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A Molecular Cavity for Tetrahedral and Y-Shaped Anions. Synthetic and Structural Studies of Macrocyclic Dicopper(I) and Disilver(I) Compounds of 1,6-Bis(diphenylphosphino)hexane

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New binuclear macrocyclic systems of 1,6-bis(diphenylphosphino)hexane (dpph) and 1,4-bis(diphenylphosphino)-butane (dppb), $[\mathrm{Cu_2(dppb)_2(ClO_4)_2}]$ (**2**), $[\mathrm{Cu_2(dpph)_2(\mu\text{-}X)_2}]$ (X = $\mathrm{ClO_4}$ (**3**), $\mathrm{NO_3}$ (**4**), $\mathrm{PF_2O_2}$ (**5**), $\mathrm{CH_3CO_2}$ (**7**), $\mathrm{C_2H_5CO_2}$ (**8**)), and $[\mathrm{Ag_2(dpph)_2(\mu\text{-}ClO_4)_2}]$ (**6**), have been synthesized and structurally characterized. A mononuclear copper(I) complex, $[\mathrm{Cu_2(dppp)_2]ClO_4}$ (**1**) (dppp = 1,3-bis(diphenylphosphino)propane), was also prepared. The crystals of **1**−**6** are all triclinic, space group $P\bar{1}$, with $Z = 1$ (**2**) and 2 (**1, 3**−**5**). Dimensions of the unit cells: **1**, a = 12.221(6) Å, b = 18.425(7) Å, c = 11.981(7) Å, α = 96.19(4)°, β = 102.42(4)°, γ = 70.57(4)°; **2**, a = 11.978(8) Å, b = 12.755(8) Å, c = 19.372(4) Å, α = 97.83(5)°, β = 111.24(4)°, γ = 64.85(5)°; **3**, a = 12.154(7) Å, b = 12.728(5) Å, c = 10.007(7) Å, α = 92.67(4)°; β = 101.57(4)°, γ = 101.56(6)°; **4**, a = 15.421(3) Å, b = 18.354(4) Å, c = 10.066(4) Å, α = 90.23(3)°, β = 97.06(2)°, γ = 89.27(2)°; **5**, a = 12.060(2) Å, b = 12.808(1) Å, c = 10.120(1) Å, α = 86.134(7)°, β = 101.299(9)°, γ = 102.367(8)°; **6**, a = 12.035(7) Å, b = 12.820(6) Å, c = 10.240(5) Å, α = 92.76(4)°, β = 101.49(4)°, γ = 101.39(4)°. For complexes of **3**−**5** each copper atom shares a tetrahedral geometry with the $\mathrm{P_2O_2}$ donor set, giving a molecular structure having two rings: the common outer large ring of $\underline{\mathrm{CuP(CH_2)_6PCuP(CH_2)_6P}}$ is composed of copper atoms and the bridging diphosphine ligands while the inner ring is $\underline{\mathrm{CuOXOCuOXO}}$ (X = Cl, N, P) for **3**−**5**, respectively. The distances of Cu−O fall within the shortest range for copper(I) complexes of each anion, indicating that copper−anion binding is strong even for anions having weak coordination ability. The size of cavity for the anion trap is estimated as the distance L between the two metal atoms in a molecule. The L values are 4.99−5.22 Å for **3**−**5**. Compound **1** shows a typical mononuclear structure with chelating dppp, while **2** gives a binuclear geometry, $[\mathrm{Cu_2(\mu\text{-}dppb)_2(ClO_4)_2}]$, with terminally coordinated $\mathrm{ClO_4}$ anions and a single macrocycle (L = 4.63 Å) of $\underline{\mathrm{CuP(CH_2)_4PCuP(CH_2)_4P}}$. The $\mathrm{ClO_4^-}$ ion is prevented from bridging coordination, and this is accounted for by the ring size and spatial blocking of the phenyl groups of dppb. On this basis, the ligand having six methylene groups provides a cavity able to include anions such as tetrahedral $\mathrm{ClO_4^-}$ and Y-shaped $\mathrm{NO_3^-}$. By $^{31}\mathrm{P}$ NMR, the mononuclear and binuclear copper(I) compounds in solution were also examined, and their exchange processes are discussed. The silver compound (**6**) as a structural analog of **3** also affords the double ring, but the Ag−O distance is not so sufficiently short that the silver atom binds $\mathrm{ClO_4}$ as strongly as copper does. Other compounds with $\mathrm{CH_3CO_2^-}$ (**7**), $\mathrm{C_2H_5CO_2^-}$ (**8**), and $\mathrm{VO_3^-}$ (**9**) were also examined by IR and $^{51}\mathrm{V}$ NMR spectroscopy. By using the copper(I) ion and diphosphine, we have succeeded in building large macrocyclic systems, where various small molecules or anions are included, proposing a new host−guest chemistry.

Introduction

Studies on the ion trap have been developed and form an important subdivision of host−guest chemistry.[1−6] In this chemistry there are two structural types of host molecules, acyclic and macrocyclic frameworks. In particular, many cyclic multidentate ligands have been synthesized, namely, cryptands, crown ethers, and other coronands. The formation of complexes between cations and these multidentate ligands is well-established. Complexes of organic molecules have also prepared and expanded to the chemistry of cagelike host compounds.[7] In contrast, the coordination chemistry of anions is noticeably undeveloped, although there are many organic and inorganic anions. This is due to the lack of systematic host molecules besides cryptands, whose protonated form has hydrogen-bonding capability. One way to obtain relevant anion receptors is to utilize coordination bonds between transition metal ions and anions and to build host macrocycles containing transition metal cations. To our best knowledge, metalloporphyrins have been

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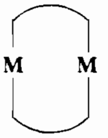
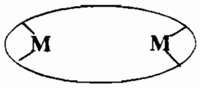
applied to anion-selective charged carriers in membranes in the mid-1980s.[8-12] There are, however, few systems in which anions are trapped by two metal ions in a macrocyclic cavity. As far as these binuclear transition metal compounds are concerned, two types of the macrocycles can be considered. Type I is a macrocycle in which metal ions are involved as a ring member. For type II, donor groups are involved in a ring member, to which metal ions are coordinated as a pendant. There have been several instances for each type; type I structures are found in binuclear $[Ag_2((C_6H_5)_2P(CH_2)_5P(C_6H_5)_2)_2(\mu\text{-}Cl)_2]$[13] and copper(II) compounds,[14] trinuclear $[Cu_3(\mu\text{-}I)(\mu\text{-dppm})_2(\mu_3\text{-}I)_2]$[15] and $[Cu_3(\mu\text{-dppm})_3(OH)](BF_4)_2$,[16] and tetranuclear $[Cu_4(\mu\text{-}I)_2(\mu\text{-dppm})_2(\mu_3\text{-}I)_2]$[17] and $[(C_2B_{10}H_{10}Hg)_4I_2]Li_2$.[18,19] Examples of type II are dipyridyl crown ether[20] and cyclic polyaza compounds of copper(II).[21-23] The anionic complexes have primarily involved halides ions, although there are various monodentate anions such as azide, hydroxide, perchlorate, and imidazolate. The structural characterization data are limited, and these data need to be systematized. However, there are few instances regarding complexaiton of other anions such as perchlorate, nitrate, etc.



Type I



Type II

Copper(I) complexes are good structural supports, providing well-designed molecular architecture and expanding supramolecular chemistry.[24,25] This is attributed to the structural characteristics of copper(I) compounds, which show various geometries with one-, two-, three- (Y and T-shaped), four- (tetrahedral), and five-coordination (square-pyramidal). Copper(I) favors soft bases such as phosphines to form very stable complexes in spite of its low oxidation state. The prominent utility of diphosphine ligands, whose general formula is $R_2P(CH_2)_nPR_2$, for transition metal complexes has made it possible to prepare various low-valent metal complexes. Especially, bis(diphenylphosphino)methane (dppm) and 1,2-bis(diphenylphosphino)ethane (dppe) are quite common in organometallic chemistry. Dppm affords binuclear metal complexes in the μ-dppm form,[26] while dppe affords both chelating[27] and bridging complexes.[28] In contrast with small-chain types ($n \le 2$), metal complexes having a long chain $R_2P(CH_2)_nPR_2$ ($n > 4$) are very few. The purpose of this work is to clarify the effect of the number n on the mode of its coordination, chelating or bridging, as shown in our figures. The second but most important purpose of this work is to build large macrocyclic systems with these ligands, in which various anions are trapped and with which new host–guest chemistry begins. This work is thus concerned with the preparation of bridging dicopper and disilver complexes having macrocyclic structures and to examine the relationship between anions and the structural factors of the cavity.

Experimental Section

Materials. Copper(I) salts, $[Cu(CH_3CN)_4]X$ ($X = ClO_4, PF_6$), were prepared according to the literature.[29,30] $AgClO_4$ was purchased from Mitsuwa Chemical Co. and dried at 40 °C under vacuum before use. 1,3-Bis(diphenylphosphino)propane (dppp), 1,4-bis(diphenylphosphino)butane (dppb), and 1,6-bis(diphenylphosphino)hexane (dpph) were purchased from Aldrich Chemical Co. All operations were carried out under dry argon by using the standard Schlenk techniques, but products were worked up in the open atmosphere.

Syntheses. $[Cu(dppp)_2]ClO_4{\cdot}0.5CH_3OH$ (1). $[Cu(CH_3CN)_4]ClO_4$ (16.4 mg, 0.050 mmol) was added to a 10 mL methanol solution of dppp (41.2 mg, 0.100 mmol), and the mixture was stirred for 10 min. A colorless solution was obtained, which was transferred to a glass tube and layered with n-hexane; the glass tube was then sealed. The contents were kept at room temperature for several days. The colorless brick-shaped crystals that were obtained (yield 65%) were stable to air. Anal. Calcd for $C_{109}H_{107}Cu_2Cl_2P_8O_9$: C, 65.24; H, 5.37. Found: C, 64.57; H, 5.52.

$[Cu_2(dppb)_2(ClO_4)_2]$ (2). Under an ethylene atmosphere, $Cu(ClO_4)_2{\cdot}6H_2O$ (9.3 mg, 0.025 mmol) was dissolved in 10 mL of acetone, and the copper was reduced with copper wire to copper(I). The addition of dppb (20.6 mg, 0.050 mmol) gave a colorless solution, and ethylene was replaced with argon. After several days, the solution, which was sealed in a glass tube, afforded colorless brick-shaped crystals at room temperature (yield 74%). Anal. Calcd for $C_{56}H_{56}Cu_2Cl_2P_4O_8$: C, 62.29; H, 5.23. Found: C, 61.69; H, 5.52.

$[Cu_2(dpph)_2(\mu\text{-}ClO_4)_2]$ (3). $[Cu(CH_3CN)_4]ClO_4$ (9.8 mg, 0.030 mmol) was added to a 10 mL THF solution of dpph (13.6 mg, 0.030 mmol), and the mixture was stirred for 10 min. A colorless solution was obtained, which was transferred to a glass tube; the tube was then sealed. The contents were kept at room temperature for several days. Colorless brick-shaped crystals were obtained (yield 57%) that were stable to air. Anal. Calcd for $C_{60}H_{64}Cu_2Cl_2P_4O_8$: C, 58.35; H, 5.22. Found: C, 58.07; H, 5.18.

$[Cu_2(dpph)_2(\mu\text{-}NO_3)_2]$ (4). $[Cu(CH_3CN)_4]ClO_4$ (19.6 mg, 0.060 mmol) was added to a 20 mL THF solution of dpph (27.3 mg, 0.060 mmol), the mixture was stirred for 10 min, and a colorless solution was obtained. Excess $NaNO_3$ (10.2 mg, 0.120 mmol) in 5 mL of methanol was added to this solution, and the mixture was stirred for 30 min. After filtration, the resultant solution was layered with n-hexane at room temperature, giving colorless brick-shaped crystals (yield 47%). Anal. Calcd for $C_{60}H_{64}Cu_2P_4N_2O_6$: C, 62.12; H, 5.56. Found: C, 62.98; H, 6.28.

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Table 1. Crystallographic Data for [Cu(dppp)$_2$]ClO$_4$·0.5CH$_3$OH (**1**), [Cu$_2$(μ-dppb)$_2$(ClO$_4$)$_2$] (**2**), [Cu$_2$(μ-dpph)$_2$(μ-ClO$_4$)$_2$] (**3**), [Cu$_2$(μ-dpph)$_2$(μ-NO$_3$)$_2$] (**4**), [Cu$_2$(μ-dpph)$_2$(μ-PF$_2$O$_2$)$_2$] (**5**), and [Ag$_2$(μ-dpph)$_2$(μ-ClO$_4$)$_2$] (**6**)

formula	$C_{109}H_{104}Cu_2Cl_2P_8O_9$ (**1**)	$C_{56}H_{54}Cu_2Cl_2P_4O_8$ (**2**)	$C_{30}H_{32}CuClP_2O_4$ (**3**)	$C_{30}H_{32}CuP_2NO_3$ (**4**)	$C_{30}H_{32}CuP_3F_2O_2$ (**5**)	$C_{30}H_{32}AgClP_2O_4$ (**6**)
fw	2003.81	1176.93	617.53	580.08	619.05	661.85
cryst dimens, mm	0.30 × 0.30 × 0.35	0.30 × 0.30 × 0.30	0.25 × 0.25 × 0.25	0.40 × 0.40 × 0.40	0.25 × 0.25 × 0.30	0.20 × 0.25 × 0.20
lattice	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
a, Å	12.221(6)	11.978(8)	12.154(7)	15.421(3)	12.060(2)	12.035(7)
b, Å	18.425(7)	12.755(8)	12.728(5)	18.354(4)	12.808(1)	12.820(6)
c, Å	11.981(7)	19.372(4)	10.007(7)	10.066(4)	10.120(1)	10.240(5)
α, deg	96.19(4)	97.83(5)	92.67(4)	90.23(3)	86.134(7)	92.76(4)
β, deg	102.42(4)	111.24(4)	101.57(4)	97.06(2)	101.299(9)	101.49(4)
γ, deg	70.57(4)	64.85(5)	101.56(6)	89.27(2)	102.367(8)	101.39(4)
V, Å^3	2483(2)	1336.7	1480(1)	2827(2)	1496.8(3)	1511(3)
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Z	1	1	2	2	2	2
ϱ(calcd) g cm^{-3}	1.348	1.464	1.386	1.363	1.373	1.454
F(000)	1048	606	640	1208	640	676
μ(Mo Kα), cm^{-1}	6.66	10.69	9.68	9.15	28.73	8.84
diffractometer	AFC6B	AFC6B	AFC6S	AFC5R	AFC5R	AFC5R
radiation (λ, Å)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Cu Kα (1.541 78)	Mo Kα (0.710 69)
temp, °C	23	23	23	23	23	23
R^a	0.061	0.094	0.051	0.051	0.036	0.041
$R_w{}^b$	0.063	0.107	0.052	0.052	0.051	0.050
no. of observns ($I > 3.00\sigma(I)$)	4105	3815	2830	4904	3866	5152
no. of variables	579	325	370	667	343	370

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)]^{1/2}$.

[Cu$_2$(dpph)$_2$(μ-PF$_2$O$_2$)$_2$] (5). [Cu(CH$_3$CN)$_4$]PF$_6$ (22.4 mg, 0.060 mmol) was added to a 10 mL THF solution of dpph (27.3 mg, 0.060 mmol), the mixture was stirred for 10 min, the colorless solution obtained was layered with *n*-pentane, and the mixture was sealed in a glass tube. Colorless brick-shaped crystals were obtained within a week. Anal. Calcd for $C_{60}H_{64}Cu_2P_6F_4O_4$: C, 58.21; H, 5.21. Found: C, 58.01; H, 5.28.

[Ag$_2$(dpph)$_2$(μ-ClO$_4$)$_2$] (6). An ethanol solution (2 mL) of AgClO$_4$ (8.3 mg, 0.040 mmol) was added to a 2 mL THF solution of dpph (9.1 mg, 0.080 mmol), the mixture was stirred for 10 min, and the resultant colorless solution, layered with *n*-hexane, was kept in the dark. Anal. Calcd for $C_{60}H_{64}Ag_2Cl_2P_4O_8$: C, 54.44; H, 4.87. Found: C, 54.07; H, 5.05.

[Cu$_2$(dpph)$_2$(μ-CH$_3$CO$_2$)$_2$] (7). An ethanol solution (5 mL) of CH$_3$COONa·3H$_2$O (20.4 mg, 0.150 mmol) was added to 5 mL of a THF solution containing 16.4 mg (0.050 mmol) of [Cu(CH$_3$CN)$_4$]ClO$_4$ and 22.7 mg of dpph (0.050 mmol), and the mixture was stirred for 10 min. A white precipitate was obtained (yield 47%). IR data: ν_{CO} 1563 cm^{-1}. Anal. Calcd for $C_{64}H_{70}Cu_2P_4O_4$: C, 66.60; H, 6.11. Found: C, 65.50; H, 5.90.

[Cu$_2$(dpph)$_2$(μ-C$_2$H$_5$O$_2$)$_2$] (8). An ethanol solution (3 mL) of C$_2$H$_5$COONa (8.6 mg, 0.090 mmol) was added to 3 mL of a THF solution containing 13.7 mg (0.042 mmol) of [Cu(CH$_3$CN)$_4$]ClO$_4$ and 19.1 mg of dpph (0.042 mmol), and the mixture was stirred for 10 min. A white precipitate was obtained (yield 30%). IR data: ν_{CO} 1566 cm^{-1}. Anal. Calcd for $C_{66}H_{74}Cu_2P_4O_4$: C, 67.05; H, 6.31. Found: C, 67.58; H, 6.34.

Physical Measurements. IR spectra were recorded as KBr disks with a Jasco FTIR-800 spectrometer. ^{1}H, ^{31}P{^{1}H}, and ^{51}V NMR spectra were recorded on a JEOL GSX-270 spectrometer operating at 270.16, 109.37, and 67.94 MHz, respectively. H$_3$PO$_4$/D$_2$O (85:15 v/v) and neat VOCl$_3$ at 23 °C were used as external shift references for ^{31}P and ^{51}V NMR, respectively. For ^{1}H NMR spectra two species, [Cu(P-dpph)$_2$]ClO$_4$ (**3'**) and [Cu$_2$(dpph)$_2$(ClO$_4$)$_2$] (**3**) were observed. The α, β, and γ-methylene ^{1}H signals for coordinated dpph (**3**) were assigned to 2.43, 1.47, and 1.47 ppm, respectively, while those of **3'** are 2.51, 1.80, and 1.80 ppm, respectively.

X-ray Data Collection. General crystallographic data and procedures for this paper are as follows. As a rule, crystals were glued on top of a glass fiber. For each compound unit-cell constants were determined from the geometric parameters of 25 well-centered reflections with 2θ values in the range 20−32 ° for Mo Kα and for Cu Kα, respectively, and all the unit cells corresponded to a triclinic cell. Then, a unique data set was measured to a 2θ limit predetermined from the scope of the data, using a Rigaku automated diffractometer fitted with a monochromatic Mo Kα or Cu Kα radiation source and operating in the conventional $\omega-2\theta$ scan mode at 23 °C. Lorenz, polarization, and absorption corrections were applied. Of the N unique reflections measured, N_o were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. On the basis of packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to $P\bar{1}$.

For the structures of **1** and **2**, the positions of the copper atoms were obtained via direct methods using MULTAN 78.[31] Fourier syntheses were then calculated to determine the positions of the remaining atoms. The structure was refined by full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. For **1**, all hydrogen atoms were placed in calculated positions, but their parameters were not refined.

For the structures of **3**−**7**, the positions of the copper, phosphorus, oxygen, and chlorine atoms were obtained by MITHRIL.[32] Fourier syntheses were then calculated to determine the positions of the remaining atoms. The structure was refined by full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. All the hydrogen atoms of the phenyl and methylene groups were located in a difference Fourier map and introduced as fixed contributors in the final stage of the refinement. The fractional positional parameters for non-hydrogen atoms are listed in Tables 2−7.

Departures from the above occurred for complexes **1**, **3**, and **6**. The ClO$_4^-$ anion is disordered with the site occupancies of 0.6:0.4 (**1**) and 0.8:0.2 (**3** and **6**) for O(2), O(3), and O(4) vs O(5), O(6), and O(7), whereas those for the Cl(1) and O(1) are 1:1. For the final refinement the multiplicities were fixed at those values. The significance of the minor sites was verified by the stable refinement and the fact that the parameters derived for the minor anion were within acceptable ranges.

Results and Discussion

Molecular Structures. [Cu(dppp)$_2$]ClO$_4$·0.5CH$_3$OH (1). The molecular structure of the cation is shown in Figure 1. The copper atom is tetrahedrally coordinated to four phosphorus atoms. The ligand dppp exhibits a chelating form. The selected

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[31] A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data, Universities of York and Louvain, 1978.

[32] Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42.

Table 2. Positional and Equivalent Isotropic Thermal Parameters for $[Cu(dppp)_2]ClO_4{\cdot}0.5CH_3OH$ (**1**)

atom	*x*	*y*	*z*	B_{eq},[a] Å^2	atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Cu(1)	0.18198(8)	0.22195(6)	0.22909(8)	2.68(5)	C(22)	0.1702(7)	0.4176(4)	0.2512(7)	3.5(5)
Cl(1)	0.6110(3)	0.3017(2)	0.7791(3)	7.1(2)	C(23)	0.2297(8)	0.3974(5)	0.1609(8)	4.1(5)
P(1)	0.3755(2)	0.1970(1)	0.3261(2)	3.2(1)	C(24)	0.273(1)	0.4488(6)	0.1229(9)	5.7(7)
P(2)	0.1193(2)	0.3471(1)	0.3019(2)	3.2(1)	C(25)	0.258(1)	0.5189(7)	0.175(1)	6.6(8)
P(3)	0.1372(2)	0.2002(1)	0.0335(2)	3.0(1)	C(26)	0.199(1)	0.5414(6)	0.265(1)	6.6(8)
P(4)	0.0533(2)	0.1667(1)	0.2775(2)	2.7(1)	C(27)	0.1549(9)	0.4904(6)	0.3010(9)	5.4(6)
O(1)	0.583(1)	0.2356(7)	0.777(1)	14.5(4)	C(28)	0.2030(8)	0.1018(5)	−0.0169(7)	3.3(5)
O(2)[b]	0.725(2)	0.289(1)	0.831(2)	10.4(5)	C(29)	0.3131(8)	0.0581(5)	0.0384(8)	4.5(6)
O(3)[b]	0.528(1)	0.364(1)	0.817(2)	9.2(4)	C(30)	0.362(1)	−0.0183(6)	0.006(1)	6.3(7)
O(4)[b]	0.615(2)	0.309(1)	0.659(2)	13.4(6)	C(31)	0.299(1)	−0.0514(7)	−0.082(1)	8(1)
O(5)[b]	0.635(3)	0.332(2)	0.907(3)	15(1)	C(32)	0.192(1)	−0.0090(8)	−0.141(1)	8(1)
O(6)[b]	0.516(2)	0.360(2)	0.737(3)	10.1(7)	C(33)	0.1434(9)	0.0669(6)	−0.1071(9)	5.5(7)
O(7)[b]	0.721(2)	0.298(1)	0.756(2)	6.6(5)	C(34)	0.1686(8)	0.2548(5)	−0.0670(6)	3.4(5)
O(8)	$^1/_2$	$^1/_2$	$^1/_2$	25(1)	C(35)	0.2702(8)	0.2255(5)	−0.1132(8)	4.3(6)
C(1)	0.4706(7)	0.0972(5)	0.3433(7)	3.7(5)	C(36)	0.302(1)	0.2698(7)	−0.1805(8)	5.4(7)
C(2)	0.592(1)	0.0748(6)	0.357(1)	7.3(8)	C(37)	0.229(1)	0.3433(8)	−0.2045(9)	6.5(9)
C(3)	0.658(1)	−0.0019(8)	0.362(1)	9(1)	C(38)	0.127(1)	0.3730(6)	−0.162(1)	6.4(8)
C(4)	0.605(1)	−0.0572(6)	0.353(1)	6.8(8)	C(39)	0.0964(9)	0.3287(5)	−0.0938(8)	5.0(6)
C(5)	0.486(1)	−0.0364(6)	0.345(1)	6.5(7)	C(40)	−0.0227(7)	0.2188(5)	−0.0106(7)	3.7(5)
C(6)	0.4199(8)	0.0409(6)	0.3407(9)	5.2(6)	C(41)	−0.0752(7)	0.1712(5)	0.0476(7)	3.8(5)
C(7)	0.4624(7)	0.2400(5)	0.2651(8)	3.6(5)	C(42)	−0.0847(7)	0.1940(5)	0.1724(7)	3.5(5)
C(8)	0.5294(7)	0.2843(6)	0.3277(8)	4.8(6)	C(43)	0.0057(7)	0.2003(4)	0.4122(7)	3.1(5)
C(9)	0.5981(9)	0.3180(6)	0.275(1)	6.1(7)	C(44)	0.0896(8)	0.1892(5)	0.5120(8)	4.4(6)
C(10)	0.5846(9)	0.3085(6)	0.161(1)	5.9(7)	C(45)	0.061(1)	0.2114(6)	0.6184(8)	4.6(6)
C(11)	0.5231(9)	0.2624(6)	0.0952(9)	5.7(7)	C(46)	−0.055(1)	0.2464(5)	0.6275(8)	4.8(6)
C(12)	0.4601(8)	0.2301(5)	0.1487(8)	4.4(6)	C(47)	−0.140(1)	0.2590(6)	0.531(1)	5.7(7)
C(13)	0.3805(8)	0.2374(5)	0.4727(7)	4.1(5)	C(48)	−0.1105(7)	0.2353(5)	0.4238(7)	4.2(5)
C(14)	0.3162(8)	0.3241(5)	0.4862(7)	4.3(6)	C(49)	0.0897(7)	0.0615(5)	0.2844(7)	3.2(5)
C(15)	0.1801(8)	0.3493(5)	0.4553(7)	4.0(5)	C(50)	0.061(1)	0.0288(6)	0.368(1)	7.4(8)
C(16)	−0.0394(7)	0.3977(4)	0.2935(8)	3.6(5)	C(51)	0.095(1)	−0.0501(7)	0.374(1)	9(1)
C(17)	−0.1059(9)	0.4166(5)	0.1881(9)	4.9(6)	C(52)	0.161(1)	−0.0978(5)	0.300(1)	5.7(7)
C(18)	−0.228(1)	0.4532(6)	0.172(1)	5.6(7)	C(53)	0.1891(8)	−0.0663(5)	0.2172(8)	4.8(6)
C(19)	−0.281(1)	0.4725(6)	0.265(1)	6.3(7)	C(54)	0.1535(8)	0.0130(5)	0.2107(7)	4.0(5)
C(20)	−0.215(1)	0.4528(6)	0.371(1)	6.1(7)	C(55)	0.567(4)	0.418(2)	0.538(3)	34(5)
C(21)	−0.0932(8)	0.4164(5)	0.3860(8)	4.7(6)					

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] The perchlorate anion is disordered. The occupancies are 0.6 and 0.4 for O(2)−O(4) and O(5)−O(7), respectively.

bond distances and angles are listed in Table 8. The Cu−P bonds are essentially equivalent, and their mean distance (2.317(3) Å) is very similar to the corresponding distances in $[Cu(dppe)_2]^+$ (2.313(4) Å (average)).[27,28] The P−Cu−P chelate angles (95.8(1)° (average)) of **1** are greater than those of $[Cu(dppe)_2]^+$ (88.5(1)° (average)). This is reasonable when the size of chelate ring is considered, the former having a six-membered ring and the latter a five-membered ring.

$[Cu_2(dppb)_2(ClO_4)_2]$ (2). The entire molecule is shown in Figure 2, which clearly shows C_i symmetry. The big difference between **1** and **2** is recognized in the coordination modes of the ligands. **2** indicates a bridging mode for the ligand, forming a macrocycle. Each copper shows a three-coordinate geometry with two dppb and a ClO_4 anion. The Cu−O(1) distance is 2.435(8) Å, short enough for perchlorate to bind copper(I).[21,33−36] All three angles P(1)−Cu−P(2), P(1)−Cu−O(1), and P(2)−Cu−O(1) are different and asymmetric, dissimilar from those of Y-shaped $[Cu(2\text{-picoline})]^+$.[37] The perchlorate anion is terminally coordinated to the copper atom in such a way that a Cu−O(1)−Cl(1) angle is 104.7(4)° and the remaining three oxygen atoms of the perchlorate anion bend away from the ring cavity. The side view of the molecule in Figure 2B clearly shows that both perchlorate anions cannot have the bridged form. This is because the two upright phenyl groups hinder approach of that anion, i.e. a substituent effect of dppb, and because the Cu⋅⋅⋅Cu distance, 4.63 Å in **2**, is too short to have a bridging perchlorate anion.

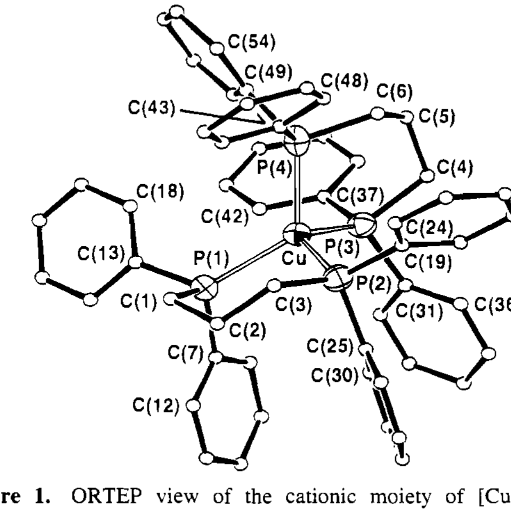

Figure 1. ORTEP view of the cationic moiety of $[Cu(dppp)_2](ClO_4){\cdot}0.5CH_3OH$ with thermal ellipsoids at the 50% level for Cu and P atoms. Ellipsoids of the carbon atoms in the methylene and phenyl groups have been arbitrarily reduced.

$[Cu_2(dpph)_2(\mu\text{-}ClO_4)_2]$ (3). The entire molecule of **3** is shown in Figure 3, where the molecule has a center of symmetry at the midpoint of the Cu(1)⋅⋅⋅Cu(1′) vector. The most interesting feature of **3** is a double-ring structure: the outer ring

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(34) Thompson, J. S.; Whitney, J. F. *Inorg. Chem.* **1984**, *23*, 2813.

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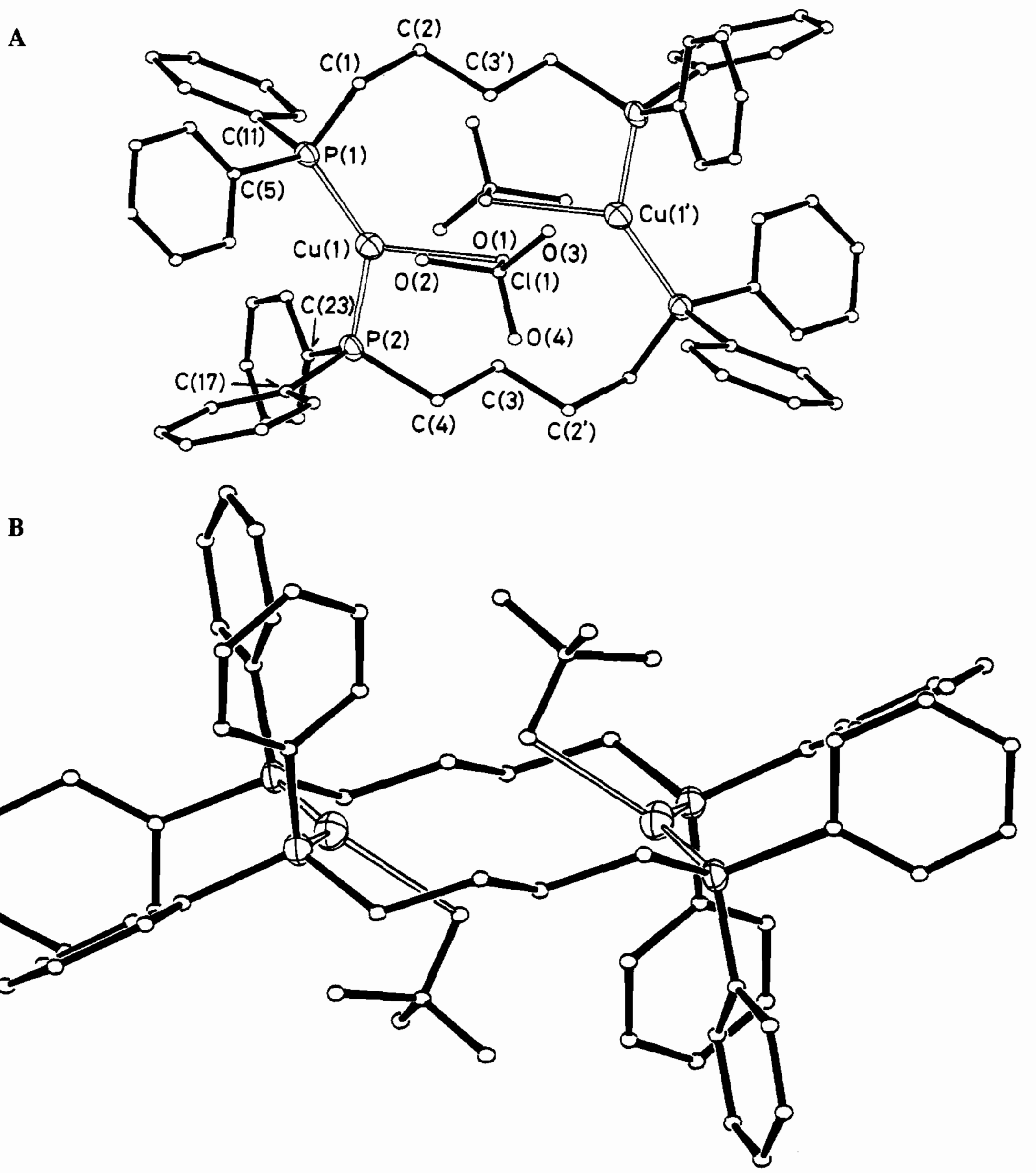

Figure 2. ORTEP drawings of the entire molecule of $[Cu_2(\mu\text{-dppb})_2(ClO_4)_2]$ with thermal ellipsoids at the 50% level for Cu, P, and O atoms. Ellipsoids of the carbon atoms in the methylene and phenyl groups have been arbitrarily reduced. The numbers of unlabeled phenyl carbon atoms follow from those given. Only half the atoms are labeled; the others are related by a center of inversion at the midpoint of the Cu–Cu vector.

consists of a Cu–dpph–Cu–dpph 18-membered ring, while the inner one consists of the two perchlorate anions and copper atoms to form an 8-membered ring. The two rings are orthogonal to each other. The copper atom has a distorted tetrahedral geometry, which is different from a normal tetrahedron such as $[Cu(C_5H_4N)_4]^+$ (N–Cu–N = 110°).[38] The coordinated perchlorate anions are disordered and have two positions, A and B, which are related to each other by rotation around the Cl(1)–O(1) axis. Both forms A [ClO(1)O(2)O(3)O(4)) and B (ClO(1)O(2)O(5)O(6)O(7)) bridge the two copper atoms. In form A the angle O(1)–Cu–O(2′) is 100.2°, close to the value of a typical tetrahedron, while P(1)–Cu–P(2) is 130.9°, opening up more than 120°. The Cu–P distances are 2.23 and 2.24 Å, indicative of the normal distance, whereas the distances of Cu–O(1) and Cu–O(2′) are 2.236(6) and 2.354(8) Å, respectively, which fall within the shortest range among copper–perchlorate systems.[21,33–36] This means that the perchlorate is strongly coordinated to copper(I). Form B also shows a structure similar to that of form A, and thus, these two structures are essentially identical with regard to coordination to perchlorate anions.

$[Cu_2(dpph)_2(\mu\text{-}NO_3)_2]$ (4). Both molecules **4A** and **4B** in a unit cell indicate the double-ring structure having a center of symmetry at the midpoint of the Cu(1)···Cu(1′) (**4A**) (or Cu(2)···Cu(2′) (**4B**)) vector. Figure 4 reveals the molecular structure of **4A**. In each structure two nitrate anions bridge the two copper atoms to form an 8-membered ring together with an 18-membered ring of Cu_2dpph_2. The two Cu–O distances are not identical. The Cu(1)–O(2′) distance (2.089(6) Å) is found to be shortest in copper(I) compounds synthesized so far, while the other distance of Cu(1)–O(2) (2.245(7) Å) is comparable with that for $[Cu\{(C_6H_5)_3P\}_2NO_3]$.[39] This trend is also recognized for structure of **4B**. The stereochemistry of each copper atom is a four-coordinate with P_2O_2 donors corresponding to a distorted tetrahedron, which comes from the

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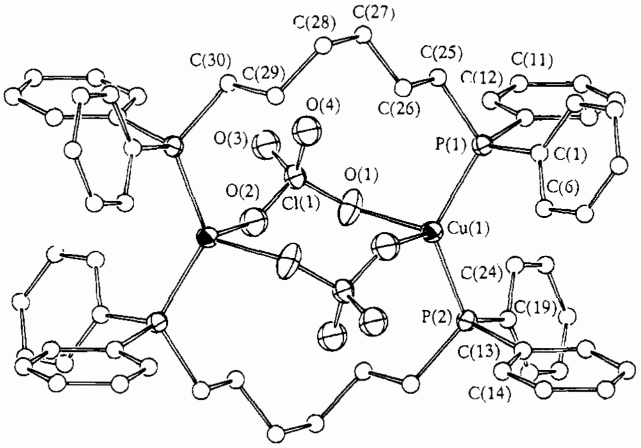

Figure 3. ORTEP drawing of entire molecule of [$Cu_2(\mu\text{-dpph})_2(\mu\text{-}ClO_4)_2$] with thermal ellipsoids at the 50% level for Cu, Cl, P, and O atoms. Ellipsoids of the carbon atoms in the methylene and phenyl groups have been arbitrarily reduced. The numbers of unlabeled phenyl carbon atoms follow from those given. Only half the atoms are labeled; the others are related by a center of inversion at the midpoint of the Cu−Cu vector. The perchlorate ions are disordered, and only the major part is drawn.

Table 3. Positional and Equivalent Isotropic Thermal Parameters for [$Cu_2(dppb)_2(ClO_4)_2$] (**2**)

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Cu	0.7835(1)	0.6211(1)	0.3880(1)	4.20(7)
Cl	0.8605(2)	0.3571(2)	0.3281(2)	4.2(1)
P(1)	0.8142(2)	0.6797(2)	0.2145(2)	3.2(1)
P(2)	0.6489(2)	0.6726(2)	0.5111(2)	3.2(1)
O(1)	0.9396(8)	0.4201(7)	0.3994(8)	6.8(6)
O(2)	0.7324(8)	0.4382(8)	0.305(1)	11.5(7)
O(3)	0.891(1)	0.2631(7)	0.406(1)	9.6(7)
O(4)	0.878(1)	0.3210(9)	0.2008(9)	9.3(7)
C(1)	0.9498(8)	0.5745(7)	0.1582(9)	3.7(5)
C(2)	1.0808(8)	0.5432(7)	0.2829(9)	3.7(5)
C(3)	0.8028(8)	0.5382(7)	0.7626(9)	3.9(5)
C(4)	0.6718(8)	0.5718(8)	0.6417(9)	3.8(5)
C(5)	0.8397(8)	0.8120(7)	0.234(1)	4.0(5)
C(6)	0.8361(9)	0.8737(6)	0.356(1)	6.2(6)
C(7)	0.858(1)	0.9773(9)	0.373(1)	7.5(7)
C(8)	0.887(1)	1.0108(9)	0.271(2)	8.1(7)
C(9)	0.887(1)	0.9519(9)	0.148(2)	7.6(7)
C(10)	0.8636(9)	0.8513(8)	0.130(1)	3.9(5)
C(11)	0.6663(8)	0.7065(7)	0.0628(8)	3.0(4)
C(12)	0.6365(9)	0.6094(8)	0.0094(9)	3.9(5)
C(13)	0.5157(9)	0.6277(8)	−0.096(1)	4.1(5)
C(14)	0.4283(9)	0.7396(8)	−0.148(1)	4.4(5)
C(15)	0.4598(9)	0.8329(8)	−0.094(1)	4.8(6)
C(16)	0.5809(8)	0.8170(8)	0.010(1)	4.2(5)
C(17)	0.6469(9)	0.8039(7)	0.6069(9)	3.9(5)
C(18)	0.538(1)	0.8939(8)	0.625(1)	4.7(6)
C(19)	0.547(1)	0.9889(9)	0.703(1)	5.9(7)
C(20)	0.670(1)	0.9951(9)	0.763(1)	6.3(8)
C(21)	0.779(1)	0.904(1)	0.745(1)	7.3(9)
C(22)	0.771(1)	0.8074(9)	0.667(1)	5.8(7)
C(23)	0.4794(8)	0.7023(7)	0.3968(9)	3.4(5)
C(24)	0.4615(9)	0.6899(8)	0.2533(9)	3.9(5)
C(25)	0.3343(9)	0.7088(8)	0.161(1)	4.8(6)
C(26)	0.2324(9)	0.7390(8)	0.208(1)	4.9(6)
C(27)	0.2501(9)	0.7508(8)	0.351(1)	5.1(6)
C(28)	0.3790(9)	0.7304(8)	0.445(1)	4.3(6)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c12\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

narrow angle of O(1)−Cu−O(2′) = 90.3(3)°. The Cu−P bond distances and P−Cu−P angles fall within normal values.

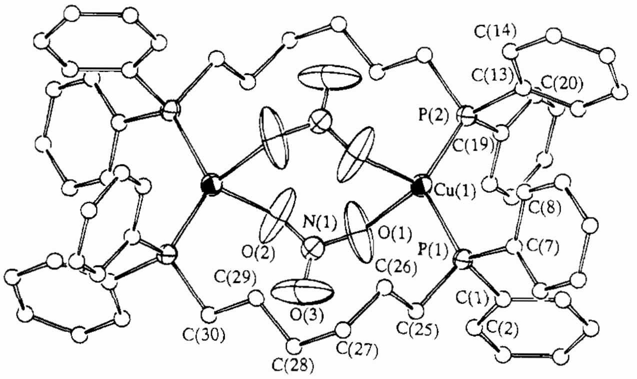

Figure 4. ORTEP drawing of the entire molecule of [$Cu_2(\mu\text{-dpph})_2(\mu\text{-}NO_3)_2$] with thermal ellipsoids at the 50% level for Cu, P, O, and N atoms. One of the two molecules in the unit cell is displayed. Ellipsoids of the carbon atoms in the methylene and phenyl groups have been arbitrarily reduced. The numbers of unlabeled phenyl carbon atoms follow from those given. Only half the atoms are labeled; the others are related by a center of inversion at the midpoint of the Cu−Cu vector.

Table 4. Positional and Equivalent Isotropic Thermal Parameters for [$Cu_2(\mu\text{-dpph})_2(\mu\text{-}ClO_4)_2$] (**3**)

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Cu(1)	0.35421(8)	0.31500(7)	0.95409(9)	3.43(4)
Cl(1)	0.6113(1)	0.4223(1)	1.1466(2)	3.29(7)
P(1)	0.2490(1)	0.2859(1)	1.1132(2)	2.74(6)
P(2)	0.3305(2)	0.2325(1)	0.7447(2)	2.82(6)
O(1)	0.5396(5)	0.3349(4)	1.0556(6)	6.3(3)
O(2)[b]	0.6579(6)	0.5041(6)	1.0673(8)	5.3(2)
O(3)[b]	0.7045(7)	0.3905(6)	1.2355(8)	5.5(2)
O(4)[b]	0.5497(7)	0.4678(7)	1.2340(8)	5.6(2)
O(5)[b]	0.574(2)	0.519(2)	1.129(2)	7.3(5)
O(6)[b]	0.581(2)	0.388(2)	1.270(2)	7.7(5)
O(7)[b]	0.724(2)	0.417(2)	1.154(2)	7.2(5)
C(1)	0.1016(6)	0.3008(5)	1.0610(7)	3.45(3)
C(3)	−0.0834(7)	0.3042(7)	1.108(1)	5.8(4)
C(4)	−0.1178(7)	0.3406(7)	0.982(1)	5.7(4)
C(5)	−0.0435(7)	0.3563(7)	0.8965(8)	5.4(4)
C(6)	0.0663(6)	0.3373(6)	0.9354(7)	4.0(3)
C(7)	0.2414(6)	0.1484(5)	1.1597(6)	3.2(3)
C(8)	0.1434(7)	0.0678(6)	1.129(1)	5.9(4)
C(9)	0.1488(8)	−0.0352(6)	1.158(1)	6.6(4)
C(10)	0.2481(8)	−0.0620(6)	1.2161(9)	5.7(4)
C(11)	0.3467(7)	0.0149(6)	1.2484(8)	5.1(4)
C(12)	0.3431(6)	0.1199(6)	1.2195(8)	4.1(3)
C(13)	0.1903(5)	0.2404(5)	0.6452(7)	3.2(3)
C(14)	0.1709(6)	0.3393(6)	0.6043(7)	4.0(3)
C(15)	0.0640(8)	0.3502(7)	0.5390(9)	5.7(4)
C(16)	−0.0273(7)	0.2660(9)	0.509(1)	6.4(4)
C(17)	−0.0094(8)	0.1679(8)	0.546(1)	7.4(5)
C(18)	0.0978(7)	0.1545(7)	0.617(1)	5.8(4)
C(19)	0.3312(6)	0.0896(5)	0.7356(7)	3.5(3)
C(20)	0.3209(6)	0.0302(5)	0.6122(7)	4.3(3)
C(21)	0.3244(7)	−0.0768(6)	0.6085(9)	5.2(4)
C(22)	0.3383(7)	−0.1272(6)	0.725(1)	5.4(4)
C(23)	0.3494(8)	−0.0713(7)	0.847(1)	6.3(4)
C(24)	0.3465(7)	0.0388(6)	0.8540(8)	5.2(4)
C(25)	0.2982(5)	0.3665(5)	1.2799(6)	2.9(2)
C(26)	0.3004(6)	0.4854(5)	1.2668(6)	3.2(3)
C(27)	0.3493(6)	0.5532(5)	1.4021(6)	3.2(3)
C(28)	0.3623(6)	0.6736(5)	1.3921(7)	3.6(3)
C(29)	0.4474(6)	0.7230(5)	1.3058(7)	3.3(3)
C(30)	0.5703(6)	0.7130(5)	1.3637(6)	3.1(3)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] Disordered. Occupancies are 0.8 and 0.2 for O(2)−O(4) and O(5)−O(7), respectively.

[$Cu_2(dpph)_2(\mu\text{-}PO_2F_2)_2$] (5). The molecular structure in Figure 5 is essentially isostructural with that of **3**. Interestingly, a tetrahedral monovalent anion is introduced into the molecule although an octahedral PF_6^- anion is used in the synthesis. This feature was unexpected, but a similar phenomenon has also been

Table 5. Positional and Equivalent Isotropic Thermal Parameters for $[Cu_2(\mu\text{-dpph})_2(\mu\text{-}NO_3)_2]$ (**4**)

atom	*x*	*y*	*z*	B_{eq},[a] Å^2	atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Cu(1)	0.66026(5)	0.02263(5)	0.03183(8)	4.11(4)	C(24)	0.7917(5)	−0.1395(4)	−0.0214(8)	5.1(4)
Cu(2)	0.16456(5)	0.47736(5)	0.05026(8)	3.52(4)	C(25)	0.6451(4)	0.0765(4)	0.3569(6)	3.6(3)
P(1)	0.7210(1)	0.0597(1)	0.2341(2)	3.28(8)	C(26)	0.5864(4)	0.1425(4)	0.3206(6)	3.7(3)
P(2)	0.7338(1)	−0.0092(1)	−0.1387(2)	3.32(8)	C(27)	0.5193(4)	0.1570(4)	0.4184(7)	4.4(4)
P(3)	0.2400(1)	0.4404(1)	−0.1181(2)	3.13(8)	C(28)	0.4517(4)	0.0977(4)	0.4245(7)	4.2(3)
P(4)	0.2167(1)	0.5118(1)	0.2587(2)	3.14(8)	C(29)	0.3936(5)	0.0859(4)	0.2953(7)	4.5(4)
O(1)	0.5779(5)	−0.0678(3)	0.096(1)	14.0(6)	C(30)	0.3295(4)	0.0236(4)	0.3013(6)	3.6(3)
O(2)	0.4522(5)	−0.0837(4)	0.0320(9)	13.4(5)	C(31)	0.3126(4)	0.5097(4)	−0.1697(6)	3.7(3)
O(3)	0.4933(8)	−0.0834(6)	0.2231(8)	17.5(8)	C(32)	0.2771(5)	0.5764(4)	−0.2106(7)	4.2(4)
O(4)	0.0444(3)	0.4240(3)	0.0175(5)	6.7(3)	C(33)	0.3287(6)	0.6326(4)	−0.2502(8)	5.6(4)
O(5)	−0.0898(3)	0.4202(3)	0.0468(6)	7.5(3)	C(34)	0.4164(6)	0.6215(6)	−0.244(1)	7.3(6)
O(6)	0.0078(5)	0.4194(4)	0.2104(6)	11.0(5)	C(35)	0.4532(5)	0.5567(6)	−0.202(1)	8.0(6)
N(1)	0.5076(4)	−0.0782(3)	0.1210(7)	4.2(3)	C(36)	0.4019(5)	0.4996(5)	−0.1658(8)	6.0(5)
N(2)	−0.0127(4)	0.4204(3)	0.0947(6)	3.6(3)	C(37)	0.3105(4)	0.3609(3)	−0.0799(6)	3.3(3)
C(1)	0.7942(5)	−0.0106(4)	0.3124(6)	3.6(3)	C(38)	0.3365(5)	0.3444(4)	0.0515(7)	4.3(4)
C(2)	0.7596(5)	−0.0766(4)	0.3472(7)	5.0(4)	C(39)	0.3894(6)	0.2849(4)	0.0865(7)	5.6(4)
C(3)	0.8131(7)	−0.1324(5)	0.3969(9)	6.8(5)	C(40)	0.4171(5)	0.2406(4)	−0.0084(9)	5.3(4)
C(4)	0.9013(8)	−0.1247(6)	0.416(1)	7.8(6)	C(41)	0.3905(5)	0.2550(4)	−0.1402(8)	5.5(4)
C(5)	0.9374(6)	−0.0623(6)	0.380(1)	7.7(6)	C(42)	0.3386(5)	0.3147(4)	−0.1767(7)	4.8(4)
C(6)	0.8850(5)	−0.0047(4)	0.3278(9)	5.9(4)	C(43)	0.2817(4)	0.4398(4)	0.3500(6)	3.6(3)
C(7)	0.7869(4)	0.1419(3)	0.2475(7)	3.5(3)	C(44)	0.3622(5)	0.4482(4)	0.4238(8)	5.6(4)
C(8)	0.7960(5)	0.1814(4)	0.1333(7)	4.9(4)	C(45)	0.4060(6)	0.3902(7)	0.487(1)	7.4(6)
C(9)	0.8441(6)	0.2451(4)	0.1419(9)	6.2(5)	C(46)	0.3716(8)	0.3230(6)	0.4795(9)	7.3(6)
C(10)	0.8829(5)	0.2691(4)	0.264(1)	5.8(4)	C(47)	0.2905(8)	0.3126(5)	0.411(1)	7.1(6)
C(11)	0.8725(5)	0.2315(4)	0.3778(8)	5.1(4)	C(48)	0.2449(5)	0.3707(5)	0.3451(7)	5.5(4)
C(12)	0.8248(4)	0.1680(4)	0.3710(7)	4.3(3)	C(49)	0.2871(4)	0.5908(4)	0.2667(6)	3.4(3)
C(13)	0.8103(4)	0.0627(4)	−0.1656(6)	3.4(3)	C(50)	0.3080(5)	0.6313(4)	0.3806(7)	5.0(4)
C(14)	0.7813(5)	0.1251(4)	−0.2320(7)	5.0(4)	C(51)	0.3586(5)	0.6929(5)	0.3816(8)	6.0(5)
C(15)	0.8379(7)	0.1832(4)	−0.2394(8)	6.2(5)	C(52)	0.3901(6)	0.7146(5)	0.267(1)	6.9(5)
C(16)	0.9214(6)	0.1807(5)	−0.179(1)	6.4(5)	C(53)	0.3709(7)	0.6743(6)	0.154(1)	9.4(7)
C(17)	0.9503(5)	0.1191(5)	−0.112(1)	6.5(5)	C(54)	0.3201(6)	0.6133(5)	0.1540(7)	7.1(5)
C(18)	0.8952(5)	0.0607(4)	−0.1038(8)	5.1(4)	C(55)	0.1749(4)	0.4183(4)	−0.2777(6)	3.6(3)
C(19)	0.8005(4)	−0.0912(4)	−0.1221(7)	3.6(3)	C(56)	0.1188(4)	0.3509(3)	−0.2712(6)	3.5(3)
C(20)	0.8554(5)	−0.1117(4)	−0.2143(8)	5.5(4)	C(57)	0.0583(4)	0.3368(3)	−0.3991(6)	3.7(3)
C(21)	0.8984(6)	−0.1781(6)	−0.206(1)	7.3(6)	C(58)	−0.0101(4)	0.3964(3)	−0.4353(6)	3.3(3)
C(22)	0.8883(7)	−0.2243(5)	−0.103(1)	7.9(6)	C(59)	−0.0754(4)	0.4063(4)	−0.3351(6)	3.6(3)
C(23)	0.8352(7)	−0.2051(5)	−0.011(1)	7.4(6)	C(60)	−0.1396(4)	0.4675(4)	−0.3782(6)	3.3(3)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

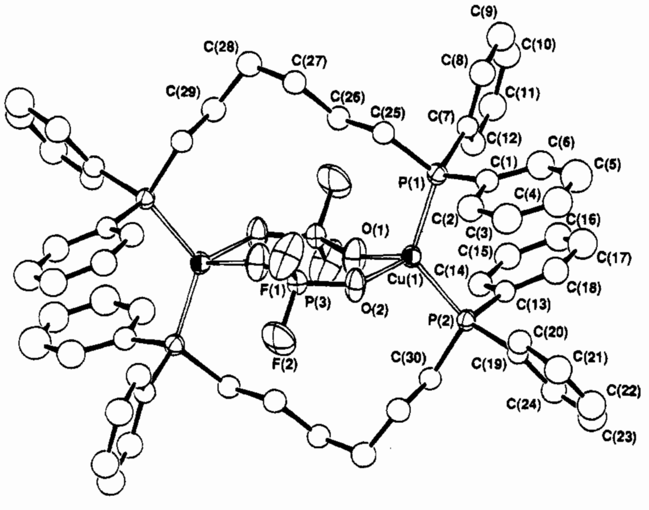

Figure 5. ORTEP drawing of the entire molecule of $[Cu_2(\mu\text{-dpph})_2(\mu\text{-}PF_2O_2)_2]$ with thermal ellipsoids at the 50% level for Cu, P, F, and O atoms. Ellipsoids of the carbon atoms in the methylene and phenyl groups have been arbitrarily reduced. The numbers of unlabeled phenyl carbon atoms follow from those given. Only half the atoms are labeled; the others are related by a center of inversion at the midpoint of the Cu−Cu vector. The perchlorate ions are disordered, and only the major part is drawn.

found in $\{[Cu(C_9H_7NS)_2]PO_2F_2\}$.[40] The $PO_2F_2^-$ anion is likely produced by partial hydrolysis of PF_6^- by water present in the starting materials or solvent.[41−44] The Cu−P distances in **3** and **5** are close to each other, while the angles P−Cu−P$_{av}$ and O−Cu−O$_{av}$ of **5** are smaller by 5° than the corresponding angles in **3**. The Cu(1)−O bond distances of the two are nearly equal, dissimilar from those of **3** and **4**. The anion PO_2F_2 shows bond distances (P(3)−F$_{av}$ = 1.504(3) and P(3)−O$_{av}$ = 1.433(2) Å) and angles (F(1)−P(3)−F(2) = 94.1°, O(1)−P(3)−O(2) = 125.1(1)°, and F−P(3)−O$_{av}$ = 108.3(2)°) very close to those of terminally coordinated PO_2F_2 in $[Cu(bpy)(PO_2F_2)_2]$,[43] indicating no apparent effect of the coordination on the structural parameters.

$[Ag_2(dpph)_2(\mu\text{-}ClO_4)_2]$ (6). Figure 6 shows an entire molecule of **6**, which has the center of symmetry at the midpoint of the Ag(1)−Ag(1′) vector. The geometry around the silver atom with the P_2O_2 donor set is tetrahedral. The average Ag−P distance of 2.418(2) Å falls within the usual distances of silver compounds.[45] This is reasonable because the Ag−P distances are insensitive to the phosphines in AgP_2L or AgP_2L_2 type complexes. The coordinated perchlorate anions are disordered as in **3** and have two positions, A and B, which are related to each other by rotation around the Cl(1)−O(1) axis. The Ag−O

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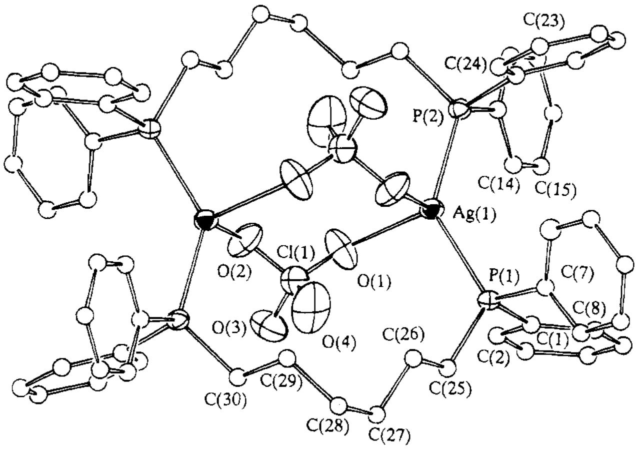

Figure 6. ORTEP drawing of the entire molecule of $[Ag_2(\mu\text{-dpph})_2(\mu\text{-ClO}_4)_2]$ with thermal ellipsoids at the 30% level for Ag, P, Cl, and O atoms. Ellipsoids of the carbon atoms in the methylene and phenyl groups have been arbitrarily reduced. The numbers of unlabeled phenyl carbon atoms follow from those given. Only half the atoms are labeled; the others are related by a center of inversion at the midpoint of the Ag−Ag vector. The perchlorate ions are disordered, and only the major part is drawn.

Table 6. Positional and Equivalent Isotropic Thermal Parameters for $[Cu_2(\mu\text{-dpph})_2(\mu\text{-PF}_2O_2)_2]$ (**5**)

atom	x	y	z	B_{eq},[a] Å^2
Cu(1)	0.35773(3)	0.31544(3)	0.96192(4)	3.79(2)
P(1)	0.26315(6)	0.30155(6)	0.74944(8)	3.67(3)
P(2)	0.30609(6)	0.21344(6)	1.13734(8)	3.37(3)
P(3)	0.62833(6)	0.42638(6)	0.93644(8)	3.71(3)
F(1)	0.6731(3)	0.4150(2)	0.8107(3)	11.2(2)
F(2)	0.7343(2)	0.4035(3)	1.0297(4)	12.1(2)
O(1)	0.5353(2)	0.3372(2)	0.9478(3)	5.9(1)
O(2)	0.6238(2)	0.5362(2)	0.9468(3)	7.1(1)
C(1)	0.2531(3)	0.1685(2)	0.6885(3)	4.4(1)
C(2)	0.3558(3)	0.1375(3)	0.6851(4)	5.9(2)
C(3)	0.3567(5)	0.0354(4)	0.6503(5)	7.9(2)
C(4)	0.2568(6)	−0.0367(4)	0.6184(5)	8.3(3)
C(5)	0.1548(5)	−0.0087(4)	0.6216(6)	9.1(3)
C(6)	0.1517(4)	0.0942(3)	0.6580(5)	6.7(2)
C(7)	0.1168(2)	0.3252(2)	0.7122(3)	3.9(1)
C(8)	0.0528(3)	0.3250(3)	0.5823(4)	5.8(2)
C(9)	−0.0548(3)	0.3510(4)	0.5579(4)	6.7(2)
C(10)	−0.1001(3)	0.3757(4)	0.6619(5)	6.6(2)
C(11)	−0.0392(3)	0.3758(4)	0.7901(4)	6.5(2)
C(12)	0.0697(3)	0.3509(3)	0.8161(4)	5.1(1)
C(13)	0.1584(2)	0.2181(2)	1.1502(3)	3.8(1)
C(14)	0.1343(3)	0.3066(3)	1.2019(4)	4.8(1)
C(15)	0.0207(3)	0.3151(3)	1.1968(4)	5.9(2)
C(16)	−0.0681(3)	0.2371(4)	1.1411(5)	6.6(2)
C(17)	−0.0458(3)	0.1505(4)	1.0893(6)	7.9(2)
C(18)	0.0668(3)	0.1410(3)	1.0940(5)	6.1(2)
C(19)	0.3082(2)	0.0711(2)	1.1469(3)	3.8(1)
C(20)	0.3505(3)	0.0283(3)	1.0522(4)	4.8(1)
C(21)	0.3567(3)	−0.0804(3)	1.0636(5)	6.7(2)
C(22)	0.3199(4)	−0.1420(3)	1.1663(6)	7.4(2)
C(23)	0.2766(5)	−0.1011(3)	1.2598(5)	7.6(2)
C(24)	0.2709(4)	0.0058(3)	1.2509(4)	5.8(2)
C(25)	0.3324(3)	0.3900(2)	0.6257(3)	4.2(1)
C(26)	0.3430(3)	0.5087(3)	0.6524(3)	4.5(1)
C(27)	0.3971(3)	0.5814(3)	0.5485(3)	4.4(1)
C(28)	0.4041(3)	0.7003(3)	0.5633(4)	5.2(1)
C(29)	0.4815(3)	0.7471(3)	0.6900(4)	4.8(1)
C(30)	0.6084(3)	0.7400(2)	0.7011(3)	4.1(1)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 7. Positional and Equivalent Isotropic Thermal Parameters for $[Ag_2(\mu\text{-dpph})_2(\mu\text{-ClO}_4)_2]$ (**6**)

atom	x	y	z	B_{eq},[a] Å^2
Ag(1)	0.65101(3)	0.18628(2)	0.55387(3)	3.59(1)
Cl(1)	0.3837(1)	0.08360(8)	0.3431(1)	4.21(4)
P(1)	0.76179(8)	0.21675(7)	0.38137(9)	2.95(3)
P(2)	0.67139(9)	0.26742(7)	0.7776(1)	3.12(3)
O(1)	0.4357(4)	0.1780(3)	0.4261(4)	8.3(2)
O(2)[b]	0.3120(6)	0.0134(5)	0.4108(7)	7.7(3)
O(3)[b]	0.3014(7)	0.1102(4)	0.2317(6)	7.9(3)
O(4)[b]	0.4566(6)	0.0285(6)	0.294(1)	11.7(4)
O(5)[b]	0.274(2)	0.055(3)	0.324(4)	11(2)
O(6)[b]	0.425(2)	0.124(2)	0.235(2)	8(1)
O(7)[b]	0.459(2)	0.014(2)	0.403(3)	9(1)
C(1)	0.7709(4)	0.3542(3)	0.3398(4)	3.6(1)
C(2)	0.6674(4)	0.3877(4)	0.2994(5)	4.8(2)
C(3)	0.6659(5)	0.4918(4)	0.2728(6)	6.3(2)
C(4)	0.7671(7)	0.5642(4)	0.2878(6)	7.3(3)
C(5)	0.8703(6)	0.5346(4)	0.3263(8)	8.7(3)
C(6)	0.8733(5)	0.4285(4)	0.3529(6)	6.5(2)
C(7)	0.9088(3)	0.1978(3)	0.4351(4)	3.4(1)
C(8)	0.9862(4)	0.2048(4)	0.3509(5)	5.5(2)
C(9)	1.0954(4)	0.1827(5)	0.3944(6)	6.8(3)
C(10)	1.1274(4)	0.1543(5)	0.5205(6)	6.0(2)
C(11)	1.0532(4)	0.1480(4)	0.6045(5)	5.7(2)
C(12)	0.9433(4)	0.1689(4)	0.5624(4)	4.4(2)
C(13)	0.6692(3)	0.4090(3)	0.7868(4)	3.5(1)
C(14)	0.6678(6)	0.4620(4)	0.6725(5)	6.2(2)
C(15)	0.6635(6)	0.5695(4)	0.6760(6)	7.5(3)
C(16)	0.6608(5)	0.6245(4)	0.7931(6)	6.1(2)
C(17)	0.6617(5)	0.5721(4)	0.9049(5)	5.5(2)
C(18)	0.6663(4)	0.4657(3)	0.9035(4)	4.7(2)
C(19)	0.8131(3)	0.2580(3)	0.8750(4)	3.5(1)
C(20)	0.9007(5)	0.3450(4)	0.9286(8)	8.0(3)
C(21)	1.0094(5)	0.3294(6)	0.991(1)	10.0(4)
C(22)	1.0319(5)	0.2315(5)	1.0024(6)	6.3(2)
C(23)	0.9458(5)	0.1454(4)	0.9529(5)	5.8(2)
C(24)	0.8376(4)	0.1591(4)	0.8899(5)	4.9(2)
C(25)	0.7096(3)	0.1380(3)	0.2193(3)	3.3(1)
C(26)	0.7056(3)	0.0201(3)	0.2306(4)	3.4(1)
C(27)	0.6565(3)	−0.0461(3)	0.0973(4)	3.5(1)
C(28)	0.6433(4)	−0.1660(3)	0.1054(4)	3.9(1)
C(29)	0.5553(3)	−0.2162(3)	0.1857(4)	3.5(1)
C(30)	0.4310(3)	−0.2102(3)	0.1225(4)	3.3(1)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] Disordered. Occupancies are 0.8 and 0.2 for O(2)−O(4), and O(5)−O(7), respectively.

bond distances of bridging ClO_4^- are different as in compounds 3 and 4. The Ag−O(1) distance of 2.639(4) Å is longer than those of μ-ClO_4 in $[Ag(C_{12}H_{10})(\mu\text{-ClO}_4)]_n$ (2.31(1)−2.58(1) Å)[46] but shorter than those of chelating ClO_4 (2.75(1) and 2.81(1) Å) in $[AgL(ClO_4)]$ (L = 2,11-bis((diphenylphosphino)methyl)-benzo[*c*]phenanthrene).[47] A strong Ag−ClO_4 interaction is inferred by the large deviation of the P−Ag−P angles from linearity: 134.33(5)°. A weaker Ag−O interaction has been found in $[Ag(napy)_2](ClO_4)_2$ (2.62(2) Å),[48] which has an angle of 167.8(5)°, much greater than that of **6**. On the basis of the distance and angles, the metal−anion interaction in the cavity of the macrocycles of $M_2(dpph)_2$ is stronger than the usual metal−anion interactions even if low coordination capability of the anion is used. A similar macrocycle has been found in $[Ag_2L_2Cl_2]$ (L = 1,5-bis(diphenylphosphino)pentane),[13] whose cavity is a smaller 16-membered ring and thus includes chloride bridges.

The Cavity for Anions. The size of cavity for each compound can be estimated by the distance, *L*, between the two

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Table 8. Selected Bond Distances (Å) and Angles (deg) for $[Cu(dppp)_2]ClO_4{\cdot}0.5CH_3OH$ (**1**)

	Distances		
Cu(1)−P(1)	2.316(3)	Cu(1)−P(2)	2.311(3)
Cu(1)−P(3)	2.312(3)	Cu(1)−P(4)	2.330(2)
P(1)−C(1)	1.825(9)	P(2)−C(15)	1.829(9)
P(1)−C(7)	1.819(9)	P(2)−C(16)	1.837(9)
P(1)−C(13)	1.829(9)	P(2)−C(22)	1.820(8)
P(3)−C(28)	1.817(8)	P(4)−C(42)	1.828(8)
P(3)−C(34)	1.825(8)	P(4)−C(43)	1.810(8)
P(3)−C(40)	1.835(8)	P(4)−C(49)	1.846(8)
	Angles		
P(1)−Cu(1)−P(2)	94.56(9)	Cu(1)−P(1)−C(1)	119.1(3)
P(1)−Cu(1)−P(3)	121.6(1)	Cu(1)−P(1)−C(7)	114.2(3)
P(1)−Cu(1)−P(4)	122.29(9)	Cu(1)−P(1)−C(13)	110.8(3)
P(2)−Cu(1)−P(3)	118.3(1)	C(1)−P(1)−C(7)	102.9(4)
P(2)−Cu(1)−P(4)	103.31(9)	C(1)−P(1)−C(13)	103.8(4)
P(3)−Cu(1)−P(4)	96.94(9)	C(7)−P(1)−C(13)	104.5(4)
Cu(1)−P(2)−C(15)	109.2(3)	Cu(1)−P(3)−C(28)	115.0(3)
Cu(1)−P(2)−C(16)	119.8(3)	Cu(1)−P(3)−C(34)	121.9(3)
Cu(1)−P(2)−C(22)	117.5(3)	Cu(1)−P(3)−C(40)	109.1(3)
Cu(1)−P(4)−C(42)	108.2(3)	C(15)−P(2)−C(16)	103.5(4)
Cu(1)−P(4)−C(43)	116.0(3)	C(15)−P(2)−C(22)	101.7(4)
Cu(1)−P(4)−C(49)	122.1(3)	C(16)−P(2)−C(22)	102.9(4)
C(28)−P(3)−C(34)	101.5(4)	C(42)−P(4)−C(43)	103.3(4)
C(28)−P(3)−C(40)	104.7(4)	C(42)−P(4)−C(49)	103.5(4)
C(34)−P(3)−C(40)	102.7(4)	C(43)−P(4)−C(49)	101.6(4)

Table 9. Selected Bond Distances (Å) and Angles (deg) for $[Cu_2(dppb)_2(ClO_4)_2]$ (**2**)

	Distances		
Cu−P(1)	2.239(3)	Cu−P(2)	2.241(3)
Cu−O(1)	2.435(8)	Cl−O(1)	1.43(1)
Cl−O(2)	1.391(8)	Cl−O(3)	1.37(8)
Cl−O(4)	1.39(1)	P(1)−C(1)	1.844(9)
P(1)−C(5)	1.81(1)	P(1)−C(11)	1.828(7)
P(2)−C(4)	1.86(1)	P(2)−C(17)	1.823(9)
P(2)−C(23)	1.843(8)	Cu−Cu′	4.631(3)[a]
Cu−O(3′)	4.47(1)[a]		
	Angles		
P(1)−Cu−P(2)	142.8(1)	P(1)−Cu−O(1)	97.2(3)
P(2)−Cu−O(1)	118.8(3)	O(1)−Cl−O(2)	104.2(5)
O(1)−Cl−O(3)	111.1(5)	O(1)−Cl−O(4)	109.4(7)
O(2)−Cl−O(3)	112.3(8)	O(2)−Cl−O(4)	109.4(6)
O(3)−Cl−O(4)	110.3(6)	Cu−P(1)−C(1)	116.1(3)
Cu−P(1)−C(5)	118.3(4)	Cu−P(1)−C(11)	107.4(4)
C(1)−P(1)−C(5)	103.6(5)	C(1)−P(1)−C(11)	105.1(4)
C(5)−P(1)−C(11)	105.0(4)	Cu(1)−P(2)−C(4)	121.3(3)
Cu−P(2)−C(17)	111.0(4)	Cu−P(2)−C(23)	110.8(3)
C(4)−P(2)−C(17)	104.1(4)	C(4)−P(2)−C(23)	101.1(5)
C(17)−P(2)−C(23)	107.4(4)	Cu−O(1)−Cl(1)	104.7(4)
P(1)−C(1)−C(2)	109.0(6)	P(2)−C(4)−C(3)	114.2(8)

[a] The nonbonded distance.

copper (or silver) atoms, which are listed in Tables 9−13 and compared in Figure 7. The value of *L* for **2** is smaller by 0.6 Å than that for **3**. The inhibition of bridging coordination of ClO_4^- is attributed to the shorter distance for the bite angle and the blocking effect of upright phenyl groups as clearly shown in Figure 2B. The NO_3 and PF_2O_2 anions are also able to bridge the two copper atoms, the distances ranging from 4.99 to 5.22 Å. For this type of cavity for the anions the distance needs to be at least 4.9 Å. Compound **4** displays two molecular structures; one has a longer *L* value than the other. On this basis, comparison of ClO_4^- and NO_3^- shows that the macrocycle of $Cu_2(dpph)_2$ is flexible enough to accept both anions. This flexibility is estimated as the range of *L* ($\Delta L = 0.23$ Å).

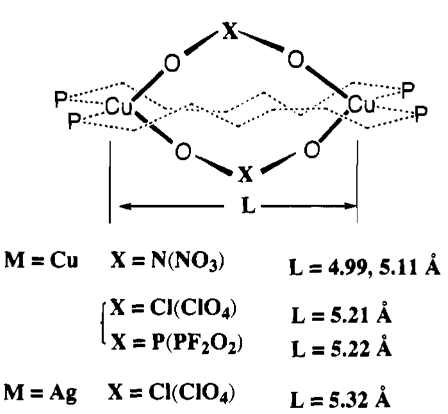

Figure 7. Schematic structure of the ring compounds and their ring size.

Table 10. Selected Bond Distances (Å) and Bond Angles (deg) for $[Cu_2(\mu\text{-dpph})_2(\mu\text{-}ClO_4)_2]$ (**3**)

	Distances		
Cu(1)−P(1)	2.234(2)	Cu(1)−P(2)	2.238(2)
Cu(1)−O(1)	2.236(6)	Cu(1′)−O(2)	2.354(8)
Cu(1′)−O(5)	2.37(2)	Cl(1)−O(1)	1.423(5)
Cl(1)−O(2)	1.433(8)	Cl(1)−O(3)	1.433(8)
Cl(1)−O(4)	1.431(8)	Cl(1)−O(5)	1.41(2)
Cl(1)−O(6)	1.42(2)	Cl(1)−O(7)	1.37(2)
P(1)−C(1)	1.813(7)	P(1)−C(7)	1.821(7)
P(1)−C(25)	1.840(6)	P(2)−C(13)	1.817(7)
P(2)−C(19)	1.818(7)	P(2)−C(30)	1.836(7)
Cu(1)−Cu(1′)	5.213(3)[a]		
	Angles		
P(1)−Cu(1)−P(2)	130.92(8)	P(1)−Cu(1)−O(1)	108.5(2)
P(1)−Cu(1)−O(2′)	96.6(2)	P(1)−Cu(1)−O(5′)	128.3(6)
P(2)−Cu(1)−O(1)	107.1(2)	P(2)−Cu(1)−O(2′)	108.7(2)
P(2)−Cu(1)−O(5′)	89.3(5)	O(1)−Cl(1)−O(2)	108.7(4)
O(1)−Cu(1)−O(2′)	100.7(2)	O(1)−Cl(1)−O(3)	112.3(4)
O(1)−Cl(1)−O(4)	112.2(4)	O(2)−Cl(1)−O(3)	108.6(5)
O(2)−Cl(1)−O(4)	109.0(5)	O(3)−Cl(1)−O(4)	106.1(5)
O(1)−Cl(1)−O(5)	112.7(8)	O(1)−Cl(1)−O(6)	97.9(8)
O(1)−Cl(1)−O(7)	108.7(9)	O(5)−Cl(1)−O(6)	105(1)
O(5)−Cl(1)−O(7)	122(1)	O(6)−Cl(1)−O(7)	108(1)
Cu(1)−P(1)−C(25)	119.3(2)	Cu(1)−P(2)−C(13)	108.7(2)
Cu(1)−P(1)−C(1)	115.1(2)	Cu(1)−P(2)−C(19)	116.4(2)
Cu(1)−P(1)−C(7)	109.2(2)	Cu(1)−P(2)−C(30)	118.3(2)
Cu(1)−O(1)−Cl(1)	128.2(3)	Cu(1)−O(2′)−Cl(1′)	134.1(5)
Cu(1)−O(5′)−Cl(1′)	134(1)	C(13)−P(2)−C(19)	104.8(3)
C(1)−P(1)−C(7)	106.2(3)	C(13)−P(2)−C(30)	103.6(3)
C(1)−P(1)−C(25)	102.6(3)	C(19)−P(2)−C(30)	103.5(3)
C(7)−P(1)−C(25)	130.0(3)		

[a] The intramolecular distance of nonbonded copper atoms.

Solution Equilibria. The formation and solution equilibria of $[Cu_2(dpph)_2X_2]$ ($X = ClO_4^-$, NO_3^-) are examined by NMR spectroscopy. Figure 8 shows the temperature dependence of ^{31}P NMR signals of the coordinated dpph. Two signals are observed at 23 °C, which are ascribed to the two compounds $[Cu_2(\mu\text{-dpph})_2X_2]$ (**3**) and $[Cu(P\text{-dpph})_2]$ (**3′**). With lowering temperature, the signal of **3′** decreases and disappears below −60 °C, while the signal of **3** increases gradually. ^1H NMR spectra at +23 to −70 °C also exhibit similar temperature dependence for the two types of signals, which are assigned and listed in the Experimental Section. In the case of ^{31}P NMR, the chemical shift of **3′** being smaller than that of **3** indicates a lower coordination species such as $[Cu(P\text{-dpph})_2)]ClO_4$, in which the dpph operates as a monodentate ligand and the two phosphorus atoms are exchanged on coordination. The absence of chelate rings for dpph is accounted for by the ring size effect, which has clearly been demonstrated for cobalt complexes of diamines; the yield of chelate ring complexes from 7- to 8-member drastically decreases and complexes with a ring size greater than 12 hardly form.[49] $[Cu(P\text{-dpph})_2)]ClO_4$ is readily used for the formation of the macrocycle when the temperature decreases, and thus the signal of **3** is assigned to the binuclear $[Cu_2(\mu\text{-dpph})_2(ClO_4)_2]$.

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(49) Ogino, H. *J. Coord. Chem.* **1987**, *15*, 187−218.

Table 11. Bond Distances (Å) and Bond Angles (deg) for $[Cu_2(\mu\text{-dpph})_2(\mu\text{-NO}_3)_2]$ (**4**)

	Distances		
Cu(1)−P(1)	2.241(2)	Cu(1)−P(2)	2.242(2)
Cu(1)−O(1)	2.245(7)	Cu(1)−O(2′)	2.089(6)
Cu(2)−P(3)	2.267(2)	Cu(2)−P(4)	2.244(2)
Cu(2)−O(4)	2.097(5)	Cu(2)−O(5′)	2.345(6)
P(1)−C(1)	1.820(7)	P(1)−C(7)	1.824(6)
P(1)−C(25)	1.826(6)	P(2)−C(13)	1.825(7)
P(2)−C(19)	1.808(7)	P(2)−C(30)	1.820(6)
P(3)−C(31)	1.823(7)	P(3)−C(37)	1.822(7)
P(3)−C(55)	1.833(6)	P(4)−C(43)	1.829(7)
P(4)−C(49)	1.817(7)	P(4)−C(60)	1.828(6)
O(1)−N(1)	1.163(7)	O(4)−N(2)	1.246(6)
O(2)−N(1)	1.164(7)	O(5)−N(2)	1.226(7)
O(3)−N(1)	1.082(8)	O(6)−N(2)	1.170(7)
Cu(1)−Cu(1′)[a]	4.985(2)	Cu(2)−Cu(2′)	5.110(2)[a]
	Angles		
P(1)−Cu(1)−P(2)	125.31(8)	P(3)−Cu(2)−P(4)	128.53(7)
P(1)−Cu(1)−O(1)	99.0(3)	P(3)−Cu(2)−O(4)	105.6(1)
P(1)−Cu(1)−O(2′)	110.9(2)	P(3)−Cu(2)−O(5′)	101.0(2)
P(2)−Cu(1)−O(1)	112.8(2)	P(4)−Cu(2)−O(4)	119.3(2)
P(2)−Cu(1)−O(2′)	112.1(3)	P(4)−Cu(2)−O(5′)	105.4(2)
O(1)−Cu(1)−O(2′)	90.3(3)	O(4)−Cu(2)−O(5′)	86.3(2)
Cu(1)−P(1)−C(1)	110.3(2)	Cu(2)−P(3)−C(31)	113.4(2)
Cu(1)−P(1)−C(7)	119.2(2)	Cu(2)−P(3)−C(37)	114.8(2)
Cu(1)−P(1)−C(25)	115.6(2)	Cu(2)−P(3)−C(55)	116.4(2)
Cu(1)−P(2)−C(13)	109.1(2)	Cu(2)−P(4)−C(43)	112.2(2)
Cu(1)−P(2)−C(19)	118.2(2)	Cu(2)−P(4)−C(49)	114.3(2)
Cu(1)−P(2)−C(30)	117.4(2)	Cu(2)−P(4)−C(60)	118.9(2)
Cu(1)−O(1)−N(1)	140.4(6)	Cu(2)−O(4)−N(2)	127.7(4)
Cu(1)−O(2′)−N(1)	133.6(5)	Cu(2)−O(5′)−N(2)	123.8(4)
C(1)−P(1)−C(7)	104.1(3)	C(31)−P(3)−C(37)	104.5(3)
C(1)−P(1)−C(25)	103.5(3)	C(31)−P(3)−C(55)	101.4(3)
C(7)−P(1)−C(25)	102.5(3)	C(37)−P(3)−C(55)	104.7(3)
C(13)−P(2)−C(19)	104.3(3)	C(43)−P(4)−C(49)	105.6(3)
C(13)−P(2)−C(30)	105.1(3)	C(43)−P(4)−C(60)	99.8(3)
C(19)−P(2)−C(30)	101.3(3)	C(49)−P(4)−C(60)	104.2(3)
O(1)−N(1)−O(2)	117.5(9)	O(4)−N(2)−O(5)	118.8(6)
O(1)−N(1)−O(3)	122(1)	O(4)−N(2)−O(6)	119.8(7)
O(2)−N(1)−O(3)	120(1)	O(5)−N(2)−O(6)	121.4(7)

[a] The intramolecular distances of nonbonded copper atoms.

Table 12. Selected Bond Distances (Å) and Angles (deg) for $[Cu_2(\mu\text{-dpph})_2(\mu\text{-PF}_2\text{O}_2)_2]$ (**5**)

	Distances		
Cu(1)−P(1)	2.2272(9)	Cu(1)−P(2)	2.2401(9)
Cu(1)−O(1)	2.131(2)	Cu(1)−O(2′)	2.119(2)
P(3)−F(1)	1.503(2)	P(3)−F(2)	1.504(3)
P(3)−O(1)	1.435(2)	P(3)−O(2)	1.431(2)
P(1)−C(1)	1.822(3)	P(1)−C(7)	1.817(3)
P(1)−C(25)	1.833(3)	P(2)−C(13)	1.825(3)
P(2)−C(19)	1.825(3)	P(2)−C(30′)	1.817(3)
Cu(1)−Cu(1′)	5.2179(8)[a]		
	Angles		
P(1)−Cu(1)−P(2)	125.75(3)	P(1)−Cu(1)−O(1)	104.68(8)
P(1)−Cu(1)−O(2′)	116.32(9)	P(2)−Cu(1)−O(1)	115.19(8)
P(2)−Cu(1)−O(2′)	95.86(9)	O(1)−Cu(1)−O(2′)	95.0(1)
F(1)−P(3)−F(2)	94.1(2)	F(1)−P(3)−O(1)	108.4(2)
F(1)−P(3)−O(2)	108.4(2)	F(2)−P(3)−O(1)	107.4(2)
F(2)−P(3)−O(2)	109.0(2)	O(1)−P(3)−O(2)	125.1(1)
Cu(1)−P(1)−C(1)	110.4(1)	Cu(1)−P(1)−C(7)	118.2(1)
Cu(1)−P(1)−C(25)	115.7(1)	C(1)−P(1)−C(7)	105.7(1)
C(1)−P(1)−C(25)	103.1(1)	C(7)−P(1)−C(25)	102.3(1)
Cu(1)−P(2)−C(13)	110.1(1)	Cu(1)−P(2)−C(19)	120.5(1)
Cu(1)−P(2)−C(30′)	113.4(1)	C(13)−P(2)−C(19)	104.3(1)
C(13)−P(2)−C(30′)	104.3(1)	C(19)−P(2)−C(30′)	102.7(1)
Cu(1)−O(1)−P(3)	136.3(1)	Cu(1)−O(2′)−P(3′)	158.4(2)

[a] The intramolecular distances of nonbonded copper atoms.

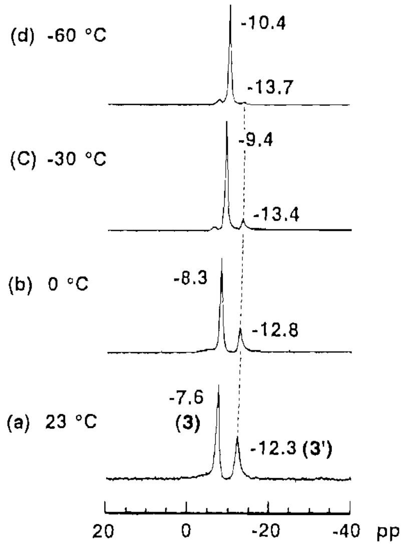

Figure 8. Temperature dependence of $^{31}P\{^1H\}$ NMR spectra of a [Cu]:[ClO$_4$]:[dpph] = 1:1:1 acetone solution ([Cu] = 10 mM). Signals (**3**) and (**3′**) denote $[Cu_2(\mu\text{-dpph})_2(\mu\text{-ClO}_4)_2]$ and $[Cu(P\text{-dpph})_2](ClO_4)_2$, respectively.

Table 13. Selected Bond Distances (Å) and Bond Angles (deg) for $[Ag_2(\mu\text{-dpph})_2(\mu\text{-ClO}_4)_2]$ (**6**)

	Distances		
Ag(1)−P(1)	2.419(2)	Ag(1)−P(2)	2.416(2)
Ag(1)−O(1)	2.639(4)	Ag(1)−O(2′)	2.712(6)
Ag(1)−O(7′)	2.74(2)	P(1)−C(1)	1.821(4)
Cl(1)−O(1)	1.402(4)	P(1)−C(7)	1.813(4)
Cl(1)−O(2)	1.424(5)	P(1)−C(25)	1.827(4)
Cl(1)−O(3)	1.456(6)	P(2)−C(13)	1.818(4)
Cl(1)−O(4)	1.380(5)	P(2)−C(19)	1.826(4)
Cl(1)−O(5)	1.27(2)	P(2)−C(30)	1.823(4)
Cl(1)−O(6)	1.39(2)	Cl(1)−O(7)	1.46(2)
Ag(1)−Ag(1′)	5.318(2)[a]		
	Angles		
P(1)−Ag(1)−P(2)	134.33(5)	P(1)−Ag(1)−O(1)	103.6(1)
P(1)−Ag(1)−O(2′)	95.0(2)	P(1)−Ag(1)−O(7′)	98.2(6)
P(2)−Ag(1)−O(1)	107.2(1)	P(2)−Ag(1)−O(2′)	104.6(2)
P(2)−Ag(1)−O(7)	96.4(7)	O(1)−Ag(1)−O(2′)	110.5(2)
O(1)−Ag(1)−O(7)	78.1(6)	O(2)−Cl(1)−O(3)	103.4(4)
O(1)−Cl(1)−O(2)	109.5(4)	O(2)−Cl(1)−O(4)	108.9(5)
O(1)−Cl(1)−O(3)	107.6(3)	O(3)−Cl(1)−O(4)	109.4(5)
O(1)−Cl(1)−O(4)	117.1(4)	O(5)−Cl(1)−O(6)	115(2)
O(1)−Cl(1)−O(5)	117(1)	O(5)−Cl(1)−O(7)	121(2)
O(1)−Cl(1)−O(6)	92(1)	O(6)−Cl(1)−O(7)	108(1)
O(1)−Cl(1)−O(7)	99(1)	Ag(1)−P(2)−C(13)	114.4(1)
Ag(1)−P(1)−C(1)	108.9(1)	Ag(1)−P(2)−C(19)	108.1(1)
Ag(1)−P(1)−C(7)	112.3(1)	Ag(1)−P(2)−C(30)	118.6(1)
Ag(1)−P(1)−C(25)	119.5(1)	C(13)−P(2)−C(19)	105.6(2)
C(1)−P(1)−C(7)	107.5(2)	C(13)−P(2)−C(30)	104.3(2)
C(1)−P(1)−C(25)	103.9(2)	C(19)−P(2)−C(30)	104.6(2)
C(7)−P(1)−C(25)	103.9(2)		

[a] The intramolecular distance of nonbonded silver atoms.

Figure 8 also shows the temperature dependence of the ^{31}P chemical shift. Generally, upfield shifts for all the signals are obtained because the point of the chemical shift for 85% H_3PO_4 and 23 °C is used as a reference position. For metal-free dpph in acetone, the observed chemical shifts are −15.8, −16.4, −17.0, and −17.6 ppm at 23, 0, −30, and −60 °C, respectively. On this basis, the signal of **3′** experiences no upfield shift while the signal of **3** still undergoes upfield shift[50] from +23 to −60 °C, implying the presence of chemical exchange. The upfield shift indicates the presence of a dominant species at low temperature whose Cu−P bonding is weaker than that for the other species. Most possible is the on−off mechanism that

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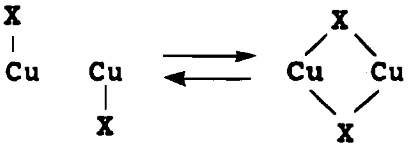
(50) From metal-free dpph the apparent shifts are estimated to be −0.6, −1.2, and −1.9 ppm at 0, −30, and −60 °C, respectively. By using these values for correction, the downfield shifts of the signal of **3** are estimated to be −0.1, −0.6, and −0.9 ppm at 0, −30, and −60 °C, respectively.

occurs upon the interconversion between terminal and bridging coordination of ClO_4^- ions:



The low temperature drives the reaction toward the right.

We have prepared other anion-trapped compounds by utilizing the exchange reaction. The anion salt was added to a solution of compound **1**. Instead of inorganic anions, organic anions such as carboxylates were also examined, and the formations of $[Cu_2(dpph)_2(\mu\text{-}RCO_2)]$ (R = CH_3 (**7**) and C_2H_5 (**8**)) were recognized. Unfortunately, the obtained compounds are microcrystals, insoluble in organic solvents and unsuitable for single-crystal X-ray crystallography. The IR spectra of the microcrystals were recorded instead of NMR spectra. The strong band ν_{CO} near 1600 cm^{-1}, characteristic of RCOO, is observed while the broad band at 1100 cm^{-1} for ClO_4^- decreases, which is attributable to $[Cu_2(dpph)_2(\mu\text{-}ClO_4)]$ as a starting material. Thus, carboxylates can be also included in the macrocycles.

In order to compare the affinity of the macrocycle moiety for anions, the nitrate anion was added to a solution of **3**. However, ^{31}P NMR failed to monitor the formation of **4** because the ^{31}P chemical shifts for both compounds are nearly equal.[51] Instead of ^{31}P NMR spectra, which provide the indirect information of anion-binding, ^{51}V NMR spectra were used to monitor the formation of $[Cu_2(\mu\text{-}dpph)_2(VO_3)_2]$ (**9**). The ^{51}V signal of VO_3^- in Figure 9b for the solution containing $[Cu(CH_3CN)_4]^+$ is essentially similar to that of the copper-free solution, indicating no significant interaction between copper ions and VO_3^- anions. Moreover, we can conclude that a simple electrostatic interaction of copper and VO_3^- ions is not strong enough to cause chemical shifts of the ^{51}V signal. On the other hand, the presence of $[Cu_2(\mu\text{-}dpph)_2]^{2+}$ affords a new signal at −532 ppm in Figure 9c, assigned to the signal of **9**. The addition of an equal amount of VO_3^- to a solution of **3** affords no signal for **9**. When the saturated solution is used, which contains precipitates of both NH_4VO_3 and **9**, the downfield signal appears with an intensity comparable to that of the upfield signal. Unfortunately, the solubility of the VO_3^- salt and compound **9** is very low, preventing quantitative analysis of the exchange reaction.[52] Qualitatively, the NMR spectra indicate that the affinity for VO_3^- is lower than that for ClO_4^-. The difference in affinities of $[Cu_2(\mu\text{-}dpph)_2]^{2+}$ for anions is unclear at present but is associated with the delicate balance of the stability of the inner and outer cycles.

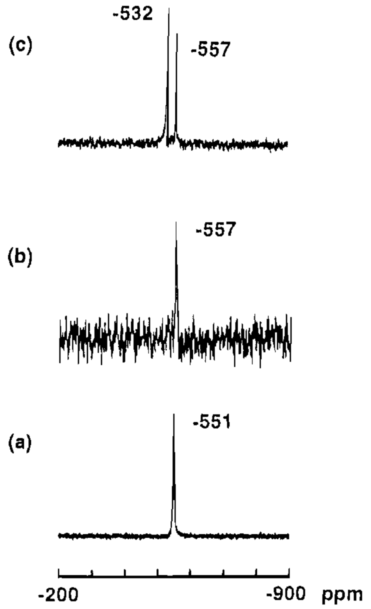


Figure 9. ^{51}V NMR spectra of THF/methanol (v/v, 1:1) solutions at 23 °C of (a) NH_4VO_3, (b) $[Cu(CH_3CN)_4]ClO_4/NH_4VO_3$, and (c) $[Cu_2(dpph)_2(ClO_4)_2]$ (5 mM) containing NH_4VO_3. For (a)−(c) the NH_4VO_3-saturated solutions are used.

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Supplementary Material Available: Listings of crystallographic data, fractional coordinates, thermal parameters, and bond distances and angles (30 pages). Ordering information is given on any current masthead page.

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(51) The signal undergoes line broadening even at low temperature. In addition to this, lowering of the solution temperature is restricted due to the very low solubility of compounds.

(52) The low solubility of these types of compounds hinders the development of chemistry concerning solution equilibria, thermodynamic stability constants, etc. The modification of dpph would solve the solubility problem.