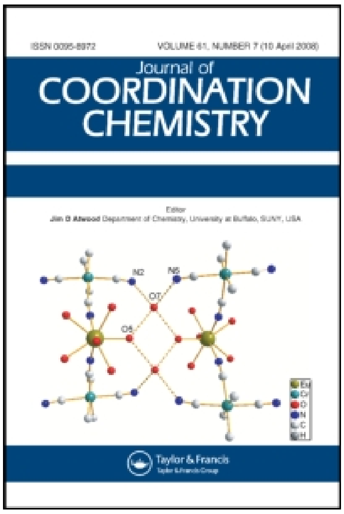

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis of asymmetric binuclear copper(I) complexes containing 4-vinylpyridine and bis(diphenylphosphino) methane

Ruina Yang[a]; Yuan Sun[b]; Dong Zhao[a]; Libing Guo[a]
[a] Henan Institute of Chemistry, Zhengzhou 450002, P.R. China [b] Zheng Light Industry College, Zhengzhou 450006, P.R. China

To cite this Article Yang, Ruina , Sun, Yuan , Zhao, Dong and Guo, Libing(2003) 'Synthesis of asymmetric binuclear copper(I) complexes containing 4-vinylpyridine and bis(diphenylphosphino) methane', Journal of Coordination Chemistry, 56: 13, 1169 — 1177

To link to this Article: DOI: 10.1080/00958970310001624465

URL: http://dx.doi.org/10.1080/00958970310001624465

J. Coord. Chem., Vol. 56, No. 13, 10 September 2003, pp. 1169–1177

SYNTHESIS OF ASYMMETRIC BINUCLEAR COPPER(I) COMPLEXES CONTAINING 4-VINYLPYRIDINE AND BIS(DIPHENYLPHOSPHINO) METHANE

RUINA YANG[a,*], YUAN SUN[b], DONG ZHAO[a] and LIBING GUO[a]

[a]*Henan Institute of Chemistry, Zhengzhou 450002, P.R. China;*
[b]*Zheng Light Industry College, Zhengzhou 450006, P.R. China*

(Received 17 June 2003; In final form 4 September 2003)

The asymmetric binuclear copper(I) complex $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}NO_3)](NO_3)$ (dppm = $Ph_2PCH_2PPh_2$, C_7H_7N = 4-vinylpyridine) has been prepared and characterized. The complex is photoluminescent at room temperature. Crystals are triclinic space group $P\bar{1}$, with cell parameters $a = 11.638(2)$, $b = 12.621(3)$, $c = 18.516(4)$ Å, $\alpha = 89.20(3)$, $\beta = 83.11(3)$, $\gamma = 76.04(3)°$, $V = 2619.5(9)$ Å^3, $D_c = 1.426\,\mathrm{g\,cm^{-3}}$, $Z = 2$, $\mu = 0.988\,\mathrm{mm^{-1}}$, $R = 0.0497$ for 6574 independently observed reflections with $I > 2\sigma(I)$. The structure consists of $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}NO_3)]^+$ cations and nitrate anions. Copper atoms show different coordination modes; Cu(2) has a distorted trigonal and Cu(1) a tetrahedral geometry.

Keywords: Copper; Binuclear complex; 4-Vinylpyridine; Crystal structure

INTRODUCTION

Many examples of complexes containing the eight-membered ring M(μ-dppm)M′ are known with a variety of metals, oxidation states and stereochemistries [1–4]. In general, bridging dppm ligands give a planar M_2P_4 core with the two metal atoms held in close proximity (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.

There is increasing interest in binuclear or cluster complexes of transition metals as models for compounds of biological and catalytic interest. The diphosphine $Ph_2PCH_2PPh_2$ (dppm) is a particularly important bridging ligand. A key feature in the chemistry of binuclear dppm complexes is the relatively stable, intrinsic $M_2(dppm)_2$ framework. The metal ions usually require additional monodentate or bidentate ligands, since each metal ion in the $M_2(dppm)_2$ framework is coordinatively unsaturated. This additional ligand influences not only the geometry around

---

*Author for correspondence. E-mail: sunstarw@371.net

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970310001624465

the metal ion but also the structure of the framework, including the conformation of the $M_2(dppm)_2$ unit. The stable $M_2(dppm)_2$ framework, while subject to 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. This adjustment may be expressed in terms of unique bonding interactions or chemical reactivity. For example, unusual reactivity with carbon disulfide was first discovered in the bimetallic dppm complex $[Cu(dppm)(NO_3)_2]$ [2]. Herein is described the first report on the preparation, and structure of an asymmetrical, binuclear copper(I) 4-vinylpyridine complex $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}NO_3)](NO_3)$, obtained by treating the complex $[Cu(dppm)(NO_3)]_2$ with 4-vinylpyridine.

EXPERIMENTAL

The compound $[Cu(dppm)(NO_3)]_2$ was prepared according to the literature procedure [4]. Solvents were dried and purified by standard methods. All other chemicals were of reagent grade quality, obtained from commercial sources and used without further purification. Elemental analyses were carried out using an ERBA-1106 instrument (Italy). Cu and P contents were determined using a JA96-970 ICP spectrometer. IR spectra were recorded on a Nicolet 170SX IR spectrophotometer. Conductivity measurements were carried out in methanol solution at 25°C using a Shanghai DDS-11A meter and a Pt black electrode. Melting points are uncorrected. Room temperature NMR spectra were recorded on a Bruker AV300 NMR spectrometer in $CDCl_3$ (^{31}P-NMR with 85% H_3PO_4 as external reference). TG-DTA traces were recorded on a PE-TGS-2 instrument. Electrospray mass spectra (ES-MS) were recorded on a LCQ system (Finngan, MAT, USA) using MeOH as the mobile phase. The spray voltage, tube lens offset, capillary voltage and capillary temperature were set at 4.5 kV, 20.0 V, 7.0 V and 200°C, respectively, and the quoted m/z values are for the major peaks in the isotope distribution. XPS spectra were recorded on a VG ESCALAB MK II instrument using Al Kα radiation. Voltage, current and vacuum were set at 12.5 kV, 20 mA and 6×10^{-8} mbar, respectively. The emission spectrum was recorded on an Aminco Bowman Series 2 spectrophotometer.

$[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}NO_3)]$ (NO_3)

4-Vinylpyridine (2 cm^3) was added with stirring to a solution of $[Cu(dppm)(NO_3)]_2$ (0.51 g, 0.5 mmol) in methanol (25 cm^3). The mixture was stirred for 16 h at room temperature. The resulting yellow solution was subsequently allowed to evaporate slowly in air at room temperature to a final volume of about 8 cm^3. Yellow crystals suitable for X-ray studies were obtained and identified as $[Cu_2(dppm)_2(C_7H_7N)(NO_3)](NO_3)$. Yield: 61%. M.p. = 180°C. Anal. Calcd. for $C_{57}H_{51}N_3O_6P_4Cu_2$ (%): C, 60.85; H, 4.57; N, 3.74; P, 11.0; Cu, 11.3. Found: C, 60.66; H, 4.49; N, 3.61; P, 11.3; Cu, 11.1. IR (CsI) data (cm^{-1}): for NO_3^-, 1380 s, 1033 m; for 4-vinylpyridine, 1633, w, 1610 s, 1583 m, 1570 m, 995 m, 930 m, 840 m; ν_{Cu-P}, 240 w; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.20 (s, 4 H, CH_2 of dppm), 6.68–8.12 (m, 44 H, C_6H_5, C_5H_4N), 6.29 (1 H, CH of $-CH{=}CH_2$), 5.92, 5.95 (2 H, CH_2 of $-CH{=}CH_2$); $^{31}P\{^1H\}$ NMR ($CDCl_3$): -10.9 ppm (s).

X-ray Structure Determination

A prismatic crystal of approximate dimensions 0.3 mm × 0.3 mm 0.2 mm was mounted on an automatic Bruker P4 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Intensity data were measured at room temperature and collected in the $\omega - 2\theta$ scan mode ($2^\circ \leq 2\theta \leq 50^\circ$). The observed index range was h, 0/13; k, −14/14; l −21/21. Of the 9191 independent reflections measured, 6574 had $I \geq 2\sigma(I)$ and these were employed in succeeding structural determination and refinement, which included 649 parameters. 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 full-matrix least-squares methods. In the final cycles of least-squares refinement, all non-H atoms were treated anisotropically; all H-atoms were then included as fixed contributors. The final R and R_w values were 0.0497 and 0.1664, respectively, and the maximum shift/e.s.d. was 0.045. The function minimized was $w = 1/[\sigma^2 F_o^2 + (0.1000P)^2 + 0.0000P]$, where $P = 1/3(F_o^2 + 2F_o^2)$. The maximum and minimum electron densities in the difference map were 1.262 and −0.615 e Å^3, respectively. Computations were performed using SHELXL-97 with Bruker XSCANS. Final atomic positions for the heavy atoms and selected bond lengths and angles are given in Tables I and II, respectively. Crystal data: $C_{57}H_{51}N_3O_6P_4Cu_2$, triclinic, space group $P\bar{1}$, with cell

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

	x/a	y/b	z/c	U_{eq}
Cu(1)	0.96303(5)	0.28636(4)	0.25596(3)	0.04135(19)
Cu(2)	0.75485(5)	0.19402(5)	0.27500(3)	0.0455(2)
P(2)	0.78588(11)	0.11519(9)	0.38259(6)	0.0398(3)
P(1)	0.99738(11)	0.21547(9)	0.36654(6)	0.0402(3)
P(4)	0.97598(10)	0.21885(9)	0.14160(6)	0.0366(3)
P(3)	0.77055(10)	0.11139(9)	0.16655(6)	0.0380(3)
C(93)	1.1965(5)	0.3456(5)	0.2292(3)	0.0621(14)
C(85)	1.1336(4)	0.1759(4)	0.1059(2)	0.0404(10)
C(4)	0.9270(4)	0.0950(4)	0.1268(2)	0.0406(10)
C(3)	0.9440(4)	0.0937(4)	0.3930(2)	0.0418(10)
N(2)	0.7019(4)	0.4328(4)	0.2887(3)	0.0622(12)
C(45)	0.7569(4)	−0.0212(4)	0.3918(3)	0.452(11)
C(3)	0.6564(3)	0.3529(3)	0.2833(2)	0.0684(11)
C(74)	0.9131(4)	0.3158(4)	0.0752(2)	0.0396(10)
N(1)	1.0810(4)	0.3908(3)	0.2412(2)	0.0513(10)
C(34)	0.7054(4)	0.1886(4)	0.4648(3)	0.0471(11)
C(92)	1.0444(6)	0.5000(4)	0.2435(3)	0.0571(13)
C(25)	0.9451(5)	0.3075(4)	0.4455(3)	0.0498(12)
C(65)	0.6834(4)	0.1812(4)	0.0969(2)	0.0436(11)
C(76)	0.8255(6)	0.5012(4)	0.0451(3)	0.0739(18)
C(73)	0.9068(5)	0.2850(4)	0.0046(3)	0.0497(12)
C(24)	0.8782(5)	0.4108(4)	0.4376(3)	0.0564(13)
C(64)	0.6937(5)	0.1357(5)	0.0272(3)	0.0542(13)
C(75)	0.8733(6)	0.4247(4)	0.0950(3)	0.0616(15)
C(84)	1.2057(4)	0.0959(4)	0.1430(3)	0.0560(13)
C(72)	0.8581(5)	0.3615(5)	−0.0451(3)	0.0606(14)
C(94)	1.2808(5)	0.4075(5)	0.2190(3)	0.0673(15)
C(95)	1.2457(6)	0.5191(5)	0.2214(3)	0.0642(16)
C(33)	0.6176(4)	0.2813(4)	0.4591(3)	0.0551(13)

(*continued*)

TABLE I Continued

	x/a	y/b	z/c	U_{eq}
C(83)	1.3259(5)	0.0649(5)	0.1222(4)	0.0714(16)
C(44)	0.6627(6)	−0.0406(5)	0.4354(4)	0.0742(17)
C(91)	1.1256(6)	0.5650(5)	0.2338(3)	0.0642(15)
C(42)	0.7036(6)	−0.2231(5)	0.3912(4)	0.0715(16)
C(26)	0.9693(7)	0.2730(5)	0.5139(3)	0.0783(19)
C(86)	1.1852(5)	0.2246(6)	0.0482(3)	0.0689(16)
C(46)	0.8252(6)	−0.1046(5)	0.3473(3)	0.0679(16)
C(66)	0.6127(5)	0.2849(4)	0.1114(3)	0.0589(14)
C(32)	0.5573(6)	0.3396(5)	0.5205(4)	0.077(2)
C(71)	0.8195(6)	0.4687(5)	−0.0252(3)	0.0703(16)
C(62)	0.5684(6)	0.2991(6)	−0.0116(3)	0.0696(16)
C(35)	0.7323(6)	0.1540(6)	0.5337(3)	0.080(2)
C(22)	0.8554(7)	0.4431(6)	0.5656(4)	0.085(2)
C(23)	0.8348(6)	0.4788(5)	0.4973(3)	0.0747(17)
C(63)	0.6368(5)	0.1962(6)	−0.0268(3)	0.0645(16)
C(82)	1.3778(5)	0.1135(6)	0.0643(3)	0.0722(17)
C(43)	0.6357(6)	−0.1410(5)	0.4346(4)	0.081(2)
C(81)	1.3083(6)	0.1900(7)	0.0282(4)	0.095(2)
C(53)	0.8111(6)	−0.2213(5)	0.1547(3)	0.0688(16)
C(41)	0.7996(6)	−0.2049(5)	0.3478(4)	0.0721(17)
C(21)	0.9229(8)	0.3408(6)	0.5739(3)	0.094(2)
C(36)	0.6729(6)	0.2140(8)	0.5945(4)	0.094(2)
C(31)	0.5876(7)	0.3059(7)	0.5876(4)	0.088(2)
C(61)	0.5545(5)	0.3431(5)	0.0570(4)	0.0727(17)
N(3)	0.1454(7)	0.8707(4)	0.2202(4)	0.098(2)
O(6)	0.2611(6)	0.8605(4)	0.2255(3)	0.1128(18)
O(5)	0.1279(5)	0.8321(4)	0.1666(3)	0.1051(17)
O(4)	0.0695(6)	0.9363(6)	0.2544(3)	0.134(3)
O(2)	0.8102(3)	0.4260(3)	0.2715(2)	0.0649(10)
C(55)	0.7450(4)	−0.0260(4)	0.1656(2)	0.0438(11)
C(15)	1.1574(5)	0.1760(4)	0.3702(3)	0.0506(12)
C(14)	1.2283(5)	0.0785(5)	0.3408(3)	0.0624(14)
C(56)	0.6301(5)	−0.0377(5)	0.1870(3)	0.0619(15)
C(54)	0.8353(5)	−0.1199(4)	0.1494(3)	0.0554(13)
C(52)	0.6968(6)	−0.2309(5)	0.1765(4)	0.0720(17)
O(1)	0.6397(5)	0.5206(4)	0.3123(4)	0.145(3)
C(1)	1.3304(7)	0.5923(6)	0.2100(4)	0.086(2)
C(51)	0.6083(6)	−0.1382(5)	0.1923(4)	0.0774(18)
C(16)	1.2128(6)	0.2526(5)	0.3936(4)	0.0781(18)
C(2)	1.4347(9)	0.5660(8)	0.2121(5)	0.109(3)
C(13)	1.3505(6)	0.0585(6)	0.3349(4)	0.0834(19)
C(12)	1.4038(6)	0.1347(8)	0.3558(4)	0.093(2)
C(11)	1.3361(7)	0.2319(8)	0.3855(5)	0.105(3)

TABLE II Selected bonddistances (Å) and angles (°)

Cu(1)–N(1)	2.115(4)	Cu(1)–Cu(2)	2.9159(11)
Cu(1)–O(2)	2.174(4)	Cu(2)–O(3)	2.052(4)
Cu(1)–P(1)	2.2638(14)	Cu(2)–P(3)	2.2432(14)
Cu(1)–P(4)	2.2681(13)	Cu(2)–P(2)	2.2433(14)
N(1)–Cu(1)–O(2)	90.94(16)	P(1)–Cu(1)–Cu(2)	84.85(4)
N(1)–Cu(1)–P(l)	102.00(12)	P(4)–Cu(1)–Cu(2)	81.39(4)
O(2)–Cu(1)–P(1)	107.97(12)	O(3)–Cu(2)–P(3)	115.87(12)
N(1)–Cu(1)–P(4)	101.56(12)	O(3)–Cu(2)–P(2)	113.92(13)
O(2)–Cu(1)–P(4)	108.29(12)	P(3)–Cu(2)–P(2)	127.69(5)
P(1)–Cu(1)–P(4)	135.95(5)	O(3)–Cu(2)–Cu(1)	85.73(12)
N(1)–Cu(1)–Cu(2)	165.49(12)	P(3)–Cu(2)–Cu(1)	100.96(4)
O(2)–Cu(1)–Cu(2)	74.72(11)	P(2)–Cu(2)–Cu(1)	97.62(5)

parameters $a = 11.638(2)$, $b = 12.621(3)$, $c = 18.516(4)$ Å, $\alpha = 89.20(3)$ $\beta = 83.11(3)$, $\gamma = 76.00(3)°$, $V = 2619.5(9)$ Å^3, $D_c = 1.426\ \mathrm{g\,cm^{-3}}$, $Z = 2$, $\mu = 0.988\ \mathrm{mm^{-1}}$.

RESULTS AND DISCUSSION

Synthesis

Displacement of weakly bonded nitrate occurs rapidly upon mixing $[Cu(dppm)(NO_3)]_2$ with 4-vinylpyridine. Substitution is accompanied by an instantaneous dissolution and colour development by formation of the charge transfer complex $[Cu_2(dppm)_2(C_7H_7N)]^{2+}$. The resulting mixed-ligand complex $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}NO_3)](NO_3)$, is stable in air. The complex gave satisfactory C, H and N analyses, and has been characterized by IR, NMR and emission spectroscopy. In methanol, the title complex displays conductance which typifies a 1 : 1 electrolyte (86 S cm^2 mol^{-1}), confirming its binuclear nature. The title complex is obtained as an air-stable solid, soluble in organic solvents such as $MeNO_2$, MeOH and $CHCl_3$. At room temperature, the complex is diamagnetic, characteristic of the presence of copper(I). The e.s. mass spectrum of the, complex includes main peaks at $m/z = 956.3$ and 1062.9, corresponding to $[Cu_2(dppm)_2(NO_3)]^+$ and $[Cu_2(dppm)_2(C_7H_7N)(NO_3)]^+$, respectively.

IR Data and NMR Spectra

The IR spectrum (in CsI) of $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}NO_3)](NO_3)$ exhibits absorptions characteristic of dppm (1482 s, 1445 s, 1095 s, 781 m, 738 s, 716 m, and 692 s cm^{-1}) and 4-vinylpyridine (1633 w, 1610 s, 1583 m, 1570 m, 995 m, 930 m, 840 m). The band expected at 1380 cm^{-1} for dppm was not resolved due to the presence of a very intense nitrate band in the same region. In the 1500–1000 cm^{-1} range, characteristic absorption bands (1380 s, 1033 m cm^{-1}) of nitrate anion appear [5]. P-Ph absorption, at 1090–1100 cm^{-1}, shows an increase in frequency and intensity, compared to the free ligand, characteristic of P–metal coordination.

^{13}P NMR spectra at room temperature show a single resonance at $\delta = -10.9$ ppm, indicating that all phosphorus atoms are chemically equivalent, in accordance with the binuclear nature of the complex. The corresponding phosphorus resonance is shifted to higher field compared to that of free dppm ($\delta = -23$ ppm). This can be compared with that shown by a similar complex $[Cu_2(dppm)_2(MeCN)_4](BF_4)_2$ ($\delta = -9.5$ ppm) [6]. ^{13}C- and ^{1}H-NMR signals of dppm and 4-vinylpyridine in the complex are shifted slightly with respect to corresponding signals in the free ligand. The ^{13}C spectrum of the title complex shows resonances in the region 119–149 ppm due to the phenyl and 4-vinylpyridine, and a signal at 25.1 ppm assignable to methylene carbons of dppm. In addition, the ^{1}H-NMR spectrum of the complex $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}NO_3)](NO_3)$ has multiplets at 6.68–8.50 ppm due to phenyl and pyridine hydrogens, at 5.92–6.29 ppm due to vinyl hydrogens, and a singlet at 3.20 ppm, attributable to the methylene protons of the dppm ligand.

XPS and DTA-TG Analysis

XPS of the Complex $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}NO_3)](NO_3)$ gives information concerning copper–ligand binding. The binding energy of the title complex is as follows: C_{1s}

(286.0 eV), O_{1s} (532.7 eV), Cu_{2p} (934.5 eV), P_{2p} (133.6 eV), N_{1s} (398.6, 406.0 eV). The binding energy (P_{2p}) of the ligand in the complex is larger than in the free ligand [P_{2p} (dppm): 132.5 eV]. This is attributed to the electron density reduction at the P atom with the formation of the P–Cu bond. There are two N_{1s} peaks in the XPS. Peaks at 398.6 and 406.0 eV are assigned to nitrogen atoms from 4-vinylpyridine and nitrate respectively.

Thermogravimetric analyses indicate that the thermal stability of dppm increases upon coordination. TG-DTA reveals that pyrolytic decomposition takes place in two steps. The first corresponds to a weight loss of 10.1% and is probably due to decomposition of 4-vinylpyridine (loss of weight 9.3%) and is confirmed by a endothermic peak at 180–210°C. The second step at 220–600°C corresponds to a pronounced weight loss due to overall organic decomposition (residue weight 13.1%; calc. 14.1%), giving CuO as the final residue.

Luminescent Properties

Excitation of a solid sample of $Cu_2(dppm)_2(C_7H_7N)(NO_3)](NO_3)$ at $\lambda = 355$ nm at room temperature produces long-lived luminescence (475, 580 nm). There is extensive literature on the emission of related copper(I) complexes [7–9]. Several assignments, such as those involving a phosphine intraligand excited state, a ligand-to-metal charge transfer state, a metal-cluster-centred excited state, or combinations of these have been made in order to explain the emission spectra of copper(I) phosphine complexes [7]. The emission spectrum of the title complex (475 nm) is similar to that of other binuclear complexes such as $[Cu_2(dppm)_2(MeCN)_4](ClO_4)_2$ (482 nm) and $[Cu_2(dppm)_2(dmcn)]Cl_2$ (480 nm) [1]. Cu–Cu distances observed in the solid-state structure of the above complexes are different. If metal-cluster-centred transitions are involved, they are likely to be affected by Cu–Cu interactions. The invariance of the high-energy emission wavelength rules out the possibility of emission from such a metal-cluster-centred excited state. On the other hand, the invariance of the high-energy emissions bands (480–490 nm) in several $Cu_m(dppm)_m$ complexes has been used to assign this band to an emission originating from an intraligand phosphine excited state [8]. Based on a literature assignment of analogous compounds and our experimental observations, the high-energy emissions (475 nm) in the title complex is most likely associated with the phosphine excited state. The complex also exhibits another emission band maximum at 580 nm. The copper(I) centre is very electron-rich in nature and can be stabilized by ligands having π-acid character, viz PPh_3, bipy, phen, py and CN, etc. Since Cu(I) is reducing, metal-to-ligand charge transfer (MLCT) transitions can occur at relatively low energies if acceptor ligands such as pyridine are present. Complexes having the general formula $[Cu(PPh_3)_2(L)]^+$ (L = CN, bipy, py), are known to exhibit emission properties at both low and room temperature. Emissions of $[Cu(PPh_3)(phen)]^+$ and $[Cu(PPh_3)(bipy)]^+$ observed at 608 and 620 nm, respectively [10]. These were tentatively assigned as metal-to-ligand charge transfers. Thus, emission bands at 580 nm in $[Cu_2(dppm)_2(C_7H_7N)(NO_3)](NO_3)$ have also been assigned to a $d(Cu) \rightarrow \pi^*(L)$ metal-to-ligand charge transfer band (MLCT).

Structure $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}NO_3)](NO_3)$

The structure provides an interesting problem of stereochemistry amongst derivatives of d^{10} metal ions. The solid-state structure of the title compound can be described as

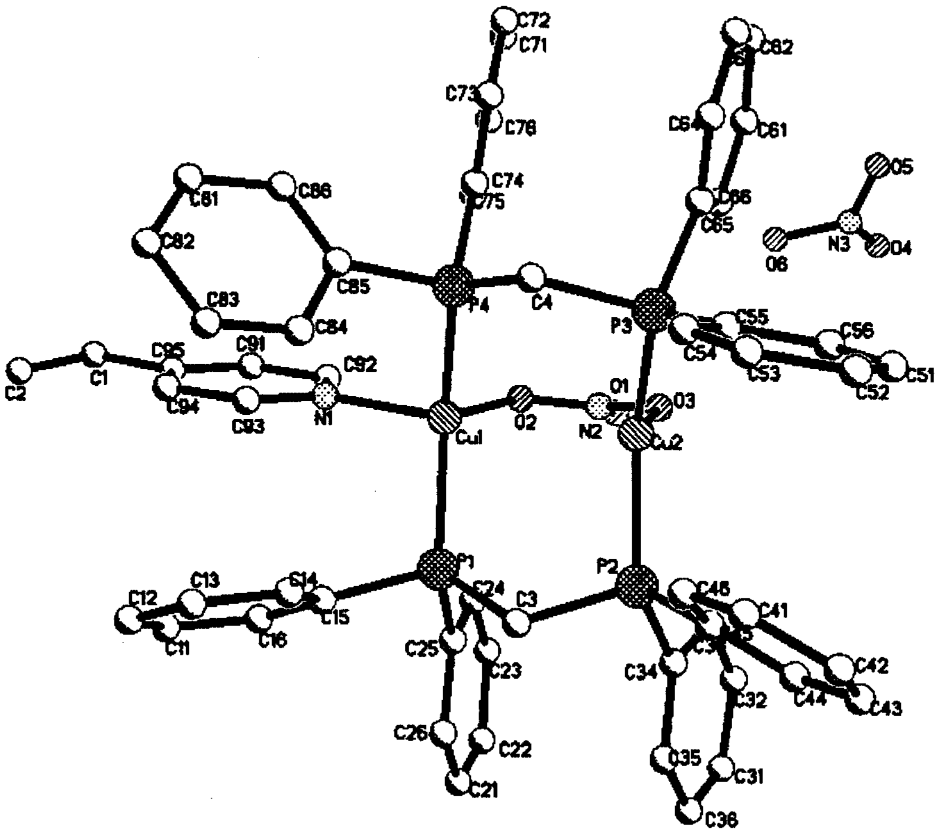

FIGURE 1 Perspective view of $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}NO_3)](NO_3)$.

a discrete cationic, $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}NO_3)]^+$ species and an isolated NO_3^- anion (Fig. 1). Two copper atoms are doubly bridged by two dppm ligands to form an eight-membered $Cu_2P_4C_2$ ring. Surprisingly, two copper atoms are coordinated in an asymmetric fashion. In $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}NO_3)](NO_3)$, the metal atoms are hold in close proximity by one nitrate anion acting as a bridge the other nitrate behaving as a free ion. As expected, Cu–P and P–Cu–P data compare favourably to those for other dppm complexes of Cu(I).

A comparison of the structural features of $Cu(NO_3)$ fragments involving nitrate coordination shows a significant lengthening of the Cu(1)–O(2) distance (2.174(4) Å) in $[Cu_2(dppm)_2(C_7H_7N)([\mu\text{-}NO_3)]^+$, due to the greater coordination number of Cu(1). Cu–P distances vary over a small range 2.243(1)–2.268(1) Å, and fall within the usual range for copper-dppm compounds so far synthesized: 2.242(3)–2.287(3) Å in $[Cu(OOCPh)(dppm)]_2$, 2.270(3)–2.283(3) Å in $[Cu_2(dppm)_2(MeCN)_4](C1O_4)_2$ and 2.245(7)–2.278(8) Å in $[Cu_3(dppm)_3(Cl)(WO_4)]$ [1,6,11]. The Cu···Cu separation in this complex [Cu (1)–Cu(2) 2.9159(11) Å] is shorter than that found in $[Cu(dppm)(NO_3)]_2$ (3.170(4) Å) due to the presence of μ-NO_3 in $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}NO_3)](NO_3)$. This distance is significantly longer than the sum of van der Waals raddi for copper (2.8 Å) suggesting that the copper atoms in the present compound are involved in any metal–metal interaction. N(2)–O(2) and N(2)–O(3) distances

(1.244(6) and 1.258(6) Å) are longer than the N(2)–O(1) distance (1.222(6) Å) because of the bridging nitrate anion.

The Cu(2) atom is coordinated by two phosphorus atoms of different dppm units and an oxygen atom of the bridging nitrate anion to give a three-coordinated copper centre with distorted trigonal planar geometry. Deviation of the copper atom from the least-squares plane of coordinated P(2), O(3) and P(3) atoms is 0.151 Å, with angles around the copper atom P(3)–Cu(2)–O(3) 115.87(12)°, P(3)–Cu(2)–P(2) 127.69(5)° and P(2)–Cu(2)–O(3) 113.92(13)°. In contrast, the tetrahedral geometry of the Cu(1) atom is satisfied by two phosphorus atoms of different dppm units, an oxygen atom of the nitrate anion and a nitrogen atom of 4-vinylpyridine. The coordination geometry around the Cu(1) atom is distorted tetrahedral, as illustrated by values of the angles around the Cu(1) atom, ranging from 90.94(16) to 135.95(5)°. Torsion angles with respect to the eight-membered $Cu_2(dppm)_2$ ring are as follows: P(2)Cu(2)Cu(1)N(1) (103.2(5)°), P(3)Cu(2)Cu(1)P(1) (131.98(5)°), P(2)Cu(2)P(3)C(4) (85.19(16)°) and Cu(2)Cu(1)P(4)C(4) (27.30(16)°). In $[Cu_2(dppm)_2(C_7H_7N)(NO_3)]^+$, conformations of the Cu(dppm)Cu fragments, as well as that of the Cu(1)O(2) N(2)O(3)Cu(2) bridge, are all approximately eclipsed and the eight-membered $Cu_2P_4C_2$ ring adopts a saddle conformation. C(3) and C(4) atoms are out by 0.7178 and 0.6985 Å from the plane P(1)Cu(1)Cu(2)P(2) and P(3)Cu(2)Cu(1)P(4), respectively. The dihedral angle between the least-squares planes through Cu(1)P(1)-P(2)Cu(2) and Cu(1)P(4)P(3)Cu(2) (130.7(4)°) gives a rough estimation of the bend of the saddle, whereas the two dihedral angles (115.3(6) and 109.4(6)°) formed by the latter planes with respect, to the least-squares plane through Cu(1)O(2)O(3)Cu(2), roughly display the asymmetric nature of the complex. This asymmetry may be due, at least in part to the structure of 4-vinylpyridine and the steric bulk of the phenyl groups of dppm. The conformation of the Cu(μ-dppm)Cu ring in $[Cu_2(dppm)_2\text{-}(C_7H_7N)(NO_3)]^+$ is similar to that found for the corresponding moiety in [Cu(dppm) $(SSCC_6H_4Me\text{-}o)]_2$ and $[Cu_2(dppm)_2(\mu\text{-mpyO})]^+$ [11]. In the latter compounds, the copper–copper separations are 3.426(3) and 2.679(6) Å, and folding extent of the eight-membered rings along the Cu···Cu direction was 135.0(1) and 124.8(2)°, respectively. The two unique P–Cu–P units in $[Cu_2(dppm)_2(C_7H_7N)(NO_3)](NO_3)$ are nonlinear and eclipsed. Inspection of structural parameters, such as angles around the copper ions, reveals steric constrains imposed on the system by the coordination of bulky ligands. Thus, the values of the P(1)–Cu(1)–P(4) and P(3)–Cu(2)–P(2) angles of 135.95(5) and 127.69(5)°, respectively, are significantly greater than the ideal values of 109.5° and 120°, decreasing interactions between phenyl rings on phosphorus.

Acknowledgments

We are grateful for financial support from National Natural Science Foundation of China (No. 20271017) and Henan Province Youth Science Foundation.

Supplementary Date

Full tables of bond lengths and angles, atomic coordinates and anisotropic thermal parameters are available from CCDC (CCDC 207324) on request.

References

[1] J.K. Bera, M. Nethaji and A.G. Samuelson, *Inorg. Chem.* **38**, 1725 (1999).
[2] R.N. Yang, Y.A. Sun and Y.M. Hou, *Inorg. Chim. Acta* **304**, 1 (2000)
[3] J. Diez, M.P. Gamasa, J. Gimeno and E. Lastra, *Organometallics* **12**, 2213 (1993).
[4] R.N. Yang, C.Y. Li and D.M. Jin, *Trans. Met. Chem.* **22**, 254 (1997).
[5] Kazuo Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds (Wiley, New York 1977), 244pp.
[6] J. Diez, M.P. Gamasa and J. Gimeno, *J. Chem. Soc. Dalton Trans.* 1275 (1987).
[7] V.W.W. Yam, *J. Photochem. Photobiol. A: Chemistry* **106**, 75 (1997).
[8] J.K. Bera, M. Nethaji and A.G. Samuelson, *Inorg. Chem.* **38**, 218 (1999).
[9] P.D. Harvey, M. Drouin and T. Zhang, *Inorg. Chem.* **36**, 498 (1997).
[10] M.T. Buckner, D.R. Mcmillin and J.C. Slater, *J. Chem. Soc. Chem. Commun.* 759 (1978).
[11] A.M.M. Lanfredi, F. Ugozzoli and A. Camus, *Inorg. Chim. Acta.* **206**, 173 (1993).