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Synthesis, Structure, and NMR Spectra of $[Cu_2(phen)_2(\mu\text{-}(C_6H_5)_2PCH_2P(C_6H_5)_2)_2](PF_6)_2$ and Its Derivatives

Susumu Kitagawa,* Hideki Maruyama, Shigetoshi Wada, Megumu Munakata,
Masaki Nakamura, and Hideki Masuda†
Department of Chemistry, Kinki University, Higashi-Osaka 577
† Institute for Molecular Science, Okazaki 444

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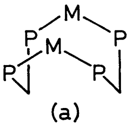
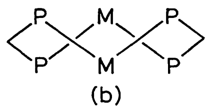
The bis(diphenylphosphino)methane(dppm) compounds of copper(I), $[Cu_2(\mu\text{-dppm})_2(biL)_2](PF_6)_2$ (biL=1,10-phenanthroline and its derivatives), have been synthesized and characterized by ^1H and ^{31}P NMR spectroscopy and X-ray crystallography. The molecules are found to contain a $[Cu_2(dppm)_2]^{2+}$ framework with the two copper atoms bridged by two dppm ligands to give eight-membered $Cu_2P_4C_2$ rings. This framework shows a staggered conformation subject to the coordination of additional ligands, biL. The coordination ^1H and ^{31}P shifts of the dppm are well-correlated with the basicity of the nitrogen donor atom of biL, sensitive to variations in the copper-ligand binding as well as their metal-to-ligand charge-transfer band. Crystallographic data of $[Cu_2(dppm)_2(phen)_2]$ are as follows. monoclinic space group $P2_1/c$, $a=11.515(2)$ Å, $b=27.922(4)$ Å, $c=12.493(2)$ Å, $\beta=107.68(1)°$, $U=3827(1)$ Å^3, and $Z=2$.

Bis(diphenylphosphino)methane (dppm) has served to afford an eight-membered ring dimer, $M_2P_4C_2$ of M_2 (μ-dppm)$_2$. This stable framework adopts the three conformations shown below. The group IB metal monocation (Cu^+, Ag^+, and Au^+) gives this framework with an eclipsed (a) and (c), and a staggered (b) conformation; type (a) is found in $[Cu_2(\mu\text{-dppm})_2L_n]$ ($L=CH_3CN$ ($n=4$),[1] S$_2$ct ($n=2$)[2]) and $[Ag_2(\mu\text{-dppm})_2(NO_3)_2]$;[3] type (b) is found in $[Au_2(\mu\text{-dppm})_2Cl_2]$.[4] 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 $M_2(dppm)_2$. There are sparse literature data concerning investigations of the structure and properties of the $Cu_2(dppm)_2$ framework in relation to the additional ligand. In the present work, 1,10-phenanthroline (phen) and its derivatives were used as an additional ligand (biL), from which copper(I) complexes of $[Cu_2(\mu\text{-dppm})_2(biL)_2]^{2+}$ were synthesized. Their geometrical and electronic structures have been characterized by NMR spectroscopy and X-ray crystallography.


(a)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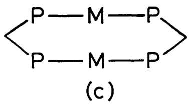

(c)

Experimental

Materials. $[Cu(CH_3CN)_4]PF_6$ was synthesized according to a method described in the literature.[5] Bis(diphenylphosphino)methane (dppm), 1,10-phenanthroline (phen) and its derivatives were obtained from Aldrich Co.

All operations were carried out under dry and purified argon by using the standard Schlenk or vacuum-line technique.

Preparation of $[Cu_2(\mu\text{-dppm})_2(phen)_2](PF_6)_2$. A 10 cm^3 acetone solution of phen (0.180 g, 1.0 mmol) and dppm (0.384 g, 1.0 mmol) was added to $[Cu(CH_3CN)_4]PF_6$ (0.373 g, 1.0 mmol), and the mixture stirred for 1 h. The resultant pale-yellow clear solution was transferred into a glass tube (7 mm inner diameter). The pale-yellow crystals were obtained after standing for 24 h at room temperature. Although most of the crystals were not suitable for X-ray crystallographic measurements, a few crystals were used.

Other phen derivatives, $[Cu_2(\mu\text{-dppm})_2(phen)_2](PF_6)_2$, were also prepared in a similar way.

Physical Measurements. The electronic absorption spectra were obtained with a Hitachi 200-10 spectrophotometer for an acetone solution in 1-cm quartz cells.

The ^1H NMR spectra were obtained on a JEOL FX200 NMR spectrometer operating in the Fourier-transform mode (16 K data points transform of 2500 Hz spectral width after 200—500 puleses) at 23 °C. ^{31}P NMR spectra were measured at 23 °C without ^1H irradiation. Between 20—50 K transients were accumulated using a 18.0 μs pulse (90°): 16 K data points were collected over a band width of 4 kHz. H_3PO_4 (85%) was used as an external standarad.

Crystallography. Crystal Data. $C_{80}H_{72}Cu_2N_4O_2F_{12}P_6$, monoclinic, space group $P2_1/c$, $a=11.515(2)$, $b=27.922(4)$, $c=12.493(2)$ Å, $\beta=107.68(1)$°, $U=3827(1)$ Å^3, $Z=2$, $D_c=1.442$ g cm^{-3}, $F(000)=1704$, $\lambda(MoK\alpha)=0.71069$ Å, $\mu=7.56$ cm^{-1}, $T=23$ °C.

X-Ray Data Collection. A single crystal (0.5×0.4×0.4 mm) of the compound was glued on top of a glass fiber and then studied on a Rigaku AFC5R automatic diffractometer. Unit-cell constants and an orientation matrix for data collection, obtained from a least squares refinement using the setting angles of 25 carefully centered reflections over the range $20°<2\theta<32°$, corresponded to a monoclinic cell.

The space group $P2_1/c$ was chosen on the basis of the observed systematic absences ($h0l$: $l=2n$; $0k0$: $k=2n$) and a successful determination of the structure.

Solution and Refinement of the Structure of $[Cu_2(\mu\text{-dppm})_2(phen)_2](PF_6)_2\cdot 2(CH_3)_2CO$. A total of 5121 reflections having $I>3\sigma(I)$ were used. The structure was solved by a direct method,[6] and refined by full-matrix least-squares calculations with anisotropic thermal parameters, including

Table 1. Fractional Coordinates for $[Cu_2(phen)_2(\mu\text{-dppm})_2](PF_6)_2\cdot 2(CH_3)_2CO$

Atom	x	y	z	Atom	x	x	z
Cu	0.9214(1)	0.07139(4)	0.4019(1)	C(15)	0.462(1)	0.0702(5)	0.199(1)
P(1)	1.0954(2)	0.04290(8)	0.3727(2)	C(16)	0.446(1)	0.0314(5)	0.129(1)
P(2)	0.7711(2)	0.03822(8)	0.4551(2)	C(17)	0.525(1)	−0.0066(5)	0.1572(9)
P(3)	0.3412(3)	0.1606(1)	0.8639(3)	C(18)	0.621(1)	−0.0064(3)	0.2566(8)
F(1)	0.2007(8)	0.1668(4)	0.830(1)	C(19)	0.7146(8)	0.0753(3)	0.5508(7)
F(2)	0.331(1)	0.1157(5)	0.929(1)	C(20)	0.783(1)	0.1138(4)	0.6051(9)
F(3)	0.4773(9)	0.1541(6)	0.893(1)	C(21)	0.741(1)	0.1406(4)	0.678(1)
F(4)	0.343(1)	0.2051(5)	0.801(1)	C(22)	0.631(1)	0.1305(4)	0.696(1)
F(5)	0.357(1)	0.1865(8)	0.972(1)	C(23)	0.564(1)	0.0927(4)	0.643(1)
F(6)	0.316(1)	0.1304(5)	0.757(1)	C(24)	0.604(1)	0.0641(4)	0.5702(9)
O(1)	0.731(1)	0.2395(4)	0.838(1)	C(25)	1.2261(8)	0.0221(3)	0.4909(8)
N(1)	0.8390(6)	0.1066(2)	0.2477(6)	C(26)	0.7637(9)	0.0903(3)	0.1523(8)
N(2)	0.9845(7)	0.1428(3)	0.4457(6)	C(27)	0.727(1)	0.1176(4)	0.0540(8)
C(1)	1.0776(9)	−0.0018(3)	0.2650(8)	C(28)	0.770(1)	0.1633(4)	0.0537(9)
C(2)	0.973(1)	−0.0276(4)	0.231(1)	C(29)	0.851(1)	0.1823(4)	0.1524(8)
C(3)	0.958(1)	−0.0639(4)	0.147(1)	C(30)	0.902(1)	0.2284(4)	0.159(1)
C(4)	1.050(2)	−0.0712(6)	0.100(1)	C(31)	0.978(1)	0.2477(3)	0.257(1)
C(5)	1.151(1)	−0.0446(5)	0.132(1)	C(32)	1.008(1)	0.2171(3)	0.356(1)
C(6)	1.169(1)	−0.0102(4)	0.2141(9)	C(33)	1.087(1)	0.2326(3)	0.459(1)
C(7)	1.1641(8)	0.0920(4)	0.3199(8)	C(34)	1.115(1)	0.2038(5)	0.551(1)
C(8)	1.245(1)	0.1233(4)	0.392(1)	C(35)	1.058(1)	0.1594(3)	0.5400(8)
C(9)	1.288(1)	0.1635(4)	0.352(1)	C(36)	0.9583(8)	0.1713(3)	0.3532(8)
C(10)	1.248(1)	0.1744(4)	0.239(1)	C(37)	0.8787(8)	0.1517(3)	0.2486(7)
C(11)	1.167(1)	0.1456(4)	0.167(1)	C(38)	0.643(1)	0.2650(5)	0.812(1)
C(12)	1.124(1)	0.1045(3)	0.2068(9)	C(39)	0.611(2)	0.290(1)	0.900(2)
C(13)	0.6357(8)	0.0336(3)	0.3287(7)	C(40)	0.566(2)	0.2699(8)	0.702(2)
C(14)	0.555(1)	0.0718(4)	0.2986(9)				

isotropic H atoms located by a difference Fourier synthesis. Finally, a two-cycle refinement led to a convergence at $R=\sum[||F_o|-|F_c||]/\sum|F_o|=0.082$, $R_w=[\sum w(|F_o-|F_c|)^2/\sum w|F_o|^2]^{1/2}=0.127$, $w=4F_o^2/\sigma^2(F_o^2)$, $\Delta e=0.79$ Å^{-3}, and the largest shift estimated standard deviation at the final cycle (0.13). The atomic parameters of non-hydrogen atoms are given in Table 1.⁷⁾

Results and Discussion

Description of Molecular Structure. The crystal structure comprises of dimeric complex molecules $[(phen)Cu(\mu\text{-dppm})_2Cu(phen)]^{2+}$ (**1**); a perspective view of the inner skeleton is given in Fig. 1. The important bond lengths and angles are summarized in Table 2. This cation has an inversion center. The two copper atoms are doubly bridged by two dppm ligands to form an eight-membered $Cu_2P_4C_2$ ring. Each copper atom displays a four-coordinate form having P_2N_2 donors. The dihedral angle between the (N(1)–Cu–N(2)) and (P(1)–Cu–P(2)) planes is 84.5°, indicating a slightly distorted tetrahedral geometry around the copper atom.

In each copper moiety, all of the distances between the copper and donor atoms are different: both Cu–N(1) and Cu–N(2) are longer by 0.065—0.087 Å than the usual distaces (2.049(9) Å for $[Cu(phen)_2]ClO_4$),⁸⁾ and the gap in the two Cu–N distances is 0.022 Å. Similarly, the two Cu–P distances, 2.286(3) and 2.234(3) Å, are also different (0.052 Å), falling within the usual range for copper–dppm compounds so far synthesized: 2.296(8) Å in $[Cu_4(dppm)_4(CS_3)_2]$,⁹⁾ 2.22 Å in $[(CuI)_2(dppm)]_2$,¹⁰⁾

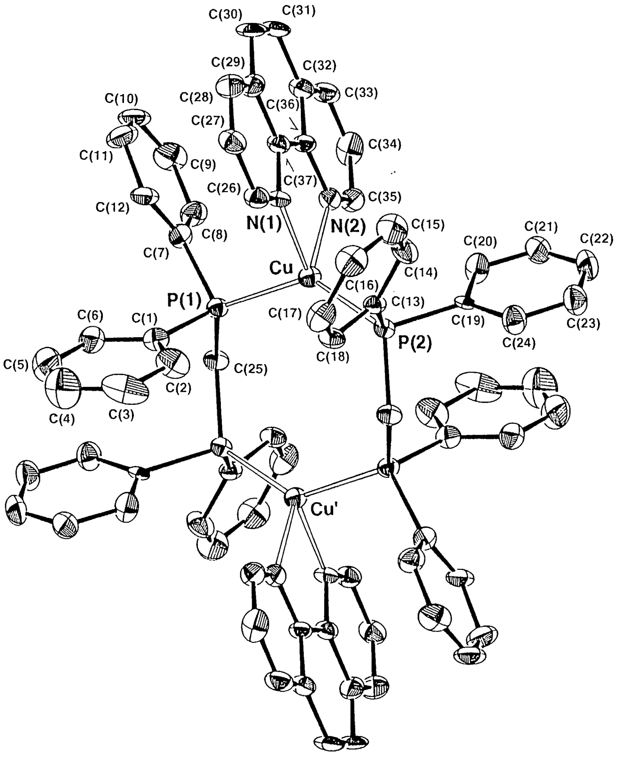


Fig. 1. View of $[Cu_2(\mu\text{-dppm})_2(phen)_2]^{2+}$ with the atomic numbering scheme. Only half the atoms are labeled, the others are related by a center of inversion at the midpoint of the Cu···Cu′ vector.

Table 2. Selected Bond Distances (Å) and Angles (degree) for $[Cu_2(phen)_2(\mu\text{-dppm})_2](PF_6)_2\cdot 2(CH_3)_2CO$

Cu–P(1)	2.286(3)	Cu–P(2)	2.234(3)
Cu–N(1)	2.114(7)	Cu–N(2)	2.136(8)
P(1)–C(1)	1.801(9)	P(1)–C(7)	1.80(1)
P(1)–C(25)	1.854(9)	P(2)–C(13)	1.856(9)
P(2)–C(19)	1.843(9)	P(2)–C(25′)	1.811(9)
N(1)–C(26)	1.32(1)	N(1)–C(37)	1.34(1)
N(2)–C(35)	1.31(1)	N(2)–C(36)	1.36(1)
O(1)–C(38)	1.20(1)	C(38)–C(39)	1.44(2)
C(38)–C(40)	1.40(2)		
P(1)–Cu–P(2)	134.34(9)	P(1)–Cu–N(1)	100.9(2)
P(1)–Cu–N(2)	96.8(2)	P(2)–Cu–N(1)	106.9(2)
P(2)–Cu–N(2)	123.0(2)	N(1)–Cu–N(2)	79.8(3)
Cu–P(1)–C(1)	117.0(3)	Cu–P(1)–C(7)	107.3(3)
Cu–P(1)–C(25)	121.4(3)	C(1)–P(1)–C(7)	102.5(5)
C(1)–P(1)–C(25)	105.0(4)	C(7)–P(1)–C(25)	100.9(4)
Cu–P(2)–C(13)	107.6(3)	Cu–P(2)–C(19)	114.7(3)
Cu–P(2)–C(25′)	124.6(3)	C(13)–P(2)–C(19)	102.7(4)
C(13)–P(2)–C(25′)	99.7(4)	C(19)–P(2)–C(25′)	104.5(4)
Cu–N(1)–C(26)	130.6(6)	Cu–N(1)–C(37)	111.8(6)
Cu–N(2)–C(35)	129.6(7)	Cu–N(2)–C(36)	111.0(6)
P(1)–C(25)–P(2′)	120.5(5)	O(1)–C(38)–C(39)	118(2)
O(1)–C(38)–C(40)	124(2)	C(39)–C(38)–C(40)	118(2)

and 2.231(3) Å in $[Cu_3(OH)(dppm)_3](BF_4)_2$.[11]

The angle of N(1)–Cu–N(2), 79.8(3)°, is close to that of $[Cu(phen)_2]ClO_4$ (81.4(3)°)[8] and $[Cu(dppe)(phen)]PF_6$ (80.7(3)°),[12] where dppe is 1,2-bis(diphenylphosphino)ethane. On the other hand, a P(1)–Cu–P(2) angle of 134.34(9)°C in **1** is quite large. $[Cu(dppe)(phen)]PF_6$ displays an P–Cu–P angle of 91.3(1)°. Generally, the P–Cu–P angles in monomeric copper(I) compounds of dppe fall within 88—110°.[12,13] This smaller angle is not necessarily due to restraint by chelate coordination of dppe, since monodentate phosphines also give similar values:[14] P–Cu–P=109.3°, 115.9(1)°, and 125.4(1)° for $[Cu(Pph_3)_4]ClO_4$, $[Cu(Pph_3)_2(py)_2]ClO_4$, and $[Cu(Pph_3)_2(bpy)]ClO_4$, respectively. On the other hand the large P–Cu–P angle of 134.34(9)° is not simply ascribed to a restriction by the bridged form of dppm, since $[Cu(\mu\text{-dppm})(CH_3CN)_2]_2(ClO_4)_2$ (119.9(1)°)[1] and $[Cu(S_2ct)(\mu\text{-dppm})]_2$ (114.2°)[2] have normal P–Cu–P angles. Among the various $M_2(dppm)_2$ (M=Cu, Ag, and Au) frameworks, as illustrated in the inserted figures (a), (b), and (c), the staggered conformation (b) tends to open the P–M–P angle rather than the eclipsed one (non-planar type, (a)). The P–Ag–P angle of 138.3(1)° in eclipsed $[Ag_2(dppm)_2(NO_3)_2]$[3] is smaller than that of 155.9(1)° in staggered $[Au_2(dppm)_2Cl_2]$.[4] Hence, the P–Cu–P angle is greatly associated with the conformation of the $M_2(dppm)_2$ framework. Complex **1**, indeed, has a rare staggered framework, while both $[Cu(\mu\text{-dppm})(CH_3CN)_2]_2(ClO_4)_2$[1] and $[Cu(S_2ct)(\mu\text{-dppm})]_2$[2] show an eclipsed framework.

In spite of the significant degree in the opening of the P–Cu–P angle in **1**, the Cu···Cu separation of **1** is 4.742(2) Å, much greater than that of $[Cu_2(dppm)_2(CH_3CN)_2]^{2+}$ (**2**) (3.757(3) Å) and $[Cu_2(dppm)_2(S_2ct)_2]$ (**3**) (3.426(3) Å). This is because a conformation occurs in order to avoid close contact between the two coordinated bulky phen ligands, resulting in a large separation of the copper pair. Hence, each copper(I) moiety in **1** seems to be monomer-like, more than in **2** and **3**.

NMR Chemical Shifts and Metal-Ligand Binding. $[Cu(\mu\text{-dppm})(biL)]_2(PF_6)_2$ gave well-resolved ^1H NMR signals of coordinated biL and dppm, of which chemical shifts are listed in Table 3. For all of the complexes given in Table 3, large coordination shifts ($\delta_{coord}=\delta_{complex}-\delta_{metal\text{-}free}$) were obtained. In the case of phen derivative, for instance, the δ_{coord} of 2,9-H, phenyl-H, and CH_2 protons are −0.59, −0.32, and 1.11, respectively. These are clearly illustrated in Fig. 2. An inspection of Table 3 shows that δ_{coord} (2,9-H) of the dimers is much greater than that in monomeric $[Cu(dppe)(phen)]^+$. This large upfield shift can be accounted for by an anisotropic magnetic effect (ring current effect) of the coordinated dppm. Figure 1 reveals that one of the four phenyl groups of a dppm sits over the nearest-neighbor phen plane in a face-to-face fashion: the phenyl ring of C(7)–C(8)–C(9)–C(10)–C(11)–C(12) and the phen plane of N(1), N(2), and C(26)—C(35). The dihedral angle between the two

Table 3. Observed $^1H^{a)}$ and $^{31}P^{b)}$ NMR Shifts and Absorption Bands of $[Cu_2(dppm)_2(biL)_2](PF_6)_2$

biL	$pK_a^{c)}$	2-H(CH_3) 9-H(CH_3)	4-H(CH_3) 7-H(CH_3)	5-H(CH_3) 6-H	3-H(CH_3) 8-H(CH_3)	$CH_2^{d)}$	$^{31}P^{e)}$	$\lambda_{max}^{f)}$
5-Clphen	4.07	9.64(9.20)	8.77(8.74)		7.96(7.90)	4.07	−5.86	362
		8.64(9.13)	8.56(8.45)	8.17(8.14)	7.88(7.78)			(5230)
Phen	4.93	8.61(9.12)	8.56(8.44)	7.94(7.97)	7.84(7.74)	4.05	−5.97	355
								(4900)
5-Mephen	5.27	8.53(9.11)	8.64(8.55)	2.73(2.66)	7.85(7.76)	4.03	−6.03	364
		8.53(9.04)	8.46(8.32)	7.77(7.77)	7.81(7.68)			(5200)
4,7-Me_2phen	5.95	8.47(8.94)	2.84(2.86)	8.15(8.16)	7.70(7.56)	3.88	−6.36	370
								(5100)
3,4,7,8-Me_4phen	—	8.21(8.84)	2.76(2.71)	8.20(8.16)	2.49(2.54)	—	—	—
$[Cu(dppe)(phen)]PF_6$		9.10(9.12)	8.90(8.44)	8.34(7.97)	8.08(7.74)	2.92(2.15)		

a) Acetone solution at 23 °C. Shifts in ppm referenced against $(CH_3)_4Si$. Chemical shifts of metal-free biL are shown in parenthesis. b) Shifts in ppm referenced against 85% H_3PO_4. c) Ref. 18. d) Metal-free ligand, 2.94 ppm. e) Metal-free ligand, −22.9 ppm. f) Absorption maximum in nm. Molar extinction coefficients ($M^{-1}\ cm^{-1}$) are shown in parenthesis.

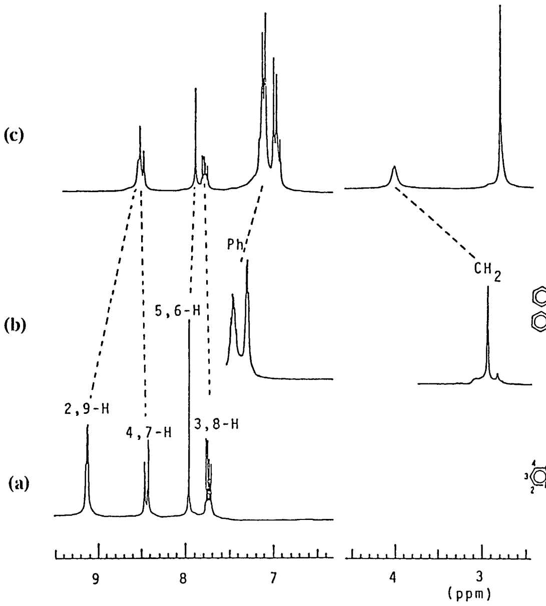
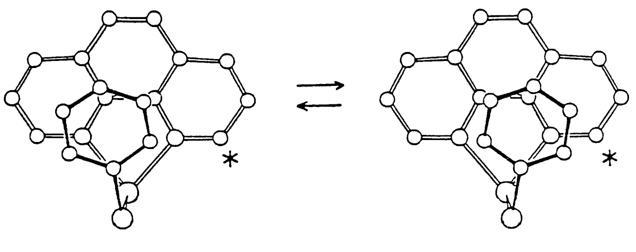


Fig. 2. ${}^{1}H$ NMR spectra at 23° of metal-free phen (a), dppm (b), and $[Cu_2(\mu\text{-dppm})_2(phen)_2]^{2+}$ (c) in acetone-d_6.

mean planes of the phenyl group and phen is 19.02°, indicating that protons on both planes experience an up-field shift. The distance between the nearest-neighbor atoms on the two plane is ca. 3.4 Å, sufficiently close to cause ring a current shift. Accordingly, the phenyl protons also undergo a ring current effect due to the phen ring. This intramolecular magnetic interaction is characteristic of the dimeric structure of $[Cu(\mu\text{-dppm})(phen)]_2^{2+}$.

The molecular structure shown in Fig. 1 also indicates a magnetic inequivalence of 2- and 9-H of phen (similarly 3- to 8-H) concerning the ring current effect of a phenyl group. However, their signals are not separated. This reveals that a low-energy fluxional process is present in solution because of the flexibility of the $Cu_2C_2P_4$ framework. The phenyl ring moves around above a phen plane, depending on the ring motion, as illustrated below.



All of the biL derivatives of $[Cu(\mu\text{-dppm})(biL)]_2^{2+}$ also provided specific large shifts of these proton signals in question. Hence, all of the complexes studied here afford the dimeric form, even in solution, as well as in the solid state.

The ${}^{31}P$ spectra showed a single signal, which is ascribed to $[Cu_2(\mu\text{-dppm})_2(biL)_2]^{2+}$. The observed ${}^{31}P$ chemical shifts are plotted against the pK_a values of biL, together with the ${}^{1}H$ chemical shifts of the CH_2 of dppm (Fig. 3). Figure 3 indicates that since biL has a higher basicity, this causes up-field shifts of both the ${}^{1}H$ and ${}^{31}P$ NMR signals. It has been demonstrated[14,15] that the higher is the basicity of biL the stronger is the copper–biL bonding. The upfield ${}^{1}H$ and ${}^{31}P$ shifts indicate that Cu–P bonding is weakened. Thus, the relationship shown in Fig. 3 well demonstrates the competition between Cu–P and Cu–N bonding. Consequently, the Cu–P bonding tends to be weak when the Cu–biL bonding becomes strong.

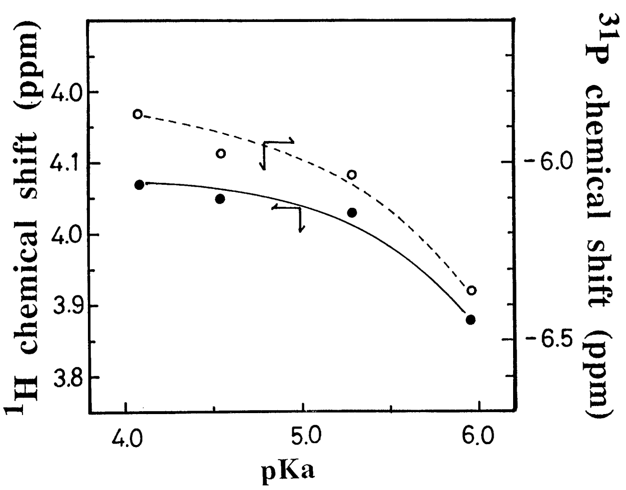


Fig. 3. Plots of the observed ^{1}H and ${}^{31}P$ NMR chemical shifts of coordinated dppm vs. pK_a of biL in $[Cu_2(\mu\text{-dppm})_2(biL)_2](PF_6)_2$. The plotted data are listed in Table 3.

The electronic absorption spectra of these solutions also give information concerning copper–ligand binding. A strong absorption band is observed for each solution in the region 360—370 nm, as shown in Table 3. There is no band in the case of binary systems, such as Cu/dppm and Cu/biL (biL=phen derivatives). The latter system affords a metal-to-ligand charge transfer (MLCT) band in the region greater than 400 nm.[15–17] On this basis, the band in Table 3 has been assigned to the metal-to-ligand charge-transfer bands between Cu and biL in ternary complexes. For instance, the band for $[Cu_2(\mu\text{-dppm})_2(phen)_2]^{2+}$ appears at 355 nm, while $[Cu(phen)_2]^{+}$ provides a band at 440 nm.[17] This remarkable blue shift (by 85 nm) shows that Cu–phen bonding is weaker in $[Cu_2(\mu\text{-dppm})_2(phen)_2]^{2+}$ than in $[Cu(phen)_2]^{+}$. This is consistent with the fact that the Cu–N bond distance in **1** is greater than that in $[Cu(phen)_2]^{+}$,[8] as mentioned above. This trend has been found for all of the complexes studied here.

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