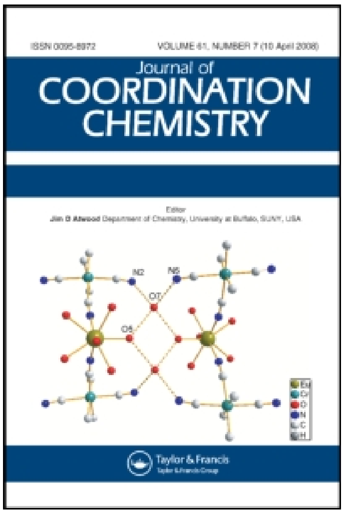
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Tetranuclear Copper(I) Complex Containing Bis (Diphenylphosphino) Methane Bridging Ligands. Crystal Structure of [Cu 4 (C 7 H 4 NO 4) 2 (dppm) 4] (NO 3) 2

Ruina Yang[a]; Yingfan Liu[a]; Douman Jin[a]
[a] Henan Institute of Chemistry, Zhengzhou, P.R. China

Online publication date: 15 September 2010

To cite this Article Yang, Ruina , Liu, Yingfan and Jin, Douman(2002) 'Tetranuclear Copper(I) Complex Containing Bis (Diphenylphosphino) Methane Bridging Ligands. Crystal Structure of [Cu 4 (C 7 H 4 NO 4) 2 (dppm) 4] (NO 3) 2', Journal of Coordination Chemistry, 55: 2, 179 — 188

To link to this Article: DOI: 10.1080/00958970211885

URL: http://dx.doi.org/10.1080/00958970211885

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Coord. Chem., 2002, Vol. 55(2), pp. 179–188

Taylor & Francis
Taylor & Francis Group

TETRANUCLEAR COPPER(I) COMPLEX CONTAINING BIS (DIPHENYLPHOSPHINO) METHANE BRIDGING LIGANDS. CRYSTAL STRUCTURE OF $[Cu_4(C_7H_4NO_4)_2(dppm)_4]$ $(NO_3)_2$

RUINA YANG[a,]*, YINGFAN LIU[a] and DOUMAN JIN[b]

[a]*Henan Institute of Chemistry, Zhengzhou 450002, P.R. China;*
[b]*State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P.R. China*

(Received 11 July 2000)

Downloaded At: 14:08 23 January 2011

The tetranuclear copper complex $[Cu_4(C_7H_4NO_4)_2(dppm)_4]$ $(NO_3)_2$ ($C_7H_4NO_4 =$ pyridine-2, 6-dicarboxylic acid) has been synthesized and characterized spectroscopically. The compound crystallizes in the triclinic space group $P\bar{1}$, with $a = 12.592(3)$, $b = 14.187(4)$, $c = 17.038(3)$ Å, $\alpha = 102.54(2)$, $\beta = 95.41(2)$, $\gamma = 90.33(2)°$, $V = 2956.7(2)$ Å^3, $Dc = 1.295\,\mathrm{g\,cm^{-3}}$ and $Z = 1$. The structure was solved and refined to a final $R = 0.055$, for 5373 independently observed reflections with $I \rangle 3\sigma(I)$. The copper(I) ion shows distorted tetrahedral coordination with dppm and pyridine-2, 6-dicarboxylic acid.

Keywords: Copper; Diphosphine; Complex; Crystal structure

INTRODUCTION

Copper(I) displays wide diversity in its structural chemistry, the coordination number ranging from two to six. Procedures to synthesize copper(I) complexes are of great interest because of the diversity of products resulting from almost the same methodology.

Copper(I) complexes containing bidentate bridging ligands have been the focus of much investigation over the last few years. [1] It has been

---

*Corresponding author.

ISSN: 0095-8972 © 2002 Taylor & Francis Ltd DOI: 10.1080/00958970290002126

pointed out and confirmed that the four-electron donor diphosphine $Ph_2PCH_2PPh_2$ (dppm) is a very efficient bridging bidentate ligand. Many examples of copper(I) complexes containing dppm are known with a variety of stereo chemistries. [2–5] A key feature in the chemistry of dinuclear bis(diphenylphosphino)methane complexes is the relatively stable $M_2(dppm)_2$ framework. This feature is presumably one of the chief reasons for the unusual bonding, reactivity and catalytic properties of $M_2(dppm)_2$ compounds. These metal ions require additional monodentate or bidentate ligands, since each metal ion in the $M_2(dppm)_2$ framework is coordinatively unsaturated. The additional ligand not only influences the geometry around a metal ion, but also the structure of the framework including the conformation of $M_2(dppm)_2$. The stable $M_2(dppm)_2$ framework, while accepting some conformational changes when interacting with small molecules, places much of the burden for any structural adjustment on the substrate species themselves and on any additional ligands present. In the present work, the binuclear compound $[Cu(dppm)(NO_3)]_2$ was reacted with pyridine-2,6-dicarboxylic acid at room temperature to give a tetranuclear copper(I) complex, $[Cu_4(C_7H_4NO_4)_2(dppm)_4]$ $(NO_3)_2$. Structural results allowed us to interpret some solution properties of the dppm derivatives.

Downloaded At: 14:08 23 January 2011

EXPERIMENTAL

The compound $[Cu(dppm)(NO_3)]_2$ was prepared by a reported method. [2] All other chemicals were of reagent grade quality obtained from commercial sources and used without further purification. All solvents were dried by standard methods and distilled under nitrogen prior to use. Elemental analyses were performed on an ERBA-1106 instrument (Italy). Cu and P content were determined using a JA96–970 spectrometer. IR spectra were recorded on a Nicolet I70SX IR spectrophotometer. TG-DTA spectra were recorded on a PE-TGS-2 instrument. Electronic spectra were observed with a Hitachi 330 spectrophotometer. Conductivity measurements were carried out in acetone solution thermostatted at 25° using a Shanghai DDS-11A conductometer and a DJS-l type platinum black electrode. Melting points were determined on an Electrothermal apparatus and are uncorrected. Room temperature ^{31}P-NMR spectra were measured on a DPX-400 NMR spectrometer $CDC1_3$ with 85% H_3PO_4 as external reference. XPS spectra were recorded on a VG ESCALAB MK II instrument with AlK α radiation. Voltage, current and vacuum were set at 12.5 kV, 20 mA and 6×10^{-6} Pa,

TABLE I Final coordinate for the non-hydrogen atoms and equivalent isotropic thermal parameters

Atom	*x*/*a*	*y*/*b*	*z*/*c*	$B(\text{Å}^2)$
Cu1	0.36125(8)	0.39993(7)	0.41440(6)	2.92(2)
Cu2	0.47791(9)	0.36766(7)	0.24555(6)	3.23(2)
P1	0.3785(2)	0.2392(2)	0.4023(1)	2.90(5)
P2	0.2328(2)	0.4698(2)	0.3476(1)	3.02(5)
P3	0.3699(2)	0.4794(2)	0.2068(1)	3.02(5)
P4	0.4539 (2)	0.2091 (2)	0.2314(1)	3.38(5)
O1	0.145(1)	0.212(1)	0.7739(9)	15.7(5)
O2	0.004(1)	0.148(1)	0.7135(7)	16.3(5)
O3	0.004(1)	0.2888(9)	0.7868 (7)	12.4(4)
O11	0.5051(4)	0.4459(4)	0.3755(3)	3.6(1)
O12	0.3787(5)	0.4548(5)	0.5379(3)	4.6(2)
O21	0.5636(6)	0.3377(6)	0.1007(4)	6.2(2)
O22	0.7300(6)	0.3495(7)	0.0698(4)	8.0(2)
N	0.6300(5)	0.4356(5)	0.2570(4)	2.8(1)
N1	0.051(1)	0.216(1)	0.7578(7)	10.3(4)
C1	0.5901(6)	0.4953(5)	0.3957(5)	2.8(2)
C2	0.6525(8)	0.3693(7)	0.1182(5)	4.8(2)
C3	0.3607(7)	0.1705(6)	0.2963(5)	3.4(2)
C4	0.2878(7)	0.5461(6)	0.2852(5)	3.4(2)
C11	0.5033(7)	0.1989(6)	0.4446(5)	3.1(2)
C12	0.5213(8)	0.0991(6)	0.4377(6)	4.3(2)
C13	0.6199(8)	0.0707(7)	0.4683(6)	5.1(3)
C14	0.6993(9)	0.1389(8)	0.5056(7)	6.0(3)
C15	0.6798(8)	0.2365(8)	0.5129(7)	5.9(3)
C16	0.5809(8)	0.2675(7)	0.4821(6)	4.5(2)
C21	0.2804(6)	0.1783(6)	0.4489(5)	3.4(2)
C22	0.2847(7)	0.2045(6)	0.5334(5)	4.1(2)
C23	0.2116(8)	0.1617(7)	0.5736(6)	4.7(2)
C24	0.1354(8)	0.0943(7)	0.5282(6)	5.3(2)
C25	0.1320(8)	0.0679(7)	0.4454(6)	5.1(2)
C26	0.2041(7)	0.1100(6)	0.4039(6)	4.4(2)
C31	0.1328(6)	0.3885(6)	0.2813(5)	3.6(2)
C32	0.0748(7)	0.4117(7)	0.2147(6)	4.6(2)
C33	−0.0026(9)	0.3455(9)	0.1679(7)	6.0(3)
C34	−0.0207(9)	0.2566(8)	0.1895(7)	6.4(3)
C35	0.0344(9)	0.2347(8)	0.2569(7)	6.0(3)
C36	0.1121(7)	0.2996(7)	0.3032(6)	4.4(2)
C41	0.1497(7)	0.5553(6)	0.4095(5)	3.4(2)
C42	0.1464(8)	0.5496(6)	0.4992(6)	4.7(2)
C43	0.0831(9)	0.6140(8)	0.5382(6)	5.8(3)
C44	0.0241(8)	0.6825(8)	0.5066(7)	5.7(3)
C45	0.0278(8)	0.6878(7)	0.4277(6)	5.2(3)
C46	0.0890(7)	0.6237(7)	0.3766(6)	4.4(2)
C51	0.4536(7)	0.5766(6)	0.1888(5)	3.3(2)
C52	0.5046(8)	0.6444(7)	0.2526(6)	4.4(2)
C53	0.5817(8)	0.7106(7)	0.2370(6)	5.3(3)
C54	0.6049(9)	0.7076(7)	0.1585(6)	5.5(3)
C55	0.5530(9)	0.6406(7)	0.0945(6)	5.4(3)
C56	0.4769(8)	0.5733(7)	0.1083(6)	4.6(2)
C61	0.2780(7)	0.4494(7)	0.1157(5)	3.9(2)
C62	0.2151(8)	0.5213(7)	0.0899(6)	5.0(2)
C63	0.1431(9)	0.4942(9)	0.0197(6)	6.7(3)
C64	0.1376(9)	0.398(1)	−0.0247(7)	7.5(3)

Downloaded At: 14:08 23 January 2011

TABLE I (Continued)

Atom	*x/a*	*y/b*	*z/c*	*B*(Å^2)
C65	0.1992(9)	0.3271(1)	0.0009(7)	7.2(3)
C66	0.2715(8)	0.3533(8)	0.0713(6)	5.3(3)
C71	0.5738(8)	0.1415(6)	0.2475(5)	3.9(2)
C72	0.5692(9)	0.0375(7)	0.2279(6)	5.3(3)
C73	0.662(1)	−0.0098(8)	0.2428(6)	6.6(3)
C74	0.757(1)	0.0397(8)	0.2773(7)	7.5(3)
C75	0.762(1)	0.1427(9)	0.2971(8)	7.9(4)
C76	0.6677(8)	0.1917(7)	0.2813(7)	5.4(3)
C81	0.3951(8)	0.1442(6)	0.1315(5)	4.5(2)
C82	0.456(1)	0.1354(8)	0.0670(6)	6.1(3)
C83	0.413(1)	0.0942(9)	−0.0115(7)	7.7(4)
C84	0.312(1)	0.061(1)	−0.0254(7)	10.0(5)
C85	0.252(1)	0.072(1)	0.0364(9)	15.6(6)
C86	0.294(1)	0.112(1)	0.1169(8)	11.2(5)
C91	0.6903(7)	0.1359(7)	0.1957(5)	3.9(2)
C92	0.7806(7)	0.4961(7)	0.2034(6)	4.8(2)
C93	0.8123(7)	0.5567(7)	0.2775(6)	4.8(2)
C94	0.7532(7)	0.5547(6)	0.3419(5)	3.7(2)
C95	0.6615(6)	0.4936(5)	0.3282(5)	2.7(2)

Downloaded At: 14:08 23 January 2011

respectively. Emission spectra were recorded on a Luminescence Spectrophotometer(Aminco Bowman Series 2).

$[Cu_4(C_7H_4NO_4)_2(dppm)_4]$ $(NO_3)_2$

Pyridine-2,6-dicarboxylic acid (0.167 g, 1 mmol) was added with stirring to a solution of $[Cu(dppm)(NO_3)]_2$ (1.019 g, 1 mmol) in a mixed solvent of methanol (30 cm^3) and dichloromethane (20 cm^3). The resulting orange solution was subsequently allowed to evaporate slowly at room temperature to a final volume of 5–10 cm^3. Multifaceted, orange crystals of $[Cu_4(C_7H_4NO_4)_2(dppm)_4]$ $(NO_3)_2$ were obtained, and Which were separated by filtration, washed with methanol and dried in air. Yield: 69%. Mp: 189–191°C dec. Anal. $C_{114}H_{96}P_8N_4O_{14}Cu_4$ requires (%): C, 60.90; H, 4.27; N, 2.49; P, 11.0; Cu, 11.3. Found: C, 60.61; H, 4.18; N, 2.29; P, 11.5; Cu, 10.9.

X-Ray Data Collection and Structure Determination

Crystal data: $C_{114}H_{96}P_8N_4O_{14}Cu_4$, triclinic, space group $P\bar{1}$, $a = 12.592(3)$, $b = 14.187(4)$, $c = 17.038(3)$ Å, $\alpha = 102.54(2)$, $\beta = 95.41(2)$, $\gamma = 90.33(2)°$, $V = 2956.7(2)$ Å^3, $Dc = 1.295$ g cm^{-3}, $Z = 1$, $F(000) = 1224$, $\mu(\mathrm{MoK}\alpha) = 0.87$ mm^{-1}. A single crystal of dimensions 0.1 × 0.1 × 0.15 mm, of the title complex was selected and mounted on an automatic Enraf-Nonius CAD-4 four-circle diffractometer equipped with a graphite monochromator

Downloaded At: 14:08 23 January 2011

TABLE II Selected bond distances (Å) and angles(°) for title complex

Cu(1)–P(1)	2.258(2)	Cu(1)–P(2)	2.248(3)	Cu(1)–O(11)	2.132(6)
Cu(1)–O(12)	2.069(6)	Cu(2)–P(3)	2.260(3)	Cu(2)–P(4)	2.226(3)
Cu(2)–O(11)	2.245(5)	Cu(2)–N	2.112(6)	Cu(1)–Cu(2)	3.2978(2)
P(1)–Cu(1)–P(2)		125.20(8)	P(1)–Cu(1)–O(11)		104.2(2)
P(1)–Cu(1)–O(12)		103.9(2)	P(2)–Cu(1)–O(11)		103.7(2)
P(2)–Cu(1)–O(12)		114.0(2)	O(11)–Cu(1)–O(12)		103.5(2)
P(3)–Cu(2)–P(4)		130.99(9)	P(3)–Cu(2)–O(11)		95.2(2)
P(3)–Cu(2)–N		102.1(2)	P(4)–Cu(2)–O(11)		112.6(2)
P(4)–Cu(2)–N		123.2(2)	O(11)–Cu(2)–N		75.0(2)
O(1)–N(1)–O(2)		119.(1)	O(1)–N(1)–O(3)		120.(1)

employing MoKα radiation ($\lambda = 0.71073$ Å). Intensity data were measured at room temperature and collected in the $\omega - 2\theta$ scan mode up to $2\theta_{\max} = 55°$ ($0 \leq h \leq 15$, $-16 \leq k \leq 16$, $-20 \leq l \leq 20$). Of the 10899 independent reflections measured, 5373 had $I \geq 3\sigma(I)$ and these were employed in the succeeding structural determination and refinement, which included 694 parameters. No significant change was detected in the intensity of three standard reflections during data collection. Lorentz, polarization and absorption corrections (empirical method, Ψ-scan) were applied to the intensity data. The structure was solved by direct methods and Fourier syntheses. The structure was refined by the full-matrix least-squares method. In the final cycles of least squares refinement, all non-H atoms were treated anisotropically; all H-atoms were then included as fixed contributors with one refined common isotropic temperature factor [8Å^2]. The refinement converged to final $R = 0.055$ and $R_W = 0.068$ (unit weights). In the final refinement cycle, the maximum and minimum electron densities in the difference map were 0. 866 and 0. 305 e Å^3, respectively. Computations were performed using the SDP program on a PDP11/44 computer. Final atomic positions for the heavy atoms and selected bond lengths and angles are given in Tables I and II. H-atom parameters, anisotropic thermal parameters and observed and calculated structure factors are available from the authors on request.

RESULTS AND DISCUSSION

Preparation of the Complex

According to colour changes correlating with the procedure for preparing the complex [Cu(dppm)(NO$_3$)]$_2$, cupric nitrate is reduced to a white copper(I) complex. [2] 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. The compound $[Cu(dppm)(NO_3)]_2$ reacts with pyridine-2,6-dicarboxylic acid at room temperature to give $[Cu_4(C_7H_4NO_4)_2(dppm)_4](NO_3)_2$. Orange crystals were deposited in good yield from methanol and dichloromethane. Molar conductivity measurement ($130\,S\,cm^2\,mol^{-1}$) suggested the title complex behaved as a uni–univalent electrolyte in acetone solution. Elemental analysis of the title complex agreed well with its formulation. When melted in air, the complex decomposed and turned blue. At room temperature, the product is orange, crystalline and diamagnetic, is fairly stable in air in the solid state, and soluble in polar solvents such as CH_2Cl_2, $CHCl_3$, acetonitrile, dimethylformamide, and dimethylsulfoxide. The complex has limited solubility in methanol, ethanol and is insoluble in toluene, ether, hexane and tetrahydrofuran.

IR Data and ^{31}P NMR Spectra

The infrared spectra(in CsI) of the title complex exhibited the expected bands due to the dppm ligand. For example, for $[Cu_4(C_7H_4NO_4)_2(dppm)_4](NO_3)_2$, these occur at 1485 s, 1385 s, 1186 w, 1098 m, 783 m, 740 s, 718 m, and 690 s cm^{-1}. [6] The band expected at $\approx 1385\,cm^{-1}$ was not resolved in the title complex due to the very intense nitrate band in the same region. The P-Ph absorption, at about $1100\,cm^{-1}$, shows an increase in frequency and intensity, which is characteristic of P-metal coordination. In the $1500-700\,cm^{-1}$ range, the characteristic absorption bands of nitrate anion appear, exhibiting a broad band at ca. $1380-85cm^{-1}$. In ^{31}P-NMR spectra 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 appears as a single resonance (δ:$^{31}P = -13.9$ ppm).

XPS Spectra

XPS spectra of the complex gives information concerning copper-ligand binding. The binding energies of P_{2p}, N_{1s} and Cu_{2p} in the title complex are at 136.10, 403.5 and 938.15 eV, respectively. The binding energy P_{2p}(136.10 eV) and N_{1s}(403.5 eV) in the complex is larger than the corresponding values for free dppm (P_{2p} : 132.5 eV) and pyridine-2,6-dicarboxylic acid (N_{1s} : 400.0 eV), and of the precursor complex $[Cu(dppm)(NO_3)]_2$ (P_{2p} : 134.6 eV, Cu_{2p} : 936.3 eV). This is attributed to electronic density decrease at P and N because of the formation of $Cu \leftarrow P$ and $Cu \leftarrow N$ bonds in $[Cu_4(C_7H_4NO_4)_2(dppm)_4](NO_3)_2$.

Downloaded At: 14:08 23 January 2011

DTA-TG Analysis

The results of thermo-gravimetric analyses of the title complex, compared with those of free dppm, indicate that the thermal stability of dppm increases upon coordination. TG-DTA thermograms of the complex reveal that pyrolytic decomposition takes place in two steps. The first corresponds to a weight loss of 12.6% and is probably due to decomposition of pyridine-2,6-dicarboxylic acid (loss of weight calc. 14.8%) and is confirmed by a endothermic peak at 190 – 270°C. The second step in the 270 – 700°C range corresponds to a pronounced weight loss due to the decomposition of the organic moiety (residue weight 17.6%; calc. 14.2%), giving CuO as the final residue.

Luminescence Properties

The electronic absorption spectrum of the title complex in CH_2Cl_2 exhibits low-energy bands in the 330 – 350 nm region. Excitation of a solid sample of the complex at $\lambda = 355$ nm at room temperature produces long-lived luminescence at $\lambda = 520$ nm. The low-energy and long lifetime emission is most likely associated with the metal-centred excited state $3d^9 4s^1$ of Cu(I) modified by copper – copper interactions due to configurational mixing of filled orbitals of d parentage with appropriate empty orbitals derived from the higher-energy 4s and 4p atomic orbitals of the tetrameric unit(d→s). There is extensive literature on the emission of polynuclear copper(I) complexes. [8 – 11] In the tri-nuclear copper(I) complex $[Cu_3(dpmp)_2(MeCN)_2Cl_2]^+$, where dpmp is bis (diphenylphosphinomethyl) methane, emission at 560 nm was assigned as a metal-centred $3d^9 4s^1 \rightarrow 3d^{10}$ transition. [8] In the binuclear copper(I) complex $[(PPh_3)Cu_2Cl_2(py)]$ a similar assignment was made by Jink *et al.* [9].

Crystal Structure of $[Cu_4(C_7H_4NO_4)_2(dppm)_4]\ (NO_3)_2$

The molecular structure of the complex cation is depicted in Figure 1. The solid-state structure of $[Cu_4(C_7H_4NO_4)_2(dppm)_4]\ (NO_3)_2$ consists of discrete tetranuclear cations $[Cu_4(C_7H_4NO_4)_2(dppm)_4]^{2+}$ and nitrate anions. The tetranuclear complex consists of two $[Cu_2(dppm)_2]^{2+}$ subunits bound together by two bridging pyridine-2,6-dicarboxylic acid. Each pyridine-2,6-dicarboxylic acid ligand is involved in the bridge-bonding mode with the two copper atoms bound to different pyridirie-2,6-dicarboxylic acid oxygen atoms, and with one copper atom bound to the nitrogen atom of

Downloaded At: 14:08 23 January 2011

Downloaded At: 14:08 23 January 2011

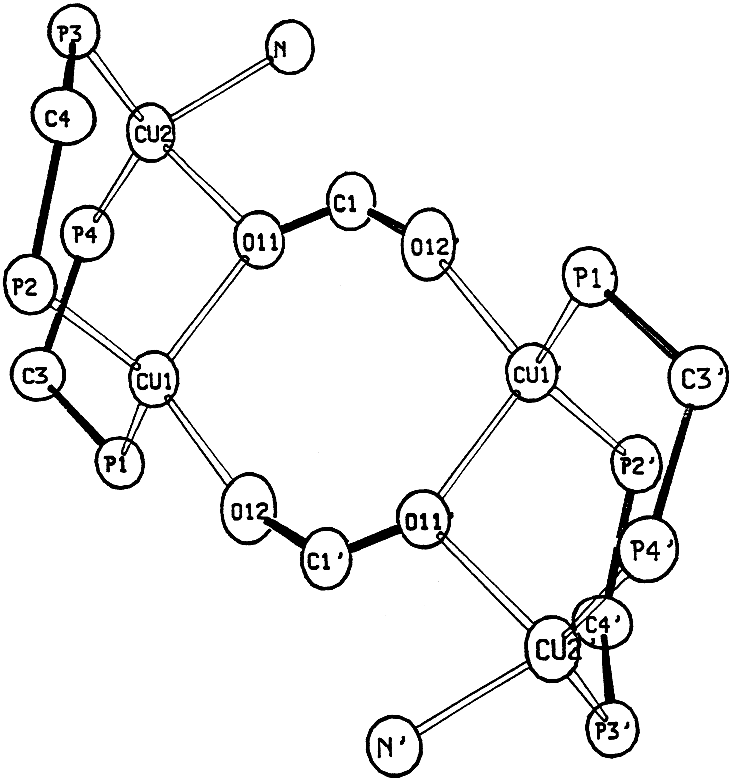


FIGURE 1 Coordination mode of the $[Cu_4(C_7H_4NO_4)_2(dppm)_4]^{2+}$ cation. Hydrogen atoms and phenyl groups are omitted for clarity.

pyridine-2,6-dicarboxylic acid. Hence, each copper atom is four-coordinate, with phosphorus atoms from each of two bridging dppm ligands occupying two of the coordination sites, the oxygen atoms or nitrogen atom from pyridine-2,6-dicarboxylic acid occupying the third and the fourth. It has been already observed that Cu-P bonds lengths are mainly influenced by the number of phosphorus atoms bonded to the same copper atom. [10] In the present complex, all copper atoms are coordinated by two phosphorus atoms. As expected the Cu-P distances in $[Cu_4(C_7H_4NO_4)_2(dppm)_4]^{2+}$ vary from 2.226(3) to 2.260(3) Å, with a mean of 2.248(3) Å, in good agreement with the range 2.243(3) to 2.267 (3) Å for 'two-phosphorus' Cu-P distances found in $[Cu_4(S)(dppm)_4](PF_6)_2$. [11] The Cu – Cu separation of 3.2978(2) Å is significantly longer than the range of copper – copper bond lengths (2.494(5) to 2.674(5) Å) found in $[H_6Cu_6(PPh_3)_6 \cdot DMF]$, [12] suggesting that the copper atoms in the present compound are not involved in metal–metal bonding. The two unique P-Cu-P units in $[Cu_4(C_7H_4NO_4)_2(dppm)_4]^{2+}$ 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 (125.20(8)°) and the P(3)-Cu(2)-P(4) angle (130.99(9)°) are similar to the corresponding P(1)-Cu-P(2) angle of 131.8(5)° found in the related binuclear $(dppm)_2$ complex $[Cu(dppm)(NO_3)]_2$. [2] Dihedral angles of the plane defined by atoms Cu(1), O(11), C(l), O(12’), Cu(1’), O(11’), C(l’), O(12) to the plane Cu(l), P(2), C(4), P(3), Cu(2), O(11) and the plane Cu(l), P(1), C(3), P(4), Cu(2), O(11) are 115.7 and 39.90°, respectively. Structural studies involving binuclear $(dppm)_2$ species of other transition metals (Mn, [13] Mo [14]) have been much less frequent but, in general, also reveal common *trans* binding of 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 non-linear. X-ray structural characterization of the complex reported here clearly reveals 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 particular are much more bent (125. 2°) than the corresponding P-M-P values (131. 8°) found in $[Cu(dppm)(NO_3)]_2$.

In summary, the doubly bridged bis(diphenylphosphine)methane complex $[Cu_4(C_7H_4NO_4)_2(dppm)_4](NO_3)_2$ has been structurally characterized by single-crystal X-ray methods and found to contain folded M_2P_4 core structures. In addition, the weakly-coordinated unidentate nitrate in the complex $[Cu(dppm)(NO_3)]_2$ are apparently labile; the nitrate can be replaced easily by other ligands. The flexibility of the M_2P_4 core and the coordinative unsaturation of the $[Cu_2(dppm)_2]^{2+}$ dimer are particularly intriguing in that these features should facilitate the uptake and binding of larger substrate species than presently possible with known $M_2(dppm)_2$ ($M = Ag, Pd, Pt$) complexes, which are generally restricted to a square-planar coordination geometry. In addition, the tetrameric nature 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···Cu axis allows the close approach of two binuclear units to produce an enclosed central cavity. In $[Cu_4(C_7H_4NO_4)_2(dppm)_4](NO_3)_2$, this cavity is occupied by two pyridine-2,6-dicarboxylic acid ligands. 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 unit $[Cu_4(C_7H_4NO_4)_2(dppm)_4]^{2+}$ should provide a very convenient entry point for the synthesis and study of such molecules.

Downloaded At: 14:08 23 January 2011

Acknowledgements

We thank National Natural Science Foundation of China (Grant No. 29871009) and the Henan Province Outstanding Youth and Natural Science Foundation for support of this research.

References

[1] R. J. Puddephatt, *Chem. Soc. Rev.* **12**, 99 (1983).
[2] Yang Ruina, Lin Kunhua and Jin Douman, *Trans. Met. Chem.* **22**, 254 (1997).
[3] C. P. Kubiak, C. Woodcock and R. Eisenberg, *Inorg. Chem.* **19**, 2733 (1980).
[4] Ruina Yang, Xiaoyuan Hu and Douman Jin, *Trans. Met. Chem.* **25**, 174 (2000).
[5] Ruina Yang and Douman Jin, *Inorg. Chim. Acta* **304**, 1 (2000).
[6] Josefina Diez and M. Pilar Gamasa, *J. Chem. Soc. Dalton Trans.* 1275 (1987).
[7] Douman Jin and Wenxiang Zhu, *Research Methods of Coordination Chemistry* (Beijing Science Publishers, Beijing, 1996), p. 123.
[8] D. Li, H. K. Yip, C. M. Che, Z. Y. Zhou, T. C. W. Mak and S. T. Liu, *J. Chem. Soc. Dalton Trans.* 2445 (1992).
[9] M. Henry, J. L. Wotton, S. I. Khan and J. I. Zink, *Inorg. Chem.* **36**, 796 (1997).
[10] G. Nardin, *J. Chem. Soc. Dalton Trans.* 2566 (1975).
[11] V. W. Yam, W. Lee and T. F. Lai, *J. Chem. Soc. Chem. Commun.* 1571 (1993).
[12] M. R. Churchill, S. Bezman and J. A. Osborn, *Inorg. Chem.* **11**, 1818 (1972).
[13] C. J. Commons and B. F. Hoskins, *Aust. J. Chem.* **28**, 1663 (1975).
[14] E. H. Abbott, K. S. Bose and F. A. Cotton, *Inorg. Chem.* **17**, 3240 (1978).

Downloaded At: 14:08 23 January 2011