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Binuclear copper(I) complexes containing bis(diphenylphosphino)methane bridging ligands. X-ray crystal structure of $[Cu_2(dppm)_2(Py)_2(NO_3)](NO_3) \cdot CH_3OH$

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Abstract—Binuclear copper(I) complexes $[Cu(dppm)(phen)]_2(NO_3)_2$ (**1**), dppm = $Ph_2PCH_2PPh_2$, $[Cu(dppm)(2,2'\text{-bipy})]_2(NO_3)_2$(2), $[Cu_2(dppm)_2(C_7H_5O_4N)](NO_3)_2$(3), $C_7H_5O_4N$ = pyridine-2,6-dicarboxylic acid, $[Cu_2(dppm)_2(Py)_2(NO_3)](NO_3)CH_3OH$(4), Py = pyridine have been synthesized by ligand reduction of cupric nitrate with dppm and characterized by specific elemental analyses, molecular weight determination, t.g., and ^{31}PNMR; their electronic conductivities and c.v. waves have also been measured. The X-ray crystal structure of complex (**4**) shows that dppm coordinates as a bridging bidentate ligand to the Cu^I atoms, and NO_3 behaves as a bidentate ligand or free ion in these new binuclear $copper^I$ complexes. © 1997 Elsevier Science Ltd

Keywords: copper; dppm; py; complex; binuclear; reduction.

Copper(I) displays wide diversity in its structural chemistry, the copper coordination number ranging from 2 to 4. Procedures to synthesize copper(I) complexes are of great interest because of the diversity of products resulting from almost the same methodology. In order to imitate the structure and functions of the active center of oxydase which contains mono- and divalent copper complexes, artificial systems should be developed. Coordination compounds with latent biological significance or with novel structures should be prepared. Binuclear copper(I) complexes containing bidentate bridging ligands have been the focus of much investigation in the last few years. It has been pointed out and confirmed that the four-electron-donor diphosphine ligand $Ph_2PCH_2PPh_2$ (dppm) is a very efficient bridging bidentate ligand [1]. Many examples of binuclear complexes containing the eight-membered ring $M(\mu\text{-dppm})M'$ are known with a variety of metals, oxidation and stereochemistries [1]. In general, this has consisted of *trans*-bound, bridging dppm ligands to give a planar M_2P_4 core structure with the two metal atoms held in close proximity to each other (regardless of whether a metal–metal bond is present or not). This feature is presumably one of the chief reasons for the unusual bonding, reactivity, and catalytic properties of $M_2(dppm)_2$ compounds [2–4].

Copper(I) complexes can be obtained directly from copper(II) compounds by ligand reduction, the most important fact in this procedure is that there must be an excess of ligand to stabilize the state of the resulting copper(I). In the present paper we describe an easy way to synthesize copper(I) complexes using the diphosphine ligand, dppm, as ligand reductant, where dppm, acting as a bridging ligand, forms binuclear complexes. Structural results allowed us to interpret some solution properties of the dppm derivatives, such as molecular weight and conductivity measurements.

EXPERIMENTAL

General considerations

All reactions were carried out under N_2 using standard Schlenk techniques. Commercially available purest samples of various chemicals were used for the

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preparation of the complexes. All solvents were dried by standard methods and distilled under nitrogen prior to use. The ligand dppm was prepared by a advanced method. Elemental analysis were performed on an ERBA-1106 instrument (Italy). Cu and the P content were determined using a JA96-970 spectrometer. Molecular weight determinations were made on $CHCl_3$ solutions at 25° using CORONA-117 analyser (American instrument). IR spectra were recorded on a Nicolet 170SX IR spectrophotometer. TG-DTA spectra were recorded on a PE-TGS-2 instrument. Conductivity measurements were carried out in MeOH solutions thermostatted at 25° using a Shanghai DDS-11A conductometer and DJS-1 type platinum black electrode. Melting points were determined on an Electrothermal apparatus and are uncorrected. Room temperature ^{31}P NMR. spectra were taken on a DPX-400 NMR spectrometer.

^{31}P NMR. spectra were measured in $CDCl_3$ with 85% H_3PO_4 as external reference. Cyclic voltammograms were obtained in CH_2Cl_2 (0.1 MBu_4NClO_4) by using an MEC-12A analyzer and a conventional three-electrode system at 25°C. The platinum working electrode was in the form of a disc and used in a stationary mode, the auxiliary electrode was a platinum plate with an area of $2 \times 8mm^2$, the reference electrode was a saturated calomel electrode (SEC).

Synthesis of dppm

Li (1.88 g, 0.25 mol) was added to Ph_3P(32.8 g, 0.125 mol) dissolved in THF (150 cm^3) at room temperature. The resulting mixture was stirred for *ca* 20 h, then filtered to remove the excessive Li. Me_3CCl (10.3 g, 0.11 mol) was added to decompose PhLi. CH_2Cl_2 (0.06 mol) was added dropwise at 0°C, and the solvent was then removed *in vacuo* (50 mm Hg). The product was recrystallized from EtOH-THF. (Found, C: 78.0; H: 5.5; P: 15.8, $C_{25}H_{22}P_2$ Calc: C: 78.1, H: 5.7, P: 16.1%, M.p. = 120−122°C.[5])

$$Ph_3P + 2Li \rightarrow Ph_2PLi + PhLi$$

$$Me_3CCl + PhLi \rightarrow Me_2C = CH_2 + LiCl + C_6H_6$$

$$Ph_2PLi + CH_2Cl_2 \rightarrow Ph_2PCH_2PPh_2 + 2LiCl$$

Synthesis of complexes

[Cu(dppm)(NO$_3$)]$_2$. Dppm (4 mmol) was added to hot EtOH (30 cm^3) to form a colorless solution. Then while heated and stirred, in the solution was added solid $Cu(NO_3)_2$. $3H_2O$ (2 mmol) during 30 min. The addition of the first portion of $Cu(NO_3)_2$. $3H_2O$ caused the colorless solution immediately turn to grey and then light yellow. The addition of the remaining $Cu(NO_3)_2 \cdot 3H_2O$ caused precipitation of a white powder. The mixture was stirred and heated at its reflux temperature for 30 min, then cooled, filtered out and washed with MeOH and Et_2O, then dried *in vacuo* at room temperature. Colorless cubic crystals were obtained by recrystallization of the product from CH_2Cl_2 and MeOH. (Yield: 75%)

[Cu(dppm)(phen)]$_2$(NO$_3$)$_2$ (**1**). To a suspension of $[Cu(dppm)(NO_3)]_2$ (1 mmol) in MeOH (25 cm^3) and benzene (20 cm^3), was added phen (2 mmol). The suspension was stirred for 6 h to give a yellow precipitate. The product was collected by filtration and washed with MeOH and Et_2O. The complex $[Cu(dppm)(bipy)]_2$ $(NO_3)_2$ (**2**), $[Cu_2(dppm)_2(Py)_2(NO_3)](NO_3)CH_3OH$ (**4**) was prepared by a similar method. Yield: 65–80%.

[Cu$_2$(dppm)$_2$(C$_7$H$_5$O$_4$N)](NO$_3$)$_2$ (**3**). Pyridine-2,6-dicarboxylic acid (1 mmol) was added to a suspension of $[Cu(dppm)(NO_3)]_2$ (1 mmol) in MeOH (35 cm^3). The mixture was stirred for 12 h at room temperature. Concentration of the resulting solution and addition of diethyl ether (20 cm^3) led to the precipitation of an orange yellow solid which was recrystallized from dichloromethane and THF and vacuum dried. Yield: 80%.

X-ray data collection and structure determination

A single crystal of dimensions (0.1 × 0.1 × 0.15 mm) of complex (**4**) was selected and mounted on an automatic Enraf–Nonius CAD-4 four-circle diffractometer equipped with a graphite monochromator and Mo-Kα radiator ($\lambda = 0.71073$ Å). Unit-cell dimensions and intensity data were measured at room temperature. Final unit cell dimensions, calculated from a least-squares treatment of the angles of 25 accurately centred reflections are given in Table 1. Reflections were collected using $\omega/2\theta$ scans (scan width $1.00+0.35 \tan \theta$), of which 3227 were considered unique and observed [$I \geqslant 3\sigma(I)$]. No significant change was detected in the intensity of the three standard reflections. Lorentz, polarization and absorption corrections were applied to the intensity data (empirical method, ψ-scan). The structure was solved by direct methods and Fourier syntheses. The structure was refined by the full-matrix least-squares method. Computations were performed using the SPD program on a *P2P*11/44 computer. Details of the crystal data and intensity collection are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

RESULTS AND DISCUSSION

According to colour changes correlative with the procedure for preparing complex $[Cu(dppm)(NO_3)]_2$, cupric nitrate has been reduced by the diphosphine dppm to form a white copper(I) complex. What is more interesting is that the weakly bonded nitrate ligand in the complex $[Cu(dppm)(NO_3)]_2$ can be easily replaced by other ligands through ligand substitution to form various copper(I) complexes with different

Table 1. Crystallographic data and structure refinement

Empirical formula	$C_{61}H_{58}N_4O_7P_4Cu_2$
Formula weight	1210
Crystal system	monoclinic
Space group	$P2_1$
Unit cell	$a = 13.650(4)$; $c = 13.653(2)$
dimensions (Å)	$b = 15.970(7)$; $\beta = 105.4(2)°$
V (Å^3)	2868.9
Z	2
F (000)	1252
$D_{calc.}$ (g cm^{-3})	1.373
Absorption coefficient (cm^{-1})	9.0
Reflections collected	5227
2θ Range (°)	$2 \leqslant 2\theta \leqslant 50$
Range of h, k, l	$+16$, $+19$, ± 16
Reflections observed [$I > 3.0\sigma(I)$]	3227
Solution	Direct methods
Weighting scheme	$w = s(F)^2 + 0.0003F^2$
Final R indices	$R = 0.026$, $Rw = 0.028$

Table 2. Selected bond lengths (Å) and angles (°) for (**4**)

Cu(1)—P(1)	2.251(1)	Cu(1)—P(2)	2.265(2)	Cu(1)—O(2)	2.183(5)
Cu(1)—N(2)	2.123(6)	Cu(2)—P(3)	2.253(1)	Cu(2)—P(4)	2.266(2)
Cu(2)—O(1)	2.173(5)	Cu(2)—N(1)	2.121(6)	Cu(1)—Cu(2)	3.652(10)
P(1)—C(2)	1.838(6)	P(1)—C(11)	1.808(7)	P(1)—C(21)	1.832(7)
P(2)—C(1)	1.839(7)	P(2)—C(31)	1.812(5)	P(2)—C(41)	1.843(7)
P(3)—C(2)	1.840(6)	P(3)—C(51)	1.810(7)	P(3)—C(61)	1.828(7)
P(4)—C(1)	1.840(7)	P(4)—C(71)	1.821(5)	P(4)—C(81)	1.853(7)
O(1)—N	1.234(8)	O(1′)—N′	1.250(10)	O(2)—N	1.234(8)
O(2′)—N′	1.215(12)	O(3)—N	1.229(7)	O(3′)—N′	1.221(12)
N(1)—C(91)	1.319(10)	N(1)—C(95)	1.344(9)		
P(1)—Cu(1)—P(2)	125.74(7)	P(1)—Cu(1)—O(2)	110.1(1)	P(1)—Cu(1)—N(2)	108.2(1)
P(2)—Cu(1)—O(2)	112.7(1)	P(2)—Cu(1)—N(2)	103.0(2)	O(2)—Cu(1)—N(2)	90.7(2)
P(3)—Cu(2)—P(4)	125.79(8)	P(3)—Cu(2)—O(1)	110.3(2)	P(3)—Cu(2)—N(1)	108.3(1)
P(4)—Cu(2)—O(1)	112.7(1)	P(4)—Cu(2)—N(1)	102.9(2)	O(1)—Cu(2)—N(1)	90.5(2)
Cu(1)—P(1)—C(2)	118.8(2)	Cu(1)—P(1)—C(11)	118.5(2)	Cu(1)—P(1)—C(21)	105.9(2)
Cu(1)—P(2)—C(1)	118.7(2)	Cu(1)—P(2)—C(31)	116.7(2)	Cu(1)—P(2)—C(41)	110.9(2)
Cu(2)—P(3)—C(2)	118.6(2)	Cu(2)—P(3)—C(51)	118.4(2)	Cu(2)—P(3)—C(61)	105.7(2)
Cu(2)—P(4)—C(1)	118.6(2)	Cu(2)—P(4)—C(71)	117.0(3)	Cu(2)—P(4)—C(81)	111.1(2)
Cu(2)—O(1)—N	130.7(5)	Cu(1)—O(2)—N	130.4(5)	O(1)—N—O(2)	121.6(5)
O(1)—N—O(3)	119.6(6)	O(2)—N—O(3)	118.8(6)	O(1′)—N′—O(2′)	119.4(8)
O(1′)—N′—O(3′)	120.6(8)	O(2′)—N′—O(3′)	119.9(9)	Cu(2)—N(1)—C(91)	119.2(5)
Cu(2)—N(1)—C(95)	122.8(5)	Cu(1)—N(2)—C(11)	119.4(5)	Cu(1)—N(2)—C(15)	122.6(5)

ligands (e.g. pyridine and phen). The compound $[Cu(dppm)(NO_3)]_2$ reacts with the ligand (2,2′-bipyridine, phen, pyridine-2,6-dicarboxylic acid and pyridine) at room temperature to give the complexes (**1**–**4**). The molecular weight determination strongly suggests that complexes (**1**–**4**) containing dppm, are binuclear. As a result of this ligand substitution, binuclear copper(I) complexes (**1**–**4**) can be obtained with high yields. The elemental analysis of four complexes agreed well with their formulation (Table 3). Conductance data (methanol solutions) show that the complexes belong to 1 : 2 electrolytes, confirming their binuclear nature and the bridging character of dppm [6]. All the complexes are obtained as air-stable solids in air, and soluble in organic polar solvents, such as CH_2Cl_2, DMF and $CHCl_3$. When melted in air, the complexes decomposed and turned blue.

IR data

The IR spectra (in CsI) of complex (**1**)–(**4**) exhibit the expected absorptions bands due to the dppm ligand, e.g.: (**1**), 1485s, 1186w, 1098m, 783m, 740s,

Table 3. Elemental analysis data of the complexes

Complex	C	H (calc. %)	N	P	Cu	M.p. (°C)	Λ^a	M	Colour
(1)	63.7	4.3	5.9	9.3	9.3	221	175	1376	yellow
	(64.4)	(4.4)	(6.1)	(9.0)	(9.2)			(1379)	
(2)	63.6	4.8	6.1	8.8	9.1	200	170	1334	yellow
	(63.1)	(4.5)	(6.3)	(9.3)	(9.5)			(1331)	
(3)	56.9	4.2	3.3	9.9	10.1	293	168	1183	orange
	(57.6)	(4.1)	(3.5)	(10.4)	(10.7)			(1186)	
(4)	60.9	4.9	5.0	9.8	10.2	163	165	1205	red
	(60.5)	(4.8)	(4.6)	(10.2)	(10.5)			(1209)	

[a] S cm^2 mol^{-1}.

718m, and 690s cm^{-1} [7]; **(4)**, 1481m, 1185w, 1095m, 781m, 738s, 719m, and 692 cm^{-1}. The band expected at $\approx$1385 cm^{-1} was not resolved in **(1)**, **(2)**, **(3)** and **(4)** due to the presence of the very intense nitrate band in the same region. Characteristic bands (NO_3) of the complexes are shown in Table 4. In the 1500–1700 cm^{-1} range, there the characteristic absorption bands characteristic of nitrate anion appear, exhibiting a broad band at *ca* 1380–1385 cm^{-1} [8]. The difference of the two highest bands in the complex **(4)** is 192 cm^{-1}. In the 1700–1800 cm^{-1} range, two couple of combination bands with a distance of 35 cm^{-1} appear. The above results suggest that there is bidentate NO_3^- in the complex **(4)** [9].

DTA-TG analysis

The results of the thermogravimetric analyses of the complexes, compared with those of free dppm, indicate that the thermal stability of dppm increases upon complexation. The TG-DTA thermogram of **(3)** reveals that the pyrolytic decomposition takes place in two steps. The first corresponds to a weight loss of 75.1% and is probably due to decomposition of the ligand dppm and pyridine-2,6-dicarboxylic acid (loss of weight calc. 78.8%) and is confirmed by a strong endothermic peak at 186-500°C. The second step in the 500–744°C range corresponds to, a pronounced weight loss due to the decomposition of the organic moiety, residue weight (exp. = 16.9%; calc. 13.5%), giving CuO as final residue. The DTA curve shows characteristic exothermic peaks at 500–744°C.

NMR spectra

In the ^{31}P NMR spectra of the complexes in $CDCl_3$, the corresponding phosphorus resonance shifted to higher field compared to that of free dppm ($\delta = -23$ ppm). The phosphorus of the coordinated dppm ligands appear only a single resonance [$\delta^{31}P = -8.3$ ppm **(1)**, -9.9 ppm **(2)**, -8.7 ppm **(3)**, -10.8 ppm **(4)**], showing that all the phosphorus atoms in each molecule are chemically equivalent.

UV–vis spectrum

The UV–vis spectra are complicated. Absorption peaks ($\lambda < 300$ nm) belong to π–π^* or n–π orbital transition of the ligands (Table 4). The wide band (460 nm) in the complex **(4)** belongs to the MLCT absorption bands ($d^{10} \rightarrow \pi^*$, metal-to-ligand charge transfer transition).

Compound **(4)** in methanol has three absorption peaks: 248 (phenyl), 268 (pyridine), 460 nm ($d^{10} \rightarrow \pi^*$, MLCT peak). The solution is orange yellow. The

Table 4. Absorption maxima, IR and cyclic voltammogram of the complexes

Compounds	λ max (nm)	I.r. (NO_3, cm^{-1})	Ep. a(ev)	Ep. c(ev)
phen	238, 265			
(1)	242, 267	1384, 1024, 845 (free ion)	0.76	0.37
bipy	280, 234, 198			
(2)	241, 282	1384, 1050, 830 (free ion)	0.5	0.28
L	272, 228			
(3)	264, 228	1382, 1038, 832 (free ion)	0.61	0.29
Py	256, 262, 268			
(4)	248, 268, 460	1382, 1035, 829	0.63	0.20

L = pyridine-2,6-dicarboxylic acid

absorption peak (460 nm) belongs to $d^{10} \rightarrow \pi^*$ orbital transition, because pyridine has a lower π^* antibonding orbital, electrons can transfer from d^{10} (T_{2g}) copper(I) orbital to the π^* antibonding empty orbital of the N coordination atom of pyridine (MLCT peak) [10]. This phenomenon is characteristic of copper(I) [10].

One-electron reversible redox waves were observed for the complexes. The fact that the oxidation potentials of the complexes (Table 4) are much more positive than that of free copper(I) suggests that it is much more difficult to oxidize copper(I) [11].

X-ray crystal structure of (**4**)

The molecular structure of (**4**) is depicted in Fig. 1. The solid-state consists of a neutral dimeric molecular unit with the two copper atoms bridged by a pair of dppm ligands. In addition, each copper atom is terminally bound by a single pyridine and nitrate anion in a bridged fashion. Two copper atoms are doubly bridged by two dppm ligands to form an eight-membered $Cu_2P_4C_2$ ring. The slightly distorted tetrahedral coordination around copper is completed by one nitrogen atom from the pyridine ligand and one oxygen atom from the nitrate ion. The Cu–P distances in (**4**) of 2.251(1) and 2.266(2) Å are in good agreement with the 2.240(6) and 2.249(6) Å range found in $[\{Cu(S_2CC_6H_4Me\text{-}o)(dppm)\}_2]$ [12]. The Cu–Cu separation of 3.652(10) Å is significantly longer than the range of copper-copper bond lengths [2.494(5)–2.674(5) Å] found in $H_6Cu_6(PPh_3)_6$. DMF [13], suggesting that the copper atoms in the present compound are not involved in metal–metal bonding interactions. The observed Cu–O distances of 2.173(5) Å is comparable to the values found for the nitrate in $CuNO_3\ (PPh_3)_2$ [14]. The N–O(3) distance (1.229(7) Å) in bridging NO_3 anion is shorter than N–O(1) (1.234(8) and N–O(2) (1.234(8)Å) distances because of the formation of Cu ← O(1) and Cu ← O(2) bonds. The bridging nitrate ligand is involved in the *anti–syn* bridge-bonding mode (Scheme 1) with the two copper atoms bound to different nitrate oxygen atoms. The P(1)—Cu—P(2) units are nonlinear and eclipsed, resulting in a folding of the Cu_2P_4 core along the Cu···Cu axis. The P(1)—Cu(1)—P(2) angle (125.74(7)° and the P(3)—Cu(2)—P(4) angle [125.79(8)°] are similar to the corresponding P(1)—Cu—P(2) angle of 119.9(1)° found in the related binuclear $(dppm)_2$ complex $[Cu(dppm)(MeCN)_2]_2\ (ClO_4)_2$ [15].

The torsion angles in the ring are P(2)—Cu(1)—P(1)—C(2) (47.0), P(2)—Cu(1)—P(1)—C(11) (175.7), P(2)—Cu(1)—P(1)—C(21) (−68.8) and P(1)—Cu(1)—P(2)—C(1) (−47.8°).

Thus, each copper atom is four-coordinate, with phosphorus atoms from each of two bridging dppm ligands occupying two of the coordination sites, the nitrate oxygen atom occupying the third and the nitrogen atom from pyridine occupying the fourth. Structural studies involving binuclear $(dppm)_2$ species of other transition metals (Mn^{16}, Mo^{17}) have been much less frequent but, in general, also reveal the common trans binding of the two dppm ligands, linear P—M—P fragments, and planar M_2P_4 skeletal units. For the d^{10} complexes, however, the P—M—P units are distinctly nonlinear. X-ray structural characterization of the complex $[Cu_2(dppm)_2(Py)_2(NO_3)](NO_3)CH_3OH$, reported here, clearly reveals that the P—M—P angles in $(dppm)_2$ compounds are not restricted by steric crowding of the dppm phenyl rings. The P—Cu—P angles in (**4**), in particular, are much more bent (125.7°) than the corresponding P—M—P values found in $[Au(dppm)Cl]_2$ [18].

In summary, the doubly bridged bis(diphenylphosphine)methane complex $[Cu_2(dppm)_2(Py)_2$

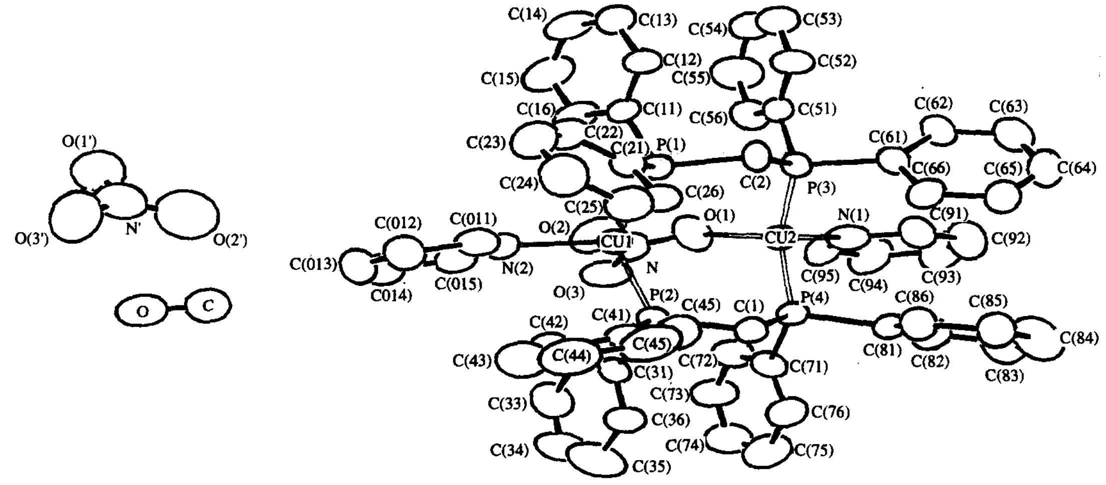
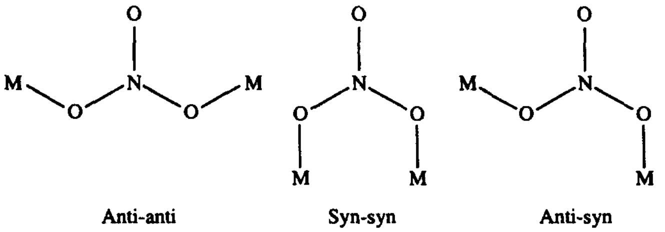


Fig. 1.



Scheme. 1.

$(NO_3)](NO_3)CH_3OH$ has been structurally characterized by single-crystal X-ray methods and found to contain folded M_2P_4 core structures. The $M_2(dppm)_2$ framework in the complex is found to be quite flexible, exhibiting folding angle (125.7°) in the solid state. In addition, the weakly-coordinated unidentate nitrate in the complex $[Cu(dppm)(NO_3)]_2$ are apparently liable, the nitrate can be replaced by other ligands. The flexibility of the M_2P_4 core and the coordinative unsaturation of the dimer are particularly intriguing in that these features should facilitate the uptake and binding of larger substrate species than presently possible with known $M_2(dppm)_2$ (M = Rh, Ir, Pd, Pt) complexes, which are generally restricted to a square-planar coordination geometry. In addition, the nature of $[Cu_2(dppm)_2(Py)_2\text{-}(NO_3)](NO_3)$ CH_3OH suggests yet another mode for the binding of small ligands by $M_2(dppm)_2$ complexes. The ability of the $[Cu_2(dppm)_2]^{2+}$ unit to fold along the $Cu \cdots Cu$ axis allows the binuclear unit to produce a central cavity. In $[Cu_2(dppm)_2(Py)_2(NO_3)](NO_3)CH_3OH$, this cavity is occupied by a nitrate anion. However, it should also be possible to introduce other species into this central cavity, as well as carry out reactions on the captured molecules. The $[Cu_2(dppm)_2]^{2+}$ unit should provide a very convenient entry point for the synthesis and study of such molecules. By replacing the nitrate in $[Cu(dppm)(NO_3)]_2$, we have prepared the following binuclear copper(I) complexes $[Cu(dppm)\text{-}(phen)]_2(NO_3)_2$ (**1**), $[Cu(dppm)(2,2'\text{-}bipy)]_2(NO_3)_2$ (**2**), $[Cu_2(dppm)_2\text{-}(C_7H_5O_4N)](NO_3)_2$ (**3**), $C_7H_5O_4N$ = pyridine-2,6-dicarboxylic acid), $[Cu_2(dppm)_2(Py)_2(NO_3)](NO_3)CH_3OH$ (**4**), Py = pyridine.

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REFERENCES

1. Puddephatt, R. J., *Chem. Soc. Rev.*, 1983, **12,** 99.
2. Benner, L. S. and Balch, A. L., *J. Am. Chem. Soc.*, 1978, **100,** 6099.
3. Kubiak, C. P., Woodcock, C. and Eisenberg, R., *Inorg. Chem.*, 1980, **19,** 2733.
4. Sanger, A. R., *Can. J. Chem.*, 1982, **60,** 1363.
5. Aguiav, A. M., Beisler, J. and Mills, A., *Org. Chem.*, 1962, **7,** 1001.
6. Geary, W. J., *Coord. Chem. Rev.*, 1971, **17,** 81.
7. Josefina Diez and Pilar Gamasa, M., *J. Chem. Soc., Dalton Trans.*, 1987, 1275.
8. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed., p. 244, John Wiley, New York (1978).
9. Jardine, F. H., Vohra, A. G. and Young, F. J., *J. Inorg. Nucl. Chem.*, 1971, **33,** 2941.
10. Lever, A. B. P., *Inorganic Electronic Spectroscopy*, p. 300, Amsterdam, Elsevier (1984).
11. Chaudret, B., *Coord. Chem. Rev.*, 1988, **86,** 191.
12. Manotti Lanfredi, A. M. and Ugozzoli, F., *Inorg. Chim. Acta.*, 1985, **99,** 111.
13. Churchill, M. R., Bezman, S. and Osborn, J. A., *Inorg. Chem.*, 1972, **11,** 1818.
14. Messmer, G. G. and Palenik, G. J., *Inorg. Chem.*, 1969, **8,** 2750.
15. Josefina Diez M. Pilar and Jose Gimeno, *J. Chem. Soc., Dalton Trans.*, 1987, 1275.
16. Commons, C. J., Hoskins, B. F., *Aust. J. Chem.*, 1975, **28,** 1663.
17. Abbott, E. H., Bose, K. S. and Cotton, F. A., *Inorg. Chem.*, 1978, **17,** 3240.
18. Schmidbaur, H., Wohlleben, A. and Huttner, G., *Chem. Ber.*, 1977, **110,** 2751.