Synthesis and Characterization of an Unexpected Asymmetric Binuclear Copper(I) Complex Containing 4-Vinyl-pyridine

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The asymmetric binuclear copper(I) complex $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}HCOO)](NO_3)$ (dppm＝$Ph_2PCH_2PPh_2$, C_7H_7N＝4-vinyl-pyridine) has been prepared and characterized by physicochemical and spectroscopic methods. The complex is photoluminescent at room temperature. It crystallizes in triclinic system, space group *P*-1 with a＝1.2719(3) nm, b＝1.8637(4) nm, c＝1.1656(2) nm, α＝97.16(3)°, β＝104.94(3)°, γ＝89.39(3)°, V＝2.648.1(9) nm^3, D_c＝1.390 g•cm^{-3}, Z＝2, μ＝0.974 mm^{-1}, R＝0.0483 for 5716 independently observed reflections with $I>2\sigma(I)$. The structure consists of $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}HCOO)]^+$ cations and nitrate anions. The copper atoms show different coordination modes: Cu(1) displays a distorted trigonal and Cu(2) a tetrahedred geometry.

Keywords   copper, binuclear complex, 4-vinyl-pyridine

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, they contain *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.

A key feature in the chemistry of binuclear dppm complexes is the relatively stable, intrinsic $M_2(dppm)_2$ framework. These 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 the metal ion, but also the structure of the framework including the conformation of the $M_2(dppm)_2$ unit. The stable $M_2(dppm)_2$ framwork while subjected 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, the unusual reactivity for carbon disulfide was first discovered in the bimetallic dppm complex $[Cu(dppm)(NO_3)]_2$.[2] To the best of our knowledge, asymmetrical 4-vinyl-pyridine $Cu_2(dppm)_2$ complex is extremely rare. Herein, is presented the first report on the preparation

and structure of an asymmetrical coordination binuclear copper(I) 4-vinyl-pyridine complex $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}HCOO)](NO_3)$, which was obtained by treating the complex $[Cu_2(dppm)_2(HCOO)(NO_3)]$ with 4-vinyl-pyridine.

Experimental

Materials

The compound $[Cu_2(dppm)_2(HCOO)(NO_3)]$ was prepared according to the literature procedure.[4a] Solvents were dried and purified by standard methods. All other chemicals were of reagent grade, obtained from commercial sources and used without further purification.

Physical measurements

Elemental analyses were carried out using an ERBA-1106 instrument (Italy). Cu and P contents were determined using a JA96-970 spectrometer (Inductively Coupled Plasmas Atomic Emission Spectrometer). IR spectra were recorded on a Nicolet 170SX IR spectrophotometer. Conductivity measurement was carried out in methanol solution at 25 ℃ using a Shanghai DDS-11A conductivity meter and a DJS-1 type Pt black electrode. Melting point was determined on an electrothermal apparatus and 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 spectrum was recorded on a PE-TGS-2 instrument. Electrospray mass spectra

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(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 ℃, 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. High voltage, electric current and vacuum were set at 12.5 kV, 20 mA and 6×10^{-8} mbar, respectively. The emission spectrum was recorded on a luminescence spectrophotometer (Aminco Bowman Series 2).

Preparation of the complex of $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-HCOO})](NO_3)$

4-Vinyl-pyridine (2 mL) was added with stirring to a solution of $[Cu_2(dppm)_2(HCOO)(NO_3)]$ (0.501 g, 0.5 mmol) in methanol (30 mL). 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 6—10 mL. Yellow crystals suitable for X-ray studies were obtained and identified as $[Cu_2(dppm)_2(C_7H_7N)(HCOO)](NO_3)$. Yield 56%, m.p. 190 ℃. ^{1}H NMR (300 MHz, CDCl$_3$) δ: 3.20 (s, 4H, CH$_2$ of dppm), 6.68—8.12 (m, 44H, C$_6$H$_5$, C$_5$H$_4$N), 6.26—6.33 (m, 1H, CH of CH=CH$_2$), 5.37—5.88 (m, 2H, CH$_2$ of CH=CH$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$) δ: -10.1 (s); IR (CsI) ν: for NO$_3^-$: 1380 s, 1033 m cm^{-1}; for 4-vinyl-pyridine: 1633 w, 1610 s, 1583 m, 1570 m, 995 m, 930 m, 840 m cm^{-1}; for HCOO$^-$: 1585 s, 1369 m cm^{-1}. Anal. calcd for C$_{58}$H$_{52}$N$_2$O$_5$P$_4$Cu$_2$: C 62.87, H 4.73, N 2.53, P 11.18, Cu, 11.47; found C 62.56, H 4.49, N 2.61, P 11.21, Cu 11.26.

X-ray structure determinations

A yellow prismatic crystal (0.28 mm×0.20 mm× 0.20 mm) was selected, mounted on a glass fiber and set on a Rigaku RAXIS-IV X-ray diffractometer equipped with an imaging plate area detector. Data were collected with graphite monochromated Mo Kα radiation ($\lambda =$ 0.071073 nm) at temperature of (291 ± 1) K to a maximum 2θ value of 55.0°. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was also applied. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. A total of 8443 reflections was collected. The final cycle of full-matrix least-squares refinement was based on 5716 observed reflections [$I > 2\sigma(I)$] and 653 variable parameters. The function minimized was $w = 1/[\sigma^2 F_o^2 + (0.0619P)^2 + 0.0000P]$, where $P = 1/3(F_o^2 + 2F_c^2)$. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. Crystal data are given in Table 1. Final atomic coordinates for all non-hydrogen atoms and equivalent thermal parameters are listed in Table 2.

Table 1 Crystal data and structure refinement for the title compound

Empirical formula	C$_{58}$H$_{52}$Cu$_2$N$_2$O$_5$P$_4$
Formula weight	1107.98
Temperature	291(2) K
Wavelength	0.071073 nm
Crystal system, space group	Triclinic, *P*-1
Unit cell dimensions	$a = 1.2719(3)$ nm, $\alpha = 97.16(3)°$ $b = 1.8637(4)$ nm, $\beta = 104.94(3)°$ $c = 1.1656(2)$ nm, $\gamma = 89.39(3)°$
Volume	2.6481(9) nm^3
Z, Calculated density	2, 1.390 Mg/m^3
Absorption coefficient	0.974 mm^{-1}
F(000)	1144
Crystal size	0.28 mm×0.20 mm×0.20 mm
θ Range for data collection	1.10° to 27.52°
Index ranges	$0 \leqslant h \leqslant 16$, $-24 \leqslant k \leqslant 24$, $-15 \leqslant l \leqslant 14$
Reflections collected/unique	8443/8443 [R(int)$=0.0000$]
Completeness to $2\theta = 27.52$	86.92%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8443/0/653
Goodness-of-fit on F^2	1.025
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0483$, $wR_2 = 0.1092$
R indices (all data)	$R_1 = 0.0919$, $wR_2 = 0.1223$
Extinction coefficient	0.0012(3)
Largest diff. peak and hole	541 and -640 e·nm^{-3}

Result and discussion

Synthesis

The displacement of the weakly-bonded nitrate occurred rapidly upon mixing $[Cu_2(dppm)_2(HCOO)(NO_3)]$ with free 4-vinyl-pyridine. The substitution was accompanied by an almost instantaneous dissolution and color development by the charge transfer $[Cu_2(dppm)_2\text{-}(C_7H_7N)]^{2+}$ complex upon introduction of 4-vinyl-pyridine. The resulting mixed-ligand complex $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-HCOO})](NO_3)$, is stable to air oxidation and ligand dissociation. The complex gave satisfactory C, H and N analyses, and was characterized by IR, NMR and emission spectroscopy. In methanol, the title complex displays conductance which typifies a 1 : 1 electrolyte (81 S·cm^2·mol^{-1}), confirming its binuclear nature. The title complex was obtained as air-stable solid, soluble in organic solvents, such as MeNO$_2$, CH$_2$Cl$_2$ and CHCl$_3$. The mass spectrum of the title complex includes main peaks at $m/z = 940.3$ and 1045.9, corresponding to the ion $[Cu_2(dppm)_2(HCOO)]^+$ and $[Cu_2(dppm)_2(C_7H_7N)(HCOO)]^+$, respectively.

IR data and NMR spectra

The IR spectrum (in CsI pellet) of the mixed-ligand

4-Vinyl-pyridine

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Table 2 Final coordinate ($\times 10^4$) for the non-hydrogen atoms and equivalent isotropic thermal parameters ($\times 10^3$)

Cu(1)	3007(1)	2228(1)	−2580(1)	40(1)	C(26)	3210(4)	3900(2)	1291(4)	37(1)
Cu(2)	2037(1)	2411(1)	−515(1)	38(1)	C(27)	4006(4)	3527(3)	031(4)	50(1)
P(1)	3826(1)	1175(1)	−2197(1)	37(1)	C(28)	4332(4)	3742(3)	3240(5)	64(2)
P(2)	2803(1)	1334(1)	−90(1)	37(1)	C(29)	3857(5)	4323(3)	3749(5)	68(2)
P(3)	2776(1)	3542(1)	−303(1)	34(1)	C(30)	3084(6)	4690(3)	3033(5)	87(2)
P(4)	3886(1)	3303(1)	−2337(1)	36(1)	C(31)	2750(5)	4480(3)	1810(4)	67(2)
O(1)	1451(3)	2157(2)	−3534(3)	57(1)	C(32)	1826(4)	4226(2)	−942(4)	37(1)
O(2)	666(3)	2253(2)	−1999(3)	55(1)	C(33)	2166(4)	4925(2)	−996(4)	45(1)
O(3)	4176(6)	7644(3)	9161(5)	174(3)	C(34)	1422(4)	5430(2)	−1438(4)	52(1)
O(4)	3359(4)	6666(3)	8656(4)	104(2)	C(35)	332(5)	5247(3)	−1813(5)	65(2)
O(5)	3584(3)	7257(2)	7293(4)	79(1)	C(36)	−10(4)	4562(3)	−1769(5)	71(2)
C(1)	3097(4)	344(2)	−3002(4)	44(1)	C(37)	736(4)	4047(2)	−1335(4)	53(1)
C(2)	3457(5)	−344(3)	−2733(5)	72(2)	C(38)	3205(4)	4021(2)	−3175(4)	41(1)
C(3)	2871(6)	−962(3)	−3317(6)	85(2)	C(39)	2167(5)	3890(3)	3913(4)	56(1)
C(4)	1944(6)	−897(3)	−4199(6)	83(2)	C(40)	1593(5)	4439(3)	−4491(5)	69(2)
C(5)	1591(5)	−227(4)	−4490(5)	78(2)	C(41)	2069(5)	5118(3)	−4320(5)	66(2)
C(6)	2165(4)	397(3)	−3898(4)	51(1)	C(42)	3092(5)	5255(3)	−3613(5)	60(2)
C(7)	5193(4)	1087(2)	−2425(4)	39(1)	C(43)	3682(4)	4704(2)	−3044(4)	49(1)
C(8)	6036(4)	1527(3)	−1719(5)	58(1)	C(44)	5275(4)	3316(2)	−2540(4)	38(1)
C(9)	7048(5)	1518(3)	−1944(5)	71(2)	C(45)	5387(4)	3103(3)	−3686(4)	55(1)
C(10)	7239(5)	1072(3)	−2897(5)	66(2)	C(46)	6408(5)	3077(3)	−3908(5)	66(2)
C(11)	6423(5)	638(3)	−3612(6)	79(2)	C(47)	7319(5)	3262(3)	−2998(5)	63(2)
C(12)	5402(5)	638(3)	−3387(5)	64(2)	C(48)	7214(4)	3474(3)	−1853(5)	59(1)
C(13)	4041(4)	1088(2)	−593(4)	39(1)	C(49)	6194(4)	3497(3)	−1621(4)	51(1)
C(14)	1911(4)	526(2)	−618(4)	40(1)	C(50)	4027(3)	3681(2)	−776(3)	36(1)
C(15)	2290(5)	−150(3)	−393(6)	76(2)	C(51)	−58(4)	2562(2)	363(5)	47(1)
C(16)	1613(5)	−760(3)	−840(7)	86(2)	C(52)	−698(4)	2668(2)	1149(5)	49(1)
C(17)	564(5)	−680(3)	−1489(5)	73(2)	C(53)	−241(4)	2795(2)	2368(5)	51(1)
C(18)	180(5)	−10(3)	−1705(5)	69(2)	C(54)	889(4)	2806(3)	2737(4)	53(1)
C(19)	864(4)	595(2)	−1266(4)	51(1)	C(55)	1495(4)	2698(2)	1902(4)	51(1)
C(20)	3216(4)	1307(2)	1538(4)	44(1)	C(56)	-929(5)	2905(3)	3229(5)	66(2)
C(21)	4193(4)	1585(3)	2243(4)	56(1)	C(57)	-653(7)	2918(4)	4338(7)	89(2)
C(22)	4400(5)	1647(3)	3494(5)	68(2)	C(58)	664(5)	2165(3)	−3062(5)	53(1)
C(23)	3629(6)	1444(3)	4022(5)	79(2)	N(1)	1032(3)	2578(2)	714(3)	44(1)
C(24)	2650(6)	1164(4)	3330(6)	88(2)	N(2)	3691(4)	7214(3)	8391(5)	72(1)
C(25)	2439(5)	1090(3)	2078(5)	68(2)					

complex [Cu$_2$(dppm)$_2$(C$_7$H$_7$N)(μ-HCOO)](NO$_3$) exhibits the expected absorptions characteristic of dppm (1482 s, 1445 s, 1095 s, 781 m, 738 s, 716 m, 692 s cm^{-1}) and 4-vinyl-pyridine (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 in the title complex due to the presence of the very intense nitrate band in the same region. In the range of 1500—1000 cm^{-1}, the characteristic absorption bands (1380s, 1033m cm^{-1}) of free nitrate anion appear,[5] exhibiting a broad band at 1380 cm^{-1}. The P—Ph absorption, in the range of 1090—1100 cm^{-1}, shows an increase in frequency and intensity, characteristic of P-metal coordination. The strong band at 1585 and weak band at 1369 cm^{-1} are assignable to v_{as}(CO$_2$) and v_s(CO$_2$), respectively. The large gap (216 cm^{-1}) between the two bands indicates a bidentate mode of coordination of the carboxylate group.[5]

The ^{31}P NMR spectrum of the title complex at room temperature shows a single resonance at δ −10.1, indicating that all phosphorus atoms are chemically equivalent, which is also in accordance with the binuclear nature of the complex. The corresponding phosphorus resonance is shifted to a higher field compared to that of free dppm (δ −23). This chemical shift can be compared with that shown by similar complex

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$[Cu_2(dppm)_2(MeCN)_4](BF_4)_2$ (δ -9.5).[6] The ^{13}C spectrum of the title complex shows resonance in the range of δ 119—149 due to the phenyl and 4-vinyl-pyridine, and a signal at 25.1 assignable to methylene carbons of dppm, respectively. In addition, the ^1H NMR spectrum of the complex $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}HCOO)](NO_3)$ has a multiplet at about δ 6.68—8.12 due to the phenyl and pyridine hydrogens, δ 5.37—6.29 due to the vinyl hydrogens, and a singlet at δ 3.20 which is attributable to the methylene protons of the dppm ligand.

XPS and DTA-TG analysis

XPS of the complex $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}HCOO)](NO_3)$ 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} (133.5eV), N_{1s} (398.5, 406.0 eV). The binding energy (P_{2p}) of the ligand in the complex is larger than the relative value of the free ligand [P_{2p} (dppm): 132.5 eV]. This is attributed to the electronic density reduction of the P atom because of the formation of the P→Cu bond in $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}HCOO)](NO_3)$. There are two N_{1s} peaks in the XPS data. The N_{1s} peaks at 398.5 and 406.0 eV are assigned to the nitrogen atom from 4-vinyl-pyridine and to the nitrogen atom from nitrate anion, respectively. The area ratio of the two peaks is 1 : 1, consistent with the composition of the complex $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}HCOO)](NO_3)$.

The results of the thermo-gravimetric analyses of the title complex, compared with those of free dppm, indicate that the thermal stability of dppm increases upon coordination. The TG-DTA thermogram of the complex reveals that the pyrolytic decomposition takes place in two steps. The first corresponds to a weight loss of 9.9% and is probably due to decomposition of the ligand 4-vinyl-pyridine (loss of weight calcd. 9.5%) and is confirmed by an endothermic peak in 180—210 ℃. The second step in 220—600 ℃ range corresponds to, a pronounced weight loss due to the decomposition of the organic moiety, residue weight (exp. 13.1%; calcd 14.3%), giving CuO as final residue.

Luminescent property

Excitation of a solid sample of the complex $[Cu_2(dppm)_2(C_7H_7N)(HCOO)](NO_3)$ at $\lambda=355$ nm at room temperature produces long-lived luminescence (480, 585 nm). Several assignments such as those involving a phosphine intra-ligand excited state, a ligand-to-metal charge transfer state, a metal-cluster-centered excited state or combinations of these have been made in order to explain the emission spectra of copper(I) phosphine complexes.[7-9] The emission spectrum of the title complex (480 nm) is similar to that of other binuclear complexes, such as $[Cu_2(dppm)_2(MeCN)_4](ClO_4)_2$ (482 nm), $[Cu_2(dppm)_2(dmcn)]Cl_2$ (480 nm).[1] If metal-cluster-centered transitions are involved, they are likely to be effected by Cu—Cu interactions. The invariance of the high-energy emission wavelength rules out the possibility of emission from such a metal-cluster-centered excited state. On the other hand, the invariance of the high-energy emission band (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 observation, the high-energy emission (480 nm) in the title complex is most likely associated with the phosphine excited state. Beside this band, the complex $[Cu_2(dppm)_2(C_7H_7N)(HCOO)](NO_3)$ also exhibits another emission band maximum at 585 nm. The copper(I) center, a d^{10} system, 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 copper(I) is reductive metal-to-ligand charge transfer (MLCT) transitions can occur at relatively low energies if acceptor ligands such as pyridine, polypyridyls are present. Complexes having general formula $[Cu(PPh_3)_2(L)]^+$ ($L=CN^-$, bipy, py), are known to exhibit emission properties both at low and room temperature. Emissions of the $[Cu(PPh_3)(phen)]^+$ and $[Cu(PPh_3)(bipy)]^+$ complexes are observed at 608 and 620 nm, respectively.[10] These emissions were tentatively assigned as metal-to-ligand charge transfers. Thus, the emission bands at 585 nm in $[Cu_2(dppm)_2(C_7H_7N)(HCOO)](NO_3)$ have also been assigned as a $d(Cu)\rightarrow\pi^*(L)$ metal-to-ligand charge transfer band (MLCT).

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

Selected bond lengths and angles are given in Table 3. The solid-state structure of the title compound can be described as a discrete cationic $[Cu_2(dppm)_2(C_7H_7N)\text{-}(\mu\text{-}HCOO)]^+$ species and an isolated NO_3^- anion (Figure 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 $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}HCOO)](NO_3)$, the metal atoms are held in a closer proximity by one $HCOO^-$ anion acting as a bridging through both the oxygen atoms, and the nitrate anion behaving as a free anion.

A comparison of the structural features of Cu(HCOO) fragments involving $HCOO^-$ coordination shows a significant lengthening of the Cu(2)—O(2) distance due to the greater coordination number of the Cu(2) metal center. The Cu—P distances vary over a small range 0.22523(13)—0.22768(13) nm. The Cu—P bond distances [0.22523(13)—0.22768(13) nm] fall within the usual range for copper-dppm compounds so far synthesized: 0.2242(3)—0.2287(3) nm in $[Cu(OOCPh)\text{-}(dppm)]_2$, 0.2270(3)—0.2283(3) nm in $[Cu_2(dppm)_2(MeCN)_4](ClO_4)_2$ and 0.2245(7)—0.2278(8) nm in $[Cu_3(dppm)_3(Cl)(WO_4)]$.[1,6,11] The Cu···Cu separation in this complex [Cu(1)—Cu(2) 0.29584 (10) nm] is shorter than that found in complex $[Cu(dppm)(NO_3)]_2$ [0.3170(4) nm] due to the presence of μ-HCOO in $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-}HCOO)](NO_3)$. This distance is significantly longer than the sum of van der Waals radii

Table 3 Selected bond distances (10^{-1} nm) and angles (°)

Cu(1)—O(1)	2.001(4)	P(2)—C(13)	1.851(4)
Cu(1)—P(1)	2.2523(13)	P(3)—C(26)	1.836(4)
Cu(1)—P(4)	2.2546(14)	P(3)—C(32)	1.838(4)
Cu(1)—Cu(2)	2.9584(10)	P(3)—C(50)	1.844(4)
Cu(2)—O(2)	2.109(3)	P(4)—C(50)	1.831(4)
Cu(2)—N(1)	2.146(4)	P(4)—C(38)	1.833(4)
Cu(2)—P(3)	2.2756(13)	P(4)—C(44)	1.842(5)
Cu(2)—P(2)	2.2768(13)	O(1)—C(58)	1.259(6)
P(1)—C(7)	1.829(5)	O(2)—C(58)	1.229(6)
P(1)—C(1)	1.833(5)	O(3)—N(2)	1.172(6)
P(1)—C(13)	1.847(4)	O(4)—N(2)	1.214(5)
P(2)—C(14)	1.838(4)	O(5)—N(2)	1.263(6)
P(2)—C(20)	1.841(5)		
O(1)-Cu(1)-P(1)	116.27(10)	C(14)-P(2)-C(13)	104.0(2)
O(1)-Cu(1)-P(4)	117.63(10)	C(20)-P(2)-C(13)	104.5(2)
P(1)-Cu(1)-P(4)	124.63(5)	C(14)-P(2)-Cu(2)	116.37(14)
O(1)-Cu(1)-Cu(2)	83.45(11)	C(20)-P(2)-Cu(2)	110.55(15)
P(1)-Cu(1)-Cu(2)	96.77(4)	C(13)-P(2)-Cu(2)	117.63(13)
P(4)-Cu(1)-Cu(2)	100.83(5)	C(26)-P(3)-C(32)	102.8(2)
O(2)-Cu(2)-N(1)	91.89(15)	C(26)-P(3)-C(50)	101.21(19)
O(2)-Cu(2)-P(3)	111.21(9)	C(32)-P(3)-C(50)	105.71(18)
N(1)-Cu(2)-P(3)	100.25(10)	C(26)-P(3)-Cu(2)	109.71(13)
O(2)-Cu(2)-P(2)	110.55(10)	C(32)-P(3)-Cu(2)	114.94(15)
N(1)-Cu(2)-P(2)	101.70(10)	C(50)-P(3)-Cu(2)	120.26(14)
P(3)-Cu(2)-P(2)	131.61(5)	C(50)-P(4)-Cu(1)	105.80(13)
O(2)-Cu(2)-Cu(1)	76.81(10)	C(38)-P(4)-Cu(1)	118.50(16)
N(1)-Cu(2)-Cu(1)	168.26(11)	C(44)-P(4)-Cu(1)	118.67(14)
P(3)-Cu(2)-Cu(1)	81.29(4)	C(58)-O(1)-Cu(1)	123.1(4)
P(2)-Cu(2)-Cu(1)	85.47(4)	C(58)-O(2)-Cu(2)	127.0(4)
C(7)-P(1)-C(1)	104.7(2)	O(2)-C(58)-O(1)	129.5(5)
C(7)-P(1)-C(13)	103.4(2)	C(51)-N(1)-C(55)	117.0(4)
C(1)-P(1)-C(13)	105.5(2)	C(51)-N(1)-Cu(2)	123.1(3)
C(7)-P(1)-Cu(1)	115.80(13)	C(55)-N(1)-Cu(2)	119.9(3)
C(1)-P(1)-Cu(1)	116.98(16)	O(3)-N(2)-O(4)	118.5(6)
C(13)-P(1)-Cu(1)	109.14(14)	O(3)-N(2)-O(5)	123.5(6)
C(14)-P(2)-C(20)	102.0(2)	O(4)-N(2)-O(5)	117.7(5)

for copper (0.28 nm), suggesting that the copper atoms in the present compound are not involved in metal-metal interaction.

The Cu(1) atom is coordinated to two phosphorus [0.2109(3) nm] in $[Cu_2(dppm)_2(C_7H_7N)(\mu\text{-HCOO})]^+$, atoms of different dppm units and an oxygen atom of the bridging $HCOO^-$ anion to give a three-coordinated copper center with a distorted trigonal planar geometry. The deviation of the copper atom from the least-squares plane of coordinated P(1), O(1) and P(4) atoms is nearly 0.01519 nm, indicative of height distortion, with angles around the copper atom P(1) — Cu(1) — O(1) 116.27(10)°, P(4)—Cu(1)—P(1) 124.63(5)° and P(4)—

Cu(1)—O(1) 117.63(10)°. In contrast, the tetrahedral geometry of Cu(2) atom is satisfied by two phosphorus atoms of different dppm units, an oxygen atom of the $HCOO^-$ anion and a nitrogen atom from 4-vinyl-pyridine. The coordination geometry around the Cu(2) atom is distorted tetrahedral, as is illustrated by the values of the angles around the Cu(2) atom which range from 91.89(15) to 131.61(5)°. The torsion angles with respect to the related eight-membered $Cu_2(dppm)_2$ ring are as follows: P(1)—Cu(1)—Cu(2)—P(3) [131.98(5)°], P(4)—Cu(1)—Cu(2)—P(3) [4.73(5)°], P(1)—Cu(1)—Cu(2)—P(2) [— 1.34(5)°], P(4) — Cu(1) — Cu(2) — P(2) [−128.60(5)°]. The C(13) and C(50) atoms are out by

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0.07178 and 0.06985 nm 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 bending of the saddle, whereas the two dihedral angles [115.3(6)° and 109.4(6)°], formed by latter planes with respect to the least-squares plane through Cu(1)O(1)O(2)Cu(2), roughly display the asymmetric property of the complex. This asymmetry may be due, at least in part, to asymmetric structure of 4-vinyl-pyridine and the steric bulk of the phenyl groups of dppm. The conformation of the Cu(μ-dppm)Cu ring in [Cu$_2$(dppm)$_2$(C$_7$H$_7$N)(HCOO)]$^+$ is similar to that found for the corresponding moiety in [Cu(dppm)(SSCC$_6$H$_4$Me-*o*)]$_2$ and [Cu$_2$(dppm)$_2$(μ-mpyO)]$^+$ cationic complex.[11] In the latter compounds, the copper-copper separations were 0.3426(3) and 0.2679(6) nm, and the folding 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$_7$H$_7$N)(HCOO)](NO$_3$) are nonlinear and eclipsed. Inspection of some structural parameters, such as the values of the angles around the copper ions, reveals the 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 124.63(5)° and 131.61(5)°, respectively, are significantly greater than the ideal values of 109.5° and 120°, decreasing the interactions between the phenyl rings on the phosphorus atoms.
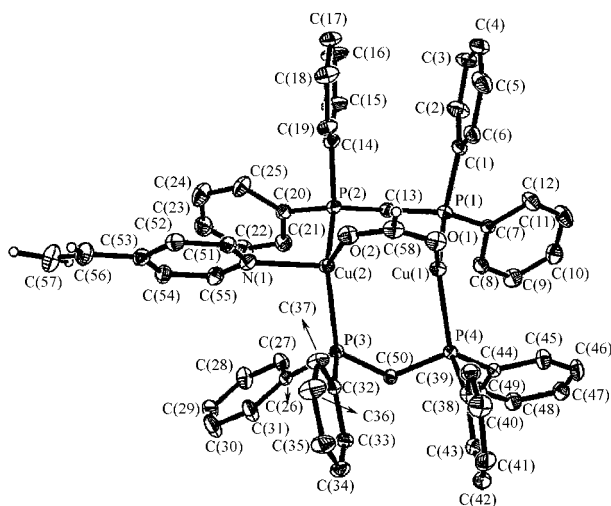
functions as monodentate ligand to the Cu(2) atom.

In summary, the present results show that the reaction of [Cu$_2$(dppm)$_2$(HCOO)(NO$_3$)] with 4-vinyl-pyridine results in the formation of the asymmetrical complex [Cu$_2$(dppm)$_2$(C$_7$H$_7$N)(μ-HCOO)](NO$_3$). This was confirmed by X-ray structural analysis. The M$_2$(dppm)$_2$ framework in the title complex is found to be quite flexible, exhibiting folding angles ranging from 124.63(5)° to 131.61(5)° in the solid state. The flexibility of the M$_2$P$_4$ 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. In addition, the unit [Cu$_2$(dppm)$_2$(C$_7$H$_7$N)(μ-HCOO)]$^+$ suggests yet another mode for the binding of small ligands by M$_2$(dppm)$_2$ complexes, and also provides a very convenient entry point for the synthesis and study of such molecules. In the [Cu$_2$(dppm)$_2$(C$_7$H$_7$N)(μ-HCOO)](NO$_3$) species, the structural parameters of the HCOO$^-$ bridge, which furnishes one oxygen atom to the tetrahedral coordination of Cu(2) and another to the trigonal arrangement of Cu(1), are in the usual range and reflect the asymmetric bonding mode of the HCOO$^-$. Although the initial aim of this reaction was to form a binuclear dppm compound as a model for the catalytic activation of 4-vinyl-pyridine, the novel copper(I) complex [Cu$_2$(dppm)$_2$(C$_7$H$_7$N)(μ-HCOO)](NO$_3$) which was obtained instead is interesting by itself for other research areas.

Figure 1 Perspective view of [Cu$_2$(dppm)$_2$(C$_7$H$_7$N)(μ-HCOO)]$^+$.

With respect to the associated phenyl moiety, they are quite coplanar, with maximum and average deviations of the ring carbon atoms being 0.001 and 0.00015 nm, respectively. The pyridine rings are essentially planar, with the C(56) atom lying approximately in the plane (0.00053 nm) of the pyridine ring to which it is bound, but the C(57) atom is out of the plane (by 0.0200 nm) of the pyridine ring. Not only do the copper atoms have different environments, but one 4-vinyl-pyridine

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