)	P(3)–Cu(1)–P(1)	112.34(5)
P(3)–Cu(1)–S(1)	131.34(4)	C(4)–S(1)–Cu(2)	118.78(14)
P(1)–Cu(1)–S(1)	103.48(4)	C(4)–S(1)–Cu(1)	104.40(13)
O(3)–Cu(1)–Cu(2)	135.06(9)	Cu(2)–S(1)–Cu(1)	79.79(4)
P(3)–Cu(1)–Cu(2)	98.57(4)	C(4)–S(2)–Cu(2)#1	91.16(14)
P(1)–Cu(1)–Cu(2)	89.78(3)	C(4)–S(2)–Cu(3)	105.92(14)
S(1)–Cu(1)–Cu(2)	48.72(3)	Cu(2)#1–S(2)–Cu(3)	101.36(4)
P(2)–Cu(2)–S(1)	114.93(4)	P(2)–Cu(2)–S(2)#1	122.27(5)
S(1)–Cu(2)–S(2)#1	120.84(4)	P(2)–Cu(2)–Cu(1)	93.48(4)
S(1)–Cu(2)–Cu(1)	51.50(3)	P(5)–O(3)–Cu(1)	125.90(19)
S(2)#1–Cu(2)–Cu(1)	109.28(3)	P(4)#1–Cu(3)–P(4)	116.51(6)
P(4)#1–Cu(3)–S(2)	95.97(4)	P(4)–Cu(3)–S(2)	118.92(4)
P(4)#1–Cu(3)–S(2)#1	118.92(4)	P(4)–Cu(3)–S(2)#1	95.97(4)
S(2)–Cu(3)–S(2)#1	112.10(6)	O(3)–P(5)–O(1)	114.4(3)
O(3)–P(5)–O(2)	109.0(2)	O(1)–P(5)–O(2)	105.1(3)
O(3)–P(5)–C(3)	115.7(2)	O(1)–P(5)–C(3)	102.1(3)
O(2)–P(5)–C(3)	109.9(2)	C(4)–C(3)–C(9)	119.5(4)
C(4)–C(3)–P(5)	122.4(3)	C(9)–C(3)–P(5)	118.1(4)
C(3)–C(4)–S(2)	122.2(3)	C(3)–C(4)–S(1)	119.5(3)
S(2)–C(4)–S(1)	118.0(2)	N(1)–C(9)–C(3)	177.5(7)

Symmetry transformations used to generate equivalent atoms: #1 $-x - 1, y, -z + 1/2$; #2 $-x - 1, -y + 2, -z + 1$.

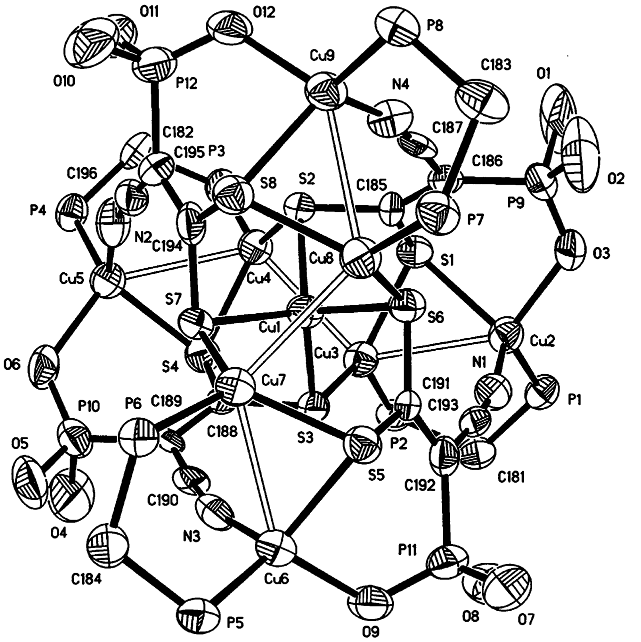


Fig. 4 The thermal ellipsoid drawing (50% probability) of the cluster cation **4** with phenyl rings and ethyl groups removed for clarity.

the Cu–S–C–C–P–O six-membered ring. Thus the free rotation of the P–C bond is hindered so that two ethoxyl groups are not chemically equivalent for the cpdt ligands. The Cu–O bond lengths average 2.155(3) Å. The average C–C–N angle of 176(2)° deviates slightly from linearity. This can be understood by the formation of the Cu–N bonds, which fall in the range 1.95(2)–2.04(2) Å. This kind of bridging mode, μ; μ, in conjunction with the oxygen atom of the phosphinyl group and the nitrogen atom of the cyano group makes the 1,1-dithiolate in **4** an extremely rare example of pentametallic hexaconnective coordination mode, η^4(μ-S-μ-S′–O–N) (**G**). The dppm ligands act as normal bridging ligands, each connecting two copper atoms. The Cu–P bond distances are in the range 2.185(5)–2.251(5) Å. Overall, the cluster itself has an idealized S_4 point group symmetry. The selected bond distances and angles are listed in Table 5.

That the cyano group of the cpdt is bonded to copper atom is of special interest by considering the emerging field in the utilization of cyanometalates to construct new porous materials.[23] Surprisingly there are only two reports of this sort regarding the coordination chemistry of either 1,1- or 1,2-dithiolates possessing the CN substituent. One is displayed in a hetero-binuclear complex, $(CH_3CN)LNi(MNT)Cu(MNT)$ (L = tetrabenzo[*b*,*f*,*j*,*n*]-1,5,9,13-tetraazacyclohexadecine and MNT = *cis*-1,2-dicyano-1,2-ethylenedithiolate),[24] in which one MNT ligand is linked through one of its cyano groups to an axial site of the Ni(II). The other is revealed from a nickel-containing chain-like polymer of $(Ni(NH_3)_4Ni(i\text{-}MNT)_2)_\infty$ where the CN group in the anionic moiety $Ni(i\text{-}MNT)_2^{2-}$ is bonded to the Ni atom of the cationic moiety $Ni(NH_3)_4^{2+}$.[25]

Bonding mode analysis

The coordination patterns **A–D** listed in Chart 1 are quite common for the 1,1-dithiolato metal complexes. Especially noted is the type **D** for phosphor-1,1-dithiolato metal complexes which were limited to cubic M_8 (M = Cu^I and Ag^I) clusters encapsulated by S^{2-}, Cl^- and Br^-,[26] but nowadays it is frequently observed in its selenium counterpart, namely the diselenophosphates, where the cluster nuclearities have been expanded to twelve.[27] However those **E–G** are unusual. Besides the connection patterns D–G mentioned above for the cpdt, type **A** was observed in two platinum complexes.[8] The simple bridging mode of **B** was identified from the dinuclear gold compound, $Au_2(\mu\text{-dppm})[\mu\text{-}S_2CC(CN)P(O)(OEt)_2]_2$.[28] To date the type **C** pattern remains unknown for any cpdt metal complexes.

Table 5 Selected bond lengths [Å] and angles [°] for **4**

Cu(1)–S(3)	2.358(5)	Cu(5)–P(4)	2.209(5)
Cu(1)–S(6)	2.363(5)	Cu(5)–S(4)	2.349(6)
Cu(1)–S(7)	2.374(5)	Cu(6)–N(3)	2.037(18)
Cu(1)–S(2)	2.387(5)	Cu(6)–O(9)	2.134(13)
Cu(2)–N(1)	1.956(16)	Cu(6)–P(5)	2.209(5)
Cu(2)–O(3)	2.159(14)	Cu(6)–S(5)	2.400(5)
Cu(2)–P(1)	2.185(5)	Cu(6)–Cu(7)	2.878(3)
Cu(2)–S(1)	2.403(6)	Cu(7)–P(6)	2.232(5)
Cu(2)–Cu(3)	2.873(3)	Cu(7)–S(5)	2.259(5)
Cu(3)–P(2)	2.223(5)	Cu(7)–S(7)	2.296(5)
Cu(3)–S(3)	2.290(5)	Cu(7)–Cu(8)	2.893(3)
Cu(3)–S(1)	2.295(5)	Cu(8)–P(7)	2.232(5)
Cu(3)–Cu(4)	2.955(3)	Cu(8)–S(6)	2.283(5)
Cu(4)–P(3)	2.251(5)	Cu(8)–S(8)	2.294(6)
Cu(4)–S(2)	2.284(5)	Cu(8)–Cu(9)	2.878(3)
Cu(4)–S(4)	2.284(5)	Cu(9)–N(4)	1.952(16)
Cu(4)–Cu(5)	2.920(3)	Cu(9)–O(12)	2.190(14)
Cu(5)–N(2)	2.023(18)	Cu(9)–P(8)	2.199(5)
Cu(5)–O(6)	2.143(14)	Cu(9)–S(8)	2.374(5)
S(3)–Cu(1)–S(6)	116.28(19)	Cu(6)–Cu(7)–Cu(8)	121.69(10)
S(3)–Cu(1)–S(7)	113.71(17)	P(7)–Cu(8)–S(6)	128.0(2)
S(6)–Cu(1)–S(7)	99.09(15)	P(7)–Cu(8)–S(8)	111.8(2)
S(3)–Cu(1)–S(2)	100.00(15)	S(6)–Cu(8)–S(8)	115.48(18)
S(6)–Cu(1)–S(2)	114.48(17)	P(7)–Cu(8)–Cu(9)	92.45(16)
S(7)–Cu(1)–S(2)	114.10(19)	S(6)–Cu(8)–Cu(9)	98.77(14)
N(1)–Cu(2)–O(3)	94.4(6)	S(8)–Cu(8)–Cu(9)	53.20(14)
N(1)–Cu(2)–P(1)	116.8(5)	P(7)–Cu(8)–Cu(7)	127.97(16)
O(3)–Cu(2)–P(1)	122.3(4)	S(6)–Cu(8)–Cu(7)	87.50(13)
N(1)–Cu(2)–S(1)	115.7(5)	S(8)–Cu(8)–Cu(7)	71.65(14)
O(3)–Cu(2)–S(1)	90.3(4)	Cu(9)–Cu(8)–Cu(7)	121.58(10)
P(1)–Cu(2)–S(1)	113.66(19)	N(4)–Cu(9)–O(12)	99.4(6)
N(1)–Cu(2)–Cu(3)	89.2(5)	N(4)–Cu(9)–P(8)	113.8(5)
O(3)–Cu(2)–Cu(3)	137.0(4)	O(12)–Cu(9)–P(8)	119.7(4)
P(1)–Cu(2)–Cu(3)	93.21(16)	N(4)–Cu(9)–S(8)	117.9(5)
S(1)–Cu(2)–Cu(3)	50.63(13)	O(12)–Cu(9)–S(8)	91.3(4)
P(2)–Cu(3)–S(3)	127.7(2)	P(8)–Cu(9)–S(8)	112.61(18)
P(2)–Cu(3)–S(1)	112.95(19)	N(4)–Cu(9)–Cu(8)	87.6(4)
S(3)–Cu(3)–S(1)	115.34(18)	O(12)–Cu(9)–Cu(8)	138.4(3)
P(2)–Cu(3)–Cu(2)	91.60(16)	P(8)–Cu(9)–Cu(8)	93.59(16)
S(3)–Cu(3)–Cu(2)	100.76(14)	S(8)–Cu(9)–Cu(8)	50.69(14)
S(1)–Cu(3)–Cu(2)	54.01(14)	N(2)–Cu(5)–P(4)	110.0(5)
P(2)–Cu(3)–Cu(4)	127.05(17)	O(6)–Cu(5)–P(4)	122.8(4)
S(3)–Cu(3)–Cu(4)	88.18(15)	N(2)–Cu(5)–S(4)	117.2(5)
S(1)–Cu(3)–Cu(4)	70.04(14)	O(6)–Cu(5)–S(4)	93.3(4)
Cu(2)–Cu(3)–Cu(4)	121.73(10)	P(4)–Cu(5)–S(4)	116.4(2)
P(3)–Cu(4)–S(2)	129.8(2)	N(2)–Cu(5)–Cu(4)	88.7(5)
P(3)–Cu(4)–S(4)	111.08(19)	O(6)–Cu(5)–Cu(4)	138.9(4)
S(2)–Cu(4)–S(4)	114.73(18)	P(4)–Cu(5)–Cu(4)	93.50(16)
P(3)–Cu(4)–Cu(5)	90.38(15)	S(4)–Cu(5)–Cu(4)	49.95(13)
S(2)–Cu(4)–Cu(5)	101.95(14)	N(3)–Cu(6)–O(9)	97.3(6)
S(4)–Cu(4)–Cu(5)	51.93(15)	N(3)–Cu(6)–P(5)	113.3(4)
P(3)–Cu(4)–Cu(3)	127.15(18)	O(9)–Cu(6)–P(5)	123.0(4)
S(2)–Cu(4)–Cu(3)	88.03(14)	N(3)–Cu(6)–S(5)	117.0(4)
S(4)–Cu(4)–Cu(3)	69.80(15)	O(9)–Cu(6)–S(5)	94.5(4)
Cu(5)–Cu(4)–Cu(3)	119.79(10)	P(5)–Cu(6)–S(5)	110.50(19)
N(2)–Cu(5)–O(6)	95.1(6)	N(3)–Cu(6)–Cu(7)	85.6(4)
P(6)–Cu(7)–Cu(6)	92.69(15)	O(9)–Cu(6)–Cu(7)	138.8(4)
S(5)–Cu(7)–Cu(6)	54.09(13)	P(5)–Cu(6)–Cu(7)	92.19(16)
S(7)–Cu(7)–Cu(6)	103.31(14)	S(5)–Cu(6)–Cu(7)	49.66(13)
P(6)–Cu(7)–Cu(8)	129.31(15)	P(6)–Cu(7)–S(5)	116.5(2)
S(5)–Cu(7)–Cu(8)	70.04(13)	P(6)–Cu(7)–S(7)	121.05(19)
S(7)–Cu(7)–Cu(8)	88.41(13)	S(5)–Cu(7)–S(7)	118.72(18)
N(4)–C(187)–C(186)	176.8(18)	N(3)–C(190)–C(189)	175.0(18)

Spectroscopy

The CN stretching frequency for clusters **1**–**4** in the IR spectra is at 2175, 2176, 2179 and 2187 cm^{-1}, respectively, with a high energy shift relative to the free ligand (ν_{CN} = 2162 cm^{-1}). Especially noted is cluster **4** which displays a 25 cm^{-1} shift. Purcell and Drago demonstrated that interaction of the nitrile unit with a Lewis acid increases its stretching frequency by increasing the CN force constant.[29] Thus it is evidence for the coordination of the nitrile to the Cu(I) ions.

While a slightly broad resonance centered at −10.2, −13.4, and −13.7 ppm for the dppm was observed for clusters **1**, **3**, and **4**, respectively, in the ^{31}P NMR spectrum at ambient temperature, only one broad methylene proton signal in the ^{1}H NMR was revealed for these clusters. This suggests the occurrence of the flipping motions of the dppm ligands. On the other hand, the chemical shifts for the cpdt ligand are at 17.1, 18.1, and 18.8 ppm and are accidentally in accordance with the cluster nuclearities. In the ^{1}H NMR of the cpdt moieties, one set of resonance frequencies of the ethyl group was found in **1** and **3** but two sets of ethyl peaks were revealed in **4**. This implies the free rotation of the P–C bond is hindered in clusters **4** and the six-membered ring of Cu–S–C–C–P–O mentioned above remains intact in solution. Besides a broad singlet centered at −14 ppm for the bridging dppm in **2**, surprisingly a set of doublets centered at 24.3 and 36.6 ppm, which can be reasonably assigned as the resonance frequency of the dangling η^1-*P*-dppmO, was identified. The chemical shift of the cpdt in **2** is at 14.9 ppm.

A unique fragmentation pattern was exhibited in the positive FAB mass spectrum for cationic clusters **3** and **4**. In addition to the molecular ion peak, additional peaks corresponding to the intact complex with the loss of one and two dppm ligands were observed.

In conclusion, the variable coordination patterns observed in clusters **1**–**4** show the cpdt ligand in a much more diverse coordination mode than expected. It will be of great interest to construct high-nuclearity metal clusters by the full use of all coordination sites of the cpdt ligands. In addition, these functionalized 1,1-dithiolates may potentially serve as building units in the field of supramolecules as demonstrated elegantly by Beer *et al.* in their recent work of dithiocarbamate–resorcarene-based nanoarchitectures,[30] and by Kim *et al.* in the inorganic "tennis ball".[31]

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References

1 D. Coucouvanis, *Prog. Inorg. Chem.*, 1970, **11**, 23; D. Coucouvanis, *Prog. Inorg. Chem.*, 1979, **26**, 301; R. Eisenberg, *Prog. Inorg. Chem.*, 1970, **12**, 295; R. P. Burns, F. P. McCullough and C. A. McAuliffe, *Adv. Inorg. Chem.*, 1980, **23**, 211.

2 J. A. Schuerman, F. R. Fronczek and J. Selbin, *J. Am. Chem. Soc.*, 1986, **108**, 336.

3 L. E. McCandlish, E. C. Bissel, D. Coucouvanis, J. P. Fackler, Jr. and K. Knox, *J. Am. Chem. Soc.*, 1968, **90**, 7357; P. J. M. W. L. Birker and G. G. Verschoor, *J. Chem. Soc., Chem. Commun.*, 1981, 322; C. W. Liu, R. J. Staples and J. P. Fackler, Jr., *Coord. Chem. Rev.*, 1998, **174**, 147; C. W. Liu, C. J. McNeal and J. P. Fackler, Jr., *J. Cluster Sci.*, 1996, **7**, 385.

4 H. Dietrich, W. Storck and G. Manecke, *J. Chem. Soc., Chem. Commun.*, 1982, 1036; H. Zhang and X. Yu, *Jieguo Hauxue*, 1987, **6**, 98.

5 M. N. I. Khan, S. Wang and J. P. Fackler, Jr., *Inorg. Chem.*, 1989, **28**, 3579.

6 G. N. George, J. Byrd and D. R. Winge, *J. Biol. Chem.*, 1988, **263**, 8199; K. H. Nakagawa, C. Inoye, B. Hedman, M. Karin, T. D. Tullius and K. D. Hodgeson, *J. Am. Chem. Soc.*, 1991, **113**, 3621; J. R. Casas-Hinets, S. Hu, D. Hamer and R. L. Karpel, *Biochemistry*, 1992, **31**, 6617; L. T. Jensen, J. M. Peltier and D. R. Winge, *J. Biol. Inorg. Chem.*, 1998, **3**, 627; K. B. Neilson and D. R. Winge, *J. Biol. Chem.*, 1985, **260**, 9698.

7 C. W. Liu, B.-J. Liaw, J.-C. Wang and T.-C. Keng, *Inorg. Chem.*, 2000, **39**, 1329.

8 J. M. Bevilacqua and R. Eisenberg, *Inorg. Chem.*, 1994, **33**, 2913; S. D. Cummings and R. Eisenberg, *J. Am. Chem. Soc.*, 1996, **118**, 1949.

9 J. Diez, M. P. Gamasa, J. Gimeno, A. Tiripicchio and M. T. Camellini, *J. Chem. Soc., Dalton Trans.*, 1987, 1275.

10 K. A. Jensen and L. Henriksen, *Acta Chem. Scand.*, 1968, **22**, 1107.

11 SMART V4.043, Software for the CCD Detector System, Bruker Analytical X-ray System, Madison, WI, 1995.

12 SAINT V4.035, Software for the CCD Detector System, Bruker Analytical X-ray System, Madison, WI, 1995.

13 G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structure, University of Göttingen, Göttingen, 1997.

14 SHELXTL 5.10 (PC-Version), Program Library for Structure Solution and Molecular Graphics, Bruker Analytical X-ray Systems, Madison, WI, 1998.

15 R. H. Holm, P. Kennepohl and E. I. Solomon, *Chem. Rev.*, 1996, **96**, 2239.

16 A. M. M. Lanfredi, A. Tiripicchio, A. Camus and N. Marsich, *J. Chem. Soc., Chem Commun.*, 1983, 1126.

17 V. W. W. Yam, W. K. Lee and T. F. Lai, *J. Chem. Soc., Chem. Commun.*, 1993, 1571; V. W. W. Yam, K. K. W. Lo and K. K. Chung, *Inorg. Chem.*, 1996, **35**, 3459; R.-N. Yang, Y.-A. Sun, Y.-M. Hou, X.-Y. Hu and D.-M. Jin, *Inorg. Chim. Acta*, 2000, **304**, 1; V. W. W. Yam, E. C. C. Cheng and N. Y. Zhu, *Chem. Commun.*, 2001, 1028.

18 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

19 P. Pyykko, *Chem. Rev.*, 1997, **97**, 597; P. Pyykko and F. Mendizabal, *Inorg. Chem.*, 1998, **37**, 3018; C. M. Che, Z. Mao, V. M. Miskowski, M. C. Tse, C. K. Chan, K. K. Cheung, D. L. Phillips and K. H. Leung, *Angew. Chem., Int. Ed.*, 2000, **39**, 4084; K. Singh, J. R. Long and P. Stavropoulos, *J. Am. Chem. Soc.*, 1997, **119**, 2942.

20 F. A. Cotton, X. Feng and D. J. Timmons, *Inorg. Chem.*, 1998, **37**, 4066; R. Clerac, F. A. Cotton, L. M. Daniels, J. Gu, C. A. Murillo and H. C. Zhou, *Inorg. Chem.*, 2000, **39**, 4488.

21 W. Oberhauser, T. Stampfl, R. Haid, C. Langes, C. Bachmann, H. Kopacka, K.-H. Ongania and P. Bruggller, *Polyhedron*, 2001, **20**, 727.

22 **Pt**: A. B. Antonova. A. A. Johansson. N. A. Deykhina. D. A. Pogrebnyakov. N. I. Pavlenko. A. I. Rubaylo. F. M. Dolgushin. P. V. Petrovskii and A. G. Ginzburg, *J. Organomet. Chem.*, 1999, **577**, 238. A. A. Frew, R. H. Hill, L. Manojlovic-Muir, K. W. Muir and R. J. Puddephatt, *Chem. Commun.*, 1982, 198. **Co**: Q.-B. Bao, S. J. Landon, A. L. Rheingold, T. M. Haller and T. B. Brill, *Inorg. Chem.*, 1985, **24**, 900; R. Weber, U. Englert, W. Keim and M. Mothrath, *Chem. Commun.*, 2000, 1419; M.-C. Hong, Z.-Y. Huang, X.-J. Lei, B.-S. Kang, F.-L. Jiang and H.-Q. Liu, *Chin. J. Chem.*, 1991, **9**, 425. **W**: D. J. Darensburg, D. J. Zalewski, C. Plepys and C. Campana, *Inorg. Chem.*, 1987, **26**, 3727. **Mo**: R. P. K. Babu, S. S. Krishnamurthy and M. Nethaji, *Organometallics*, 1995, **14**, 2947. **Re**: S. Bhattacharyya, I. Chakraborty, B. K. Dirghangi and A. Chakravoty, *Chem. Commun.*, 2000, 1813; G. A. Carriedo, M. L. Rodriguez, S. Garcia-Granda and A. Aguirer, *Inorg. Chim. Acta*, 1990, **178**, 101; X. L. R. Fontaine, E. H. Fowles, T. P. Layzell, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1991, 1519. **Au**: M. Paul and H. Schmidbaur, *Chem. Ber.*, 1996, **129**, 77.

23 K. R. Dunbar and R. A. Heitz, *Prog. Inorg. Chem.*, 1997, **45**, 283; K. K. Klausmeyer, T. B. Rauchfuss and S. R. Wilson, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1694; J. L. Heinrich, P. A. Berseth and J. R. Long, *Chem. Commun.*, 1998, 1231.

24 Z.-J. Zhong, N. Matsumoto, H. Okawa and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1989, 2095.

25 Y.-B. Zhu, S.-F. Lu, X.-Y. Huang, Q.-J. Wu, R.-M. Yu and J.-Q. Huang, *Acta Crystallogr., Sect. C*, 1995, **51**, 1515.

26 I. Haiduc, D. B. Sowerby and S. F. Lu, *Polyhedron*, 1995, **14**, 3389; C. W. Liu, R. T. Stubbs, R. J. Staples and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, 1995, **117**, 9778; Z. X. Huang, S. F. Lu, J. Q. Huang, D. M. Wu and J. L. Huang, *J. Struct. Chem.*, 1991, **10**, 213; K. Matsumoto, R. Tanaka, R. Shimomura and Y. Nakao, *Inorg. Chim. Acta*, 2000, **304**, 293.

27 C. W. Liu, H. C. Chen, J. C. Wang and T. C. Keng, *Angew. Chem., Int. Ed.*, 2001, **40**, 2342; C. W. Liu, C. M. Hung, H. C. Chen, J. C. Wang, T. C. Keng and K. M. Guo, *Chem. Commun.*, 2000, 1897; C. W. Liu, I. J. Shang, J. C. Wang and T. C. Keng, *Chem. Commun.*, 1999, 995; C. W. Liu, H. C. Chen, J. C. Wang and T. C. Keng, *Chem. Commun.*, 1998, 1831.

28 C. W. Liu, unpublished work.

29 K. F. Purcell and R. S. Drago, *J. Am. Chem. Soc.*, 1966, **88**, 919.

30 O. D. Fox, M. G. B. Drew and P. D. Beer, *Angew. Chem., Int. Ed.*, 2000, **39**, 136.

31 K. M. Kim, J. S. Park, Y. S. Kim, Y. J. Jun, T. Y. Kang, Y. S. Sohn and M. J. Jun, *Angew. Chem., Int. Ed.*, 2001, **40**, 2458.