Inorganica Chimica Acta, *183* (1991) 229–237

Synthesis and characterization of dinuclear Cu(I) complexes with two bimetallic hexadentate ligands having N_2P_4 donor sites. Crystal structure of $[Cu_2(BDPE)Cl_2]\cdot 2DMF$

M. M. Taqui Khan*, Parimal Paul, K. Venkatasubramanian and **Sapna Purohit**

Discipline of Coordination Chemistry and Homogeneous Catalysis, Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002 (India)

(Received October 30, 1990; revised February 19, 1991)

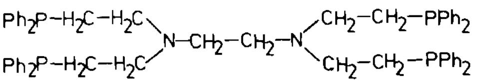
Abstract

A series of dinuclear Cu(I) complexes were synthesized from the reactions of $CuCl_2\cdot 2H_2O$, $[Cu(NCCH_3)_4](ClO_4)_2$, $CuSO_4\cdot 5H_2O$ and $Cu(CH_3COO)_2\cdot H_2O$ (where the Cu(II) ion is reduced in the reaction medium to Cu(I)), with two bimetallic hexadentate ligands BDPE and BDPX (where BDPE = α,α'-bis(bis(2-(diphenylphosphino)ethyl)amino)ethane and BDPX = α,α'-bis(bis(2-(diphenylphosphino)ethyl)amino)-*m*-xylene) having N_2P_4 donor atoms. The complexes were characterized on the basis of elemental analysis, conductivity data, IR, ^1H, ^{13}C and ^{13}P NMR spectral data. The molecular structure of the complex, $[Cu_2(BDPE)Cl_2]\cdot 2DMF$, was established by single crystal X-ray diffraction method. Crystal data: $C_{64}H_{74}Cu_2Cl_2N_4O_2P_4$, monoclinic, space group $P2_1/c$, $z = 2$, $a = 12.860(1)$, $b = 16.104(1)$, $c = 16.274(1)$ Å, $\beta = 113.24(1)°$, final R factor 0.039 ($R_w = 0.041$) for 3968 observed reflections.

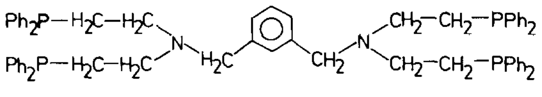
Introduction

The synthesis and characterization of copper(I) complexes with tertiary phosphine ligands have gained much importance because of their interesting stereochemical features [1] and reactivities such as photoreduction and photosensitized isomerization of diens [2], hydride mediated catalytic reduction of unsaturated organic substrates [3] and reactions with small molecules [4]. However, most of these studies are concerned mainly with monodentate tertiary phosphines, which form Cu(I) complexes, with the general composition $Lm(CuX)_n$ (where L is a nucleophile and X an anion [1]) with a wide variation of coordination geometries and stoichiometries. The monodentate tertiary phosphine ligands often undergo complicated dissociative equilibria in solution involving species with different composition [5, 6]. Sometimes such complexes show irreversibility in redox reaction due to cleavage of the metal–phosphorus bonds [7]. These problems are overcome by the use of polydentate phosphine ligands which have the ability to prevent the dissociation of the metal–phosphorus bond in solution due to stabilization provided by the chelate.

The chemistry of Cu(I) with chelated tertiary phosphines is mainly restricted to bidentate ligands such as 1,2-bis(diphenylphosphino) ethane/methane [8–15]. Such studies with polydentate phosphines, specially with dinucleating ligands is mostly unexplored. To investigate this interesting area of chemistry we have synthesized the hexadentate ligands, viz. α,α'-bis(bis(2-(diphenylphosphino)ethyl)amino)ethane (BDPE) (Structure **1**) and α,α'-bis(bis(2-(diphenylphosphino)ethyl)amino)-*m*-xylene (BDPX) (Structure **2**) which have two sets of PNP donor atoms separated by an ethylene and *m*-xylyl moiety, respectively. The PNP donors provide the hard N



1



2

---

*Author to whom correspondence should be addressed.

0020-1693/91/$3.50

and the soft P donor atoms for coordination to the metal ion which is expected to result in the extra stabilization of the (+1) oxidation state of copper in these complexes.

Here we wish to report the synthesis of a series of dinuclear Cu(I) complexes formed by the reaction of the ligands BDPE and BDPX with Cu(II) salts (Cu(II) reduces to Cu(I) in the reaction medium) and their characterization by elemental analysis, conductivity data, IR spectra, ^{1}H, ^{13}C and ^{31}P NMR spectral data. The structural characterization of a dinuclear complex, $[Cu_2(BDPE)Cl_2]\cdot 2DMF$, is also reported.

Experimental

Materials

The ligands BDPE and BDPX were prepared by the procedure developed in this laboratory [16]. $CuCl_2\cdot 2H_2O$, $CuSO_4\cdot 5H_2O$, $Cu(CH_3COO)_2\cdot H_2O$ and $AgClO_4$ were obtained from Aldrich Chemical Co. All organic solvents used were of reagent grade and were purified and dried before use. All preparations were carried out in an atmosphere of argon.

Physical measurements

Elemental analysis were performed on a Carlo Erba elemental analyser model 1106. A digisun Electronics digital conductivity meter model DI-909 was used for conductivity measurements. Magnetic measurements were carried out with a PAR model 155 vibrating sample magnetometer. IR spectra were recorded on a Carlzeiss Specord M80 spectrometer, as KBr pellets. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Jeol FX-100 FT-NMR. For ^{1}H and ^{13}C tetramethylsilane was used as an external reference and the instrument operated at 99.55 and 24.99 MHz, respectively. The ^{31}P NMR spectra were recorded at 40.27 MHz using spinning 10 mm tubes with a capillary of deuterium oxide for the internal lock and 85% H_3PO_4 as an external standard. The UV–Vis spectra were recorded on a Shimadzu UV-240 spectrometer.

Synthesis of the complexes

$[Cu_2(BDPE)Cl_2]\cdot 2DMF$ (1) and $[Cu_2(BDPX)Cl_2]$ (2)

To a refluxing solution of $CuCl_2\cdot 2H_2O$ (0.17 g, 1 mmol) in acetonitrile (20 cm^3) the ligand BDPE (0.454 g, 0.5 mmol)/BDPX (0.492 g, 0.5 mmol) dissolved in benzene (5 cm^3) was added dropwise and refluxing was continued for 2 h. The white compound which separated during reflux was collected by filtration, washed with acetonitrile and benzene, and recrystallized from DMF. Yield 60%.

$[Cu_2(BDPE)](ClO_4)_2$ (3) and $[Cu_2(BDPX)](ClO_4)_2$ (4)

$CuCl_2\cdot 2H_2O$ (0.17 g, 1 mmol) was dissolved in acetonitrile (10 cm^3) and dry $AgClO_4$ (0.41 g, 2 mmol) dissolved in acetonitrile (5 cm^3) was slowly added with stirring at room temperature. After 1 h of additional stirring the precipitated AgCl was removed by filtration and the solution dried in a rotary evaporator. The green coloured solid mass was dissolved in dry acetone (10 cm^3) and to this solution the ligand BDPE/BDPX (0.5 mmol) dissolved in benzene (5 cm^3) was added under refluxing condition. The white compounds that precipitated during reflux were collected by filtration, washed by benzene and acetone and finally recrystallized from acetonitrile. Yield 64%.

$[Cu_2(BDPE)](SO_4)$ (5) and $[Cu_2(BDPX)](SO_4)$ (6)

$CuSO_4\cdot 5H_2O$ (0.25 g, 1 mmol) was suspended in methanol (50 cm^3), the ligand BDPE/BDPX (0.5 mmol) dissolved in dichloromethane (5 cm^3) was added and the reaction mixture refluxed for 6 h. The volume of the solution was reduced to *c.* 5 cm^3 and n-hexane was added. The white compound was isolated by filtration, washed with benzene and reprecipitated from a dichloromethane–n-hexane mixture. Yield 55%.

$[Cu_2(BDPE)(CH_3COO)_2]$ (7) and $[Cu_2(BDPX)(CH_3COO)_2]$ (8)

To a solution of $Cu(CH_3COO)_2\cdot H_2O$ (0.2 g, 1 mmol) dissolved in acetone (10 cm^3) was added solid ligand BDPE/BDPX (0.5 mmol) in small portions and the reaction mixture refluxed for 4 h. In the case of BDPE a white compound separated during reflux. In the case of BDPX however, the solution was concentrated to *c.* 5 cm^3 when a white compound was separated after addition of diethyl ether. The compounds were isolated by filtration and recrystallized from a dichloromethane–ethanol mixture. Yield 50%.

X-ray structure determination of $[Cu_2(BDPE)Cl_2]\cdot 2DMF$ (1)

Preliminary data on space group and unit cell dimensions as well as intensity data were collected using a crystal of suitable dimensions on an Enraf-Nonius CAD$_4$/PDP-11/73 system with graphite-monochromatized Cu Kα radiation in the θ range 2–65°. Accurate unit cell dimensions were obtained using 25 arbitrarily chosen high order reflections (θ of 28–30°). After correcting for Lorentz and polarization factors, the intensities were corrected for absorption using the empirical absorption correction method [17] with three reflections near $\chi = 90°$. The structure was solved by Multan using the programme Multan

82 [18], which gave the positions of the metal and phosphorus atoms unambiguously and the structure was developed by alternated least-squares refinement and difference Fourier maps. Hydrogen atoms of the phenyl rings and methylene group could be generated by stereochemical constraints. Anisotropic refinement of non-hydrogen atoms by block-diagonal matrix and hydrogen held fixed by stereochemical constraints or in positions in the difference maps, with a unit weighting scheme and Dunitz–Seiler factor [19] yielded to convergence. The scattering factors for Cu, Cl, P, C, N and O were from the International Tables of Crystallography [20] while those of hydrogen were from Stewart *et al.* [21]. All the computations were carried out using the SDP package of the Enraf-Nonius system available with PDP-11/73 [22]. (For a relevant crystallographic data collection and structure solution parameters see Table 5.)

Results and discussion

The reaction of $CuCl_2 \cdot 2H_2O$, $[Cu(NCCH_3)_4](ClO_4)_2$, $CuSO_4 \cdot 5H_2O$ and $Cu(CH_3COO)_2 \cdot H_2O$ with the ligands BDPE and BDPX in 2:1 mole ratio in acetonitrile/acetone under reflux condition in argon atmosphere resulted in the formation of the dinuclear Cu(I) complexes **1**–**8** as shown in Scheme 1. The Cu(I) complexes are colorless, diamagnetic with no d–d band in the visible region of the electronic spectra (d^{10} configuration). The ligands BDPE and BDPX which contain tertiary phosphine reduced Cu(II) to Cu(I) under the reaction conditions. Similar observations were reported by others for mono- and bidentate tertiary phosphine ligands [15, 23].

Elemental analysis of the complexes are presented in Table 1. Selected IR bands and conductivity data are shown in Table 2. Tables 3 and 4 provided ^1H, ^{13}C and ^{31}P NMR spectral data.

On comparing ^1H and ^{13}C NMR spectral data of the ligands with their complexes it may be noted that the resonances of protons and carbons of x-CH_2 (CH_2 adjacent to PPh_2) are shifted to lower field by $\delta 0.20$–0.37 and $\delta 0.64$–2.64, respectively. This low field shifting of protons and carbons is due to coordination of PPh_2 to Cu(I). Similar notable deshielding of protons and carbons for y-CH_2 (CH_2 adjacent to nitrogen atom of the bridge $N-CH_2-CH_2-P$) and z-CH_2 (CH_2 of $N-CH_2-CH_2-N$ bridge for BDPE and benzyl CH_2 of BDPX) was observed for complexes **2**–**6**, which indicates that the nitrogen atoms of the ligands in these complexes are coordinated to Cu(I). For complexes **1**, **7** and **8** ^1H and ^{13}C resonances of y-CH_2 and z-CH_2 are not deshielded significantly, indicating nitrogen atoms in these complexes are not involved in coordination. The ^1H NMR spectrum of complex **1** exhibits three additional singlets (apart from peaks due to ligand) at $\delta 2.80$, $\delta 2.88$ and $\delta 7.94$. The first two peaks may be assigned to CH_3 protons and the last one to the CHO proton of two DMF molecules. The ^{13}C NMR spectrum of complex **1** gave resonances at $\delta 30.48$ and $\delta 35.34$ as singlet for CH_3 carbons and a singlet at $\delta 161.7$ for CHO carbon of DMF molecules.

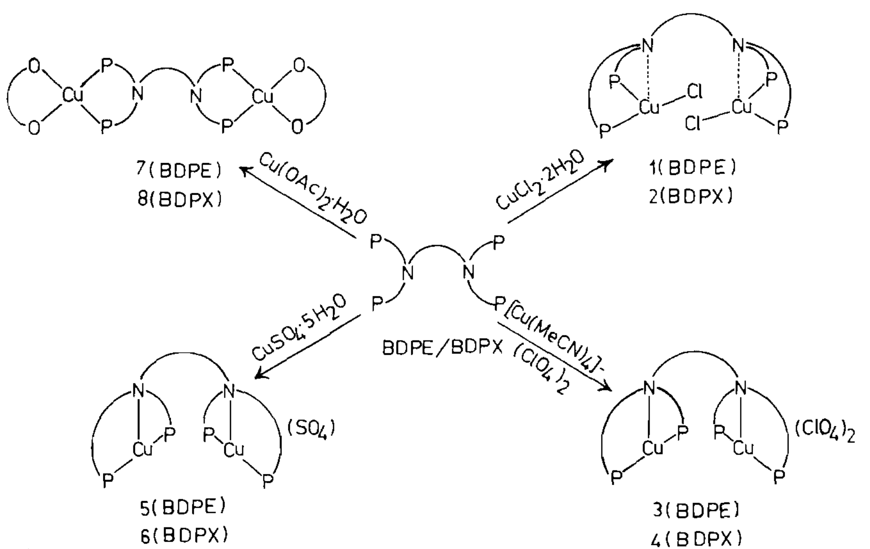
The ^1H NMR spectra of **7** and **8** exhibit singlets at $\delta 2.22$ and $\delta 2.19$, respectively, in addition to the ligand peaks, assigned to CH_3 protons of the acetate anion [13]. In ^{13}C NMR spectra CH_3 and COO carbons of the acetate anion appeared at $\delta 22.77$ and $\delta 203.84$ for **7** and at $\delta 23.81$ and $\delta 203.30$ for **8**, respectively.

The ^{31}P NMR spectra of the complexes are extremely useful for geometrical assignment. Complexes **1** and **2** show singlets at δ -17.50 and δ -17.62, respectively. The appearance of a singlet indicates the equivalence of phosphorus atoms coordinated to Cu(I). Conductivity data of **1** and **2** correspond to a non-electrolyte which indicates that the chloride ions are bonded to the Cu atom.

The IR spectra exhibit bands at 470 and 360 cm^{-1} for **1** and at 485 and 362 cm^{-1} for **2**, the higher frequency band may be assigned to $\nu(Cu-P)$ and the other one is due to $\nu(Cu-Cl)$

TABLE 1. Analytical data for Cu(I) complexes

Complex	Found (%)			Calculated (%)		
	C	H	N	C	H	N
$[Cu_2(BDPE)Cl_2] \cdot 2DMF$ (**1**)	61.12	6.02	4.31	61.34	5.91	4.47
$[Cu_2(BDPX)Cl_2]$ (**2**)	64.63	5.52	2.19	64.97	5.41	2.37
$[Cu_2(BDPE)](ClO_4)_2$ (**3**)	56.18	4.72	2.16	56.40	4.86	2.27
$[Cu_2(BDPX)](ClO_4)_2$ (**4**)	58.48	4.94	2.06	58.63	4.89	2.14
$[Cu_2(BDPE)](SO_4)$ (**5**)	61.38	5.20	2.26	61.54	5.31	2.48
$[Cu_2(BDPX)](SO_4)$ (**6**)	63.49	5.17	2.15	63.63	5.30	2.32
$[Cu_2(BDPE)(CH_3COO)_2]$ (**7**)	64.37	5.63	2.21	64.53	5.72	2.43
$[Cu_2(BDPX)(CH_3COO)_2]$ (**8**)	66.16	5.87	2.12	66.40	5.70	2.28



Scheme 1.

TABLE 2. Selected IR bands and conductivity data for Cu(I) complexes

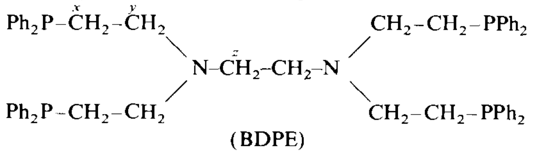
Complex	IR data (cm^{-1})[a]	Conductivity		
		Solvent	Λ_M (Ω^{-1} cm^2 mol^{-1})	Comment
$[Cu_2(BDPE)Cl_2]\cdot DMF$ (**1**)	1675s(ν(C=O))[b]; 470m(ν(Cu–P); 360m(ν(Cu–Cl))	DMF	4	Non-electrolyte
$[Cu_2(BDPX)Cl_2]$ (**2**)	485m(ν(Cu–P)); 362m(ν(Cu–Cl))	DMF	6	Non-electrolyte
$[Cu_2(BDPE)](ClO_4)_2$ (**3**)	1100br($\nu_3[ClO_4]$); 625m($\nu_4[ClO_4^-]$); 478m(ν(Cu–P))	CH_3CN	238	1:2 electrolyte
$[Cu_2(BDPX)](ClO_4)_2$ (**4**)	1100br($\nu_3[ClO_4^-]$); 625m($\nu_4[ClO_4^-]$) 478m(ν(Cu–P))	CH_3CN	226	1:2 electrolyte
$[Cu_2(BDPE)](SO_4)$ (**5**)	1120br($\nu_3[SO_4^{2-}]$); 620m($\nu_4[SO_4^{2-}]$) 478 m(ν(Cu–P))	CH_3CN	146	1:1 electrolyte
$[Cu_2(BDPX)](SO_4)$ (**6**)	1120br($\nu_3[SO_4^{2-}]$); 622m($\nu_4[SO_4^{2-}]$) 478 m(ν(Cu–P)	CH_3CN	134	1:1 electrolyte
$[Cu_2(BDPE)(CH_3COO)_2]$ (**7**)	1600s(ν_{as}[COO]); 1410m(ν_s[COO]); 480m(ν(Cu–P)); 272m(ν(Cu–O))	CH_3CN	8	Non-electrolyte
$[Cu_2(BDPX)(CH_3COO)_2]$ (**8**)	1600s(ν_{as}[COO]); 1410m(ν_s[COO]); 480m(ν(Cu–P)); 272m(ν(Cu–O))	CH_3CN	7	Non-electrolyte

[a] KBr pellets, [b] C=O of DMF, s = strong, m = medium, br = broad.

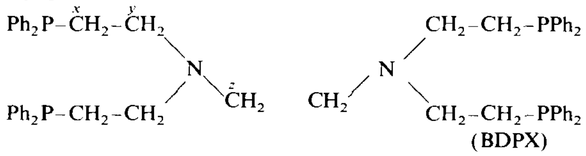
TABLE 3. ^1H NMR spectral data for the ligands and their Cu(I) complexes

Compound	Solvent	Chemical shift (δ)[a]				
		x-CH_2[b]	y-CH_2	z-CH_2	Ph[c]	Others
BDPE	$CDCl_3$	1.88m	2.22m	2.37s	7.16	
BDPX	$CDCl_3$	2.09m	2.56m	3.52s	7.14; 7.27	
1	CD_2Cl_2	2.22m	2.30m	2.40s	7.28; 7.56	2.80s[d], 2.88s[d]; 7.94s[e]
2	$CDCl_3$	2.30m	2.72m	4.09s	7.20; 7.57	
3	DMSO-d_6	2.25 m	2.41m	2.63s	7.25; 7.42	
4	DMSO-d_6	2.34m	2.74m	3.88s	7.27; 7.45	
5	DMSO-d_6	2.16m	2.53m	2.60s	7.28; 7.49	
6	DMSO-d_6	2.29m	2.78m	3.82s	7.26; 7.45	
7	$CDCl_3$	2.18m	2.21m	2.42s	7.26; 7.52	2.22s[f]
8	$CDCl_3$	2.30m	2.52m	3.62s	7.26; 7.45	2.19s[f]

[a] Relative to tetramethylsilane; m = multiplet, s = singlet. [b] See below for labelling, [c] Phenyl protons are not well resolved. [d] Due to methyl protons of DMF. [e] CH proton of DMF. [f] Due to methyl protons of acetate ion.



(BDPE)



(BDPX)

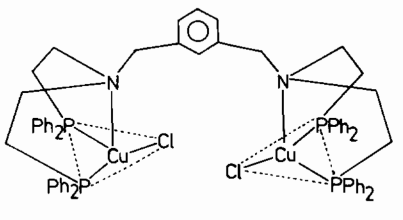
TABLE 4. $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectral data for the ligands and their complexes

Compound	Solvent	$^{13}C\{^1H\}$ NMR data: chemical shift (δ)[a]					$^{31}P\{^1H\}$ NMR data: chemical shift (δ)[b]
		x-CH_2[c]	y-CH_2	z-CH_2	Ph	Others	
BDPE	$CHCl_3$	25.57d[d]	50.33d[e]	52.06s	128.85–138.84		−19.01s
BDPX	$CHCl_3$	25.92d[f]	49.98d[g]	58.58s	127.98–139.14		−20.89s
1	$CHCl_3$	28.12	50.40	52.12	128.78–138.20	30.48s, 35.34s[h], 161.7s[i]	−17.50s
2	$CHCl_3$	28.56	50.88	59.63	127.88–134.70		−17.62s
3	CH_3CN	26.48	50.85	53.29	128.65–138.21		−12.47s
4	CH_3CN	26.57	51.45	59.74	127.95–138.11		−12.11s
5	CH_3CN	26.45	51.04	53.19	128.75–138.25		−12.47s
6	CH_3CN	26.56	50.80	59.89	128.75–138.21		−12.05s
7	$CHCl_3$	27.56	50.45	52.17	129.0–138.32	22.77s[j], 203.84s[k]	−15.92 s
8	$CHCl_3$	27.83	49.85	59.06	127.99–138.64	23.81s[j], 203.30s[k]	−16.07s

[a]Relative to teramethylsilane; d = doublet, s = singlet. [b]Relative to 85% H_3PO_4. [c]See Table 3 for labelling of CH_2. [d]$J_{c\text{-}p}$ = 13.43 Hz, [e]$J_{c\text{-}p}$ = 23.20 Hz. [f]$J_{c\text{-}p}$ = 12.2 Hz, [g]$J_{c\text{-}p}$ = 23.2 Hz, [h]Due to CH_3 of DMF. [i]Due to CHO of DMF. [j]Due to CH_3 of acetate anion. [k]Due to COO of acetate anion.

[24]. ^1H and ^{13}C NMR spectral data of **1** and **2** show nitrogen atoms of the ligand may be coordinated to Cu(I) in complex **2** but not in complex **1**. The above data therefore suggest a tricoordinated dinuclear structure for **1** in which the Cu ions are equivalent and possess PPCl coordination sites. Complex **2** has a tetracoordinated dinuclear structure with an NPPCl core for each Cu(I). The molecular structure of **1** is established from the single crystal X-ray diffraction method.

The difference in coordination in complexes **1** and **2** is not surprising. However, in complex **1** the Cu–N distance of 2.733(6) Å is not too long (see structure analysis) and may be considered as a weak interaction [25]. The molecular model of complex **2** with two PNP coordination sets of the ligand BDPX, separated by a *m*-xylyl moiety, shows that the nitrogen atom is in a favourable position to coordinate to Cu(I) through the apical position resulting in a trigonal pyramidal geometry as shown in structure **3**.



3

The ^{31}P NMR spectra of complexes **3**–**6** are similar and exhibit singlets of δ −12.47, δ −12.11, δ −12.47 and δ −12.05, respectively in acetonitrile. Conductivity measurements indicate that the anions, viz. ClO_4^- of **3** and **4** and SO_4^{2-} of **5** and **6** are not involved in coordination to Cu(I) (Table 2). This is confirmed in complexes **3** and **4** by IR bands (ν_3) centering at 1100 cm^{-1} and a sharp band (ν_4) at 625 cm^{-1}, which may be assigned to uncoordinated ClO_4^- [26]. The IR spectra of **5** and **6** also exhibit ν_3 and ν_4 frequencies at 1120 and 620 cm^{-1}, respectively, for uncoordinated SO_4^{2-} with *Td* symmetry [27]. In IR spectra ν(Cu–P) of these complexes appear at 478 cm^{-2}. The above results and ^1H and ^{13}C NMR spectral data are consistent with a tricoordinated dinuclear structure for **3**–**6** in which both the Cu ions are ligated to two phosphorus and nitrogen atoms of the ligand as shown in Scheme 1. A low-field shift of the ^{31}P resonance in complexes **3**–**6** compared to **1** and **2** may be due to the fact that in the absence of chloride ions in **3**–**6** the Cu–P bond is stronger compared to that of **1** and **2**.

The ^{31}P NMR spectra of complexes **7** and **8** show a singlet at δ −15.92 and at δ −16.07, respectively, indicating the equivalence of phosphorus atoms in each compound. Conductivity measurements show **7** and **8** to be non-electrolyte confirming the coordination of acetate ions to Cu(I) in these complexes. The IR spectra exhibit ν(Cu–P) at 480 cm^{-1} and the coordination of acetate ion is indicated by three bands at 1600, 1410 and 272 cm^{-1} which are assigned to $\nu_{as}(COO^-)$, $\nu_s(COO^-)$ and ν(Cu–O), respectively, for a bidentate coordination of acetate ion [13]. The above results together with ^{1}H and ^{13}C NMR data suggest a tetracoordinated dinuclear structure for **7** and **8** with a PPOO core for each Cu ion as shown in Scheme 1.

The ligands BDPE and BDPX confer variable geometry on coordinated Cu(I) varying from three to four coordinate depending on weak/strong coordination, respectively, of the nitrogen atom of the PNP group of the hexadentate ligands. Leaving the two P atoms that are strongly coordinated to Cu(I) the other two positions seem to be labile and can be substituted by Cl$^-$ or by bidentate CH_3COO^-. The Cu(I) ions thus seem to have low nucleophilicity in these complexes. The special features of the hexadentate bimetallic ligands BDPE and BDPX thus seem to stabilize Cu(I) with labile coordination to negative groups.

Structure of complex 1

The ORTEP diagram (DMF molecules omitted for clarity) and the packing of the unit cell in complex **1** are shown in Figs. 1 and 2, respectively. A summary of crystal and refinement data is given in Table 5. The final positional parameters are listed in Table 6; bond lengths and angles are shown in Tables 7 and 8, respectively.

The crystal structure analysis shows that the complex contains a crystallographic centre of symmetry, which is located at the middle point of the C17–C17′ bond, thus dividing the molecule into identical halves. Each identical Cu(I) atom ligates to two phosphorus atoms of the PPh_2 group and a chloride ion and the geometry is essentially trigonal planar. The three angles around Cu(I) atom deviate somewhat (5.75°) from the idealized value of 120°, which could be attributed to the different surroundings of P and Cl atoms. The angle P1–Cu–P20 of 123.85(5)° is the largest of the three and this is due to steric overcrowding of two adjacent bulky PPh_2 groups coordinated to Cu(I). The Cu atom is displaced

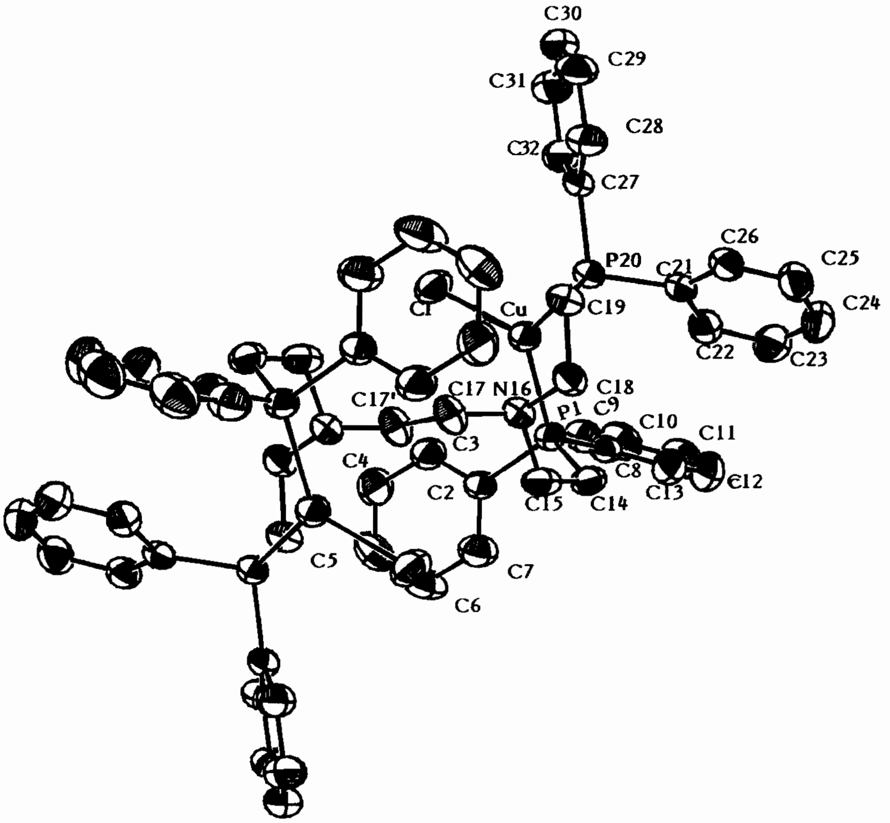


Fig. 1. ORTEP diagram of complex **1**, $[Cu_2(BDPE)Cl_2]$, showing the atom labelling scheme (DMF molecules are omitted for clarity).

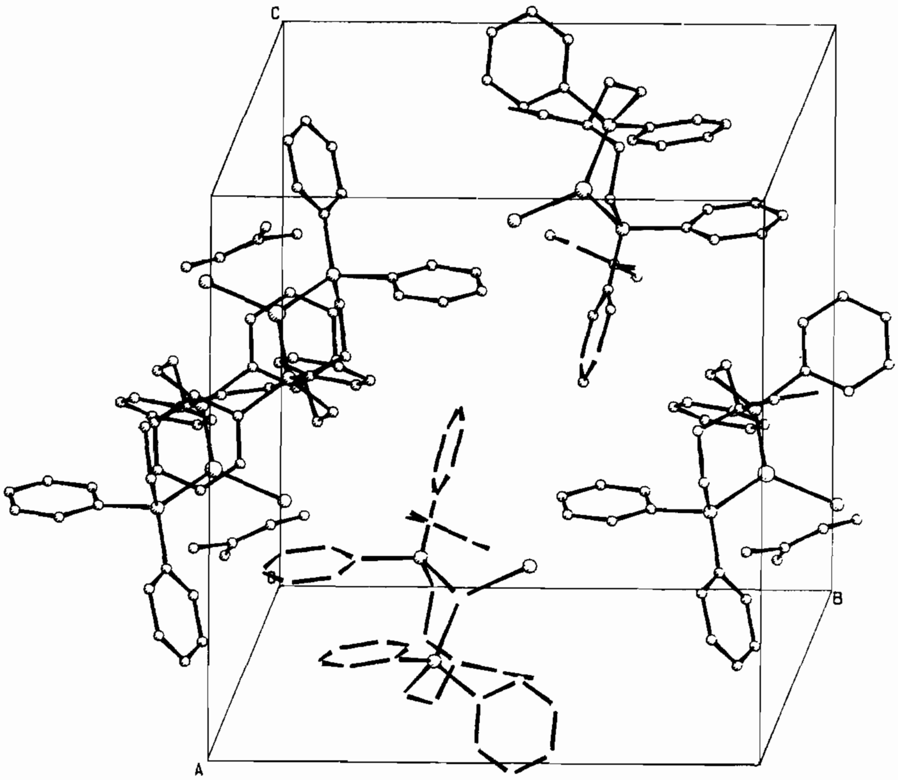


Fig. 2. A view (projected down *a* axis) of complex **1**, $[Cu_2(BDPE)Cl_2]\cdot 2DMF$, showing the crystal packing.

TABLE 5. Crystallographic data for complex **1**

Empirical formula	$C_{64}H_{74}Cu_2Cl_2N_4O_2P_4$
Formula weight	1252
Space group	$P2_1/c$(monoclinic)
a (Å)	12.860(1)
b (Å)	16.104(1)
c (Å)	16.274(1)
β (°)	113.24(1)
V (Å³)	3097.2(6)
Z	2
D_{calc} (g/cm³)	1.342
Crystal dimension (mm)	0.12 × 0.27 × 0.30
Radiation (*λ*, Å)	Cu *Kα* (1.54184)
μ (cm⁻¹)	55.378
Temperature (°C)	25
Reflections collected	5086
Reflections used in refinement ($I > 3\sigma(I)$)	3968
Parameters refined	427
R	0.039
R_w	0.041

only by the 0.011 Å from the plane defined by chloride and two phosphorus atoms. The nitrogen atom of the ligand though in a favourable position to coordinate, does not do so, but the Cu–N distance of 2.733(6) Å nevertheless indicates a moderately strong interaction between them [22].

The Cu–P bond distances of 2.235(1) Å and Cu–Cl bond distance of 2.237(1) Å are compara-

TABLE 6. Positional parameters and their e.s.d.s for complex **1**

Atom	*x*	*y*	*z*	*B* (Å²)
Cu	0.70251(5)	0.08203(4)	0.70130(4)	3.26(2)
Cl	0.7158(1)	−0.04479(7)	0.76074(8)	4.77(4)
P1	0.79663(9)	0.11687(6)	0.61660(7)	3.02(3)
P20	0.59070(8)	0.16916(6)	0.73600(6)	2.81(2)
033	0.1089(5)	0.5294(4)	0.4098(4)	10.9(2)
N16	0.5374(3)	0.1109(2)	0.5358(2)	3.08(8)
N35	0.0558(4)	0.4062(3)	0.4433(3)	6.0(1)
C2	0.8290(3)	0.0291(2)	0.5590(3)	3.2(1)
C3	0.8486(4)	−0.0470(3)	0.6010(3)	4.6(1)
C4	0.8741(5)	−0.1160(3)	0.5609(4)	5.7(2)
C5	0.8804(5)	−0.1079(3)	0.4789(4)	5.6(2)
C6	0.8610(5)	−0.0329(3)	0.4369(3)	5.7(2)
C7	0.8363(4)	0.0359(3)	0.4768(3)	4.7(1)
C8	0.9309(3)	0.1727(3)	0.6623(3)	3.3(1)
C9	1.0259(4)	0.1289(3)	0.7149(3)	4.4(1)
C10	1.1306(4)	0.1679(3)	0.7562(3)	5.3(2)
C11	1.1392(4)	0.2514(4)	0.7437(4)	5.7(2)
C12	1.0457(5)	0.2959(3)	0.6912(4)	5.7(2)
C13	0.9421(4)	0.2572(3)	0.6509(3)	4.6(1)
C14	0.7040(4)	0.1846(3)	0.5279(3)	3.6(1)
C15	0.5908(4)	0.1418(3)	0.4755(3)	3.9(1)
C17	0.4650(3)	0.0387(3)	0.4958(3)	3.7(1)
C18	0.4705(3)	0.1773(2)	0.5540(3)	3.3(1)
C19	0.4534(3)	0.1628(3)	0.6407(2)	3.3(1)
C21	0.6209(3)	0.2805(2)	0.7414(2)	3.0(1)
C22	0.7252(4)	0.3052(3)	0.7421(3)	3.9(1)
C23	0.7486(4)	0.3884(3)	0.7381(3)	4.9(1)
C24	0.6688(5)	0.4478(3)	0.7341(3)	5.1(2)
C25	0.5667(4)	0.4241(3)	0.7349(3)	4.6(1)

TABLE 6. (*continued*)

Atom	x	y	z	B (Å^2)
C26	0.5426(4)	0.3410(3)	0.7388(3)	3.7(1)
C27	0.5576(3)	0.1469(2)	0.8333(3)	3.0(1)
C28	0.4537(4)	0.1650(3)	0.8368(3)	4.0(1)
C29	0.4356(4)	0.1449(3)	0.9137(3)	4.6(1)
C30	0.5185(4)	0.1082(3)	0.9849(3)	4.6(1)
C31	0.6213(4)	0.0902(3)	0.9821(3)	4.8(1)
C32	0.6405(4)	0.1090(3)	0.9055(3)	3.9(1)
C34	0.0351(6)	0.4783(4)	0.4033(5)	8.0(2)
C36	0.1663(6)	0.3788(5)	0.4996(5)	8.4(2)
C37	−0.0356(6)	0.3478(5)	0.4239(5)	9.0(3)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)D(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

TABLE 7. Bond distances (Å) in complex **1**[a]

Cu–Cl	2.237(1)
Cu–P1	2.235(1)
Cu–P20	2.235(1)
P1–C2	1.832(5)
P1–C8	1.825(4)
P1–C14	1.827(4)
P20–C19	1.837(3)
P20–C21	1.829(4)
P20–C27	1.830(5)
O33–C34	1.23(1)
N16–C15	1.487(6)
N16–C17	1.472(5)
N16–C18	1.475(6)
N35–C34	1.305(8)
N35–C36	1.424(8)
N35–C37	1.45(1)
C2–C3	1.377(7)
C2–C7	1.382(7)
C3–C4	1.391(8)
C4–C5	1.375(9)
C5–C6	1.362(8)
C6–C7	1.383(8)
C8–C9	1.377(5)
C8–C13	1.390(6)
C9–C10	1.395(6)
C10–C11	1.371(8)
C11–C12	1.371(7)
C12–C13	1.380(7)
C14–C15	1.530(6)
C17–C17	1.513(6)
C18–C19	1.529(6)
C21–C22	1.395(7)
C21–C26	1.389(6)
C22–C23	1.381(7)
C23–C24	1.384(8)
C24–C25	1.372(8)
C25–C26	1.382(6)
C27–C28	1.390(7)
C27–C32	1.379(5)
C28–C29	1.398(7)
C29–C30	1.361(6)
C30–C31	1.372(8)
C31–C32	1.396(7)

[a]Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE 8. Bond angles (°) for complex **1**[a]

Cl–Cu–P1	121.89(6)
Cl–Cu–P20	114.25(6)
P1–Cu–P20	123.85(5)
Cu–P1–C2	114.2(2)
Cu–P1–C8	121.8(2)
Cu–P1–C14	107.1(2)
C2–P1–C8	102.7(3)
C2–P1–C14	105.4(2)
C8–P1–C14	104.3(2)
Cu–P20–C19	104.6(1)
Cu–P20–C21	118.9(2)
Cu–P20–C27	119.2(1)
C19–P20–C21	102.2(2)
C19–P20–C27	104.2(2)
C21–P20–C27	105.6(2)
N35–O33–C34	29.1(3)
C15–N16–C17	110.5(3)
C15–N16–C18	110.3(3)
C17–N16–C18	110.1(3)
C34–N35–C36	123.6(6)
C34–N35–C37	118.9(5)
C36–N35–C37	117.4(5)
P1–C2–C3	117.8(4)
P1–C2–C7	123.4(3)
C3–C2–C7	118.8(4)
C2–C3–C4	120.6(5)
C3–C4–C5	119.6(5)
C4–C5–C6	120.2(5)
C5–C6–C7	120.3(5)
C2–C7–C6	120.5(4)
P1–C8–C9	117.8(3)
P1–C8–C13	124.0(3)
C9–C8–C13	118.1(4)
C8–C9–C10	121.4(4)
C9–C10–C11	119.4(4)
C10–C11–C12	120.1(5)
C11–C12–C13	120.4(5)
C8–C13–C12	120.7(4)
P1–C14–C15	110.6(3)
N16–C15–C14	111.7(3)
N16–C17–C17′	111.2(3)
N16–C18–C19	112.5(3)
P20–C19–C18	109.3(3)
P20–C21–C22	117.7(3)
P20–C21–C26	123.3(3)
C22–C21–C26	118.9(4)
C21–C22–C23	120.3(4)
C22–C23–C24	120.1(5)
C23–C24–C25	120.2(4)
C24–C25–C26	120.1(5)
C21–C26–C25	120.5(5)
P20–C27–C28	123.3(3)
P20–C27–C32	117.3(4)
C28–C27–C32	119.4(4)
C27–C28–C29	119.4(4)
C28–C29–C30	120.7(5)
C29–C30–C31	120.3(6)
C30–C31–C32	119.7(4)
C27–C32–C31	120.6(5)
O33–C34–N35	123.7(6)

[a]Numbers in parentheses are e.s.d.s in the least significant digits.

ble to the other reported values [1, 8, 10, 24]. The interatomic distances (Table 7) and angles (Table 8) within the ligand moiety are consistent with those commonly found in similar compounds [1, 8, 10, 24]. The phenyl rings are remarkably planar, the maximum deviation from the mean place being 0.009(4) Å. The phenyl rings attached to P1 lie more or less perpendicular (interplanar angle of 95.02(1)°), whereas the phenyl rings attached to P20 lie at an angle of 65.2(2)°.

A view of the molecular packing down the *A* axis is shown in Fig. 2. An inspection of the intermolecular distances below 4 Å between the phenyl rings shows that these tend to pack rather in a random fashion and the interactions between them are of the van der Waals type. The DMF molecule is wedged between layers of the complex occupying interstitial positions. The molecule has no short intermolecular contact less than 3.358 Å and hence the structure is held in space by van der Waals contacts.

Supplementary material

Supplementary Tables S1–S6 (anisotropic thermal parameters of non-hydrogen atoms, torsional angles in the molecule, positional and thermal parameters of hydrogen atoms, bond lengths and angles involving hydrogen atoms, least-squares planes and F_o, F_c list) are available from the authors on request.

References

1 (a) J. T. Gill, J. J. Mayerle, P. S. Welcker, D. F. Lewis, D. A. Ucko, D. J. Barton, D. Stowens and S. J. Lippard, *Inorg. Chem.*, *15* (1976) 1155, and refs. therein; (b) G. A. Bowmaker, J. C. Dyason, P. C. Healy, L. M. Engelhardt, C. Pakawatchai and A. H. White, *J. Chem. Soc., Dalton Trans.*, (1987) 1089; (c) P. F. Barron, J. C. Dyason and P. C. Healy, *J. Chem. Soc., Dalton Trans.*, (1987), 1099; (d) G. A. Bowmaker, B. W. Skelton, A. H. White and P. C. Healy, *J. Chem. Soc., Dalton Trans.*, (1988) 2825.

2 (a) B. Liaw, S. W. Orchard and C. Kutal, *Inorg. Chem.*, *27* (1988) 1311; (b) S. Sakaki, K. S. Hinokuma, S. Hashimoto and K. Ohkubo, *Inorg. Chem.*, *26* (1987) 1817.

3 (a) W. S. Mahoney and J. M. Stryker, *J. Am. Chem. Soc.*, *111* (1989) 8818; (b) W. S. Mahoney, D. M. Brestensky and J. M. Stryker, *J. Am. Chem. Soc.*, *110* (1988) 291.

4 C. Bianchini, C. A. Ghilardi, A. Meli, S. Midollini and A. Orlandini, *Inorg. Chem.*, *24* (1985) 924 and 932.

5 S. J. Lippard and J. J. Mayerle, *Inorg. Chem.*, *11* (1972) 753.

6 D. J. Fife, W. M. Moore and K. W. Morse, *Inorg. Chem.*, *23* (1984) 1684.

7 G. Zotti, Z. Zecchin and G. Pilloni, *J. Organomet. Chem.*, *246* (1983) 61.

8 V. G. Albano, P. L. Bellon and G. Ciani, *J. Chem. Soc., Dalton Trans.*, (1972) 1938.

9 N. Brescani, N. Morsich, G. Nardin and L. Randaccio, *Inorg. Chim. Acta.*, *10* (1974) L5.

10 G. Nardin, L. Randaccio and E. Zangrando, *J. Chem. Soc., Dalton Trans.*, (1975) 2566.

11 N. Marsich, G. Nardin and L. Randaccio, *J. Am. Chem. Soc.*, *95* (1973) 4053.

12 G. Nardin, A. Camus and L. Randaccio, *Inorg. Chim. Acta*, *12* (1975) 23.

13 D. A. Edwards and R. Richards, *J. Chem. Soc., Dalton Trans.*, (1975) 637.

14 A. P. Gaughan, R. F. Ziolo and Z. Dori, *Inorg. Chem.*, *10* (1971) 2776.

15 S. J. Berners-Price, R. K. Johnson, C. K. Mirabelli, L. F. Faucette, F. L. McCabe and P. J. Sadler, *Inorg. Chem. 26* (1987) 3383.

16 M. M. Taqui Khan, P. Paul, K. Venkatasubramanian and S. Purohit, *J. Chem. Soc., Dalton Trans.*, accepted for publication.

17 A. C. T. North, D. C. Philips and F. S. Mathews, *Acta Crystallogr., Sec. A*, *24* (1968) 351.

18 P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq and M. M. Woolfson, *MULTAN 82*, a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data, Universities of York, U.K., and Louvain, Belgium, 1982.

19 J. D. Dunitz and P. Seiler, *Acta Crystallogr., Sect. B*, *29* (1973) 589.

20 *International Tables for Crystallography*, Vol. IV, Reidel, Dordrecht, The Netherlands, 1983.

21 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, *42* (1965) 3175.

22 *S. D. P. Structure Determination Package*, Enraf-Nonius, Delft, The Netherlands, 1986.

23 S. J. Lippard and D. A. Ucko, *Inorg. Chem.*, *7* (1968) 1051.

24 G. A. Bowmaker, J. D. Cotton, P. C. Healy, J. D. Kildea, S. B. Silong, B. W. Skelton and A. H. White, *Inorg. Chem.*, *28* (1989) 1462.

25 G. P. Marianne, H. Choi, D. R. Chapman, R. Bau, V. McKee and C. A. Reed, *Inorg. Chem.*, *29* (1990) 110.

26 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1963, p. 107.

27 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1963, p. 161.