826 *Inorg. Chem.* **1993,** *32,* 826-832

Synthesis, Structures, and Properties of the Molecular Assemblies of Copper(I) and Silver(I) Complexes with Phenazine. Novel Donor-Acceptor and Huge Polynuclear Complexes

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Received February 24, 1992

Three copper(I) and two silver(I) complexes with phenazine (phz), $[Cu_2(phz)_3(MeOH)_2](phz)(PF_6)_2$ (**1**), $[Cu(phz)_2(H_2O)]ClO_4$ (**2**), $[Cu(phz)_2(NO_3)]$ (**3**), $\{[Ag(phz)]ClO_4\}_\infty$ (**4**), and $[Ag_2(phz)(NO_3)_2]_\infty$ (**5**), were synthesized, and their molecular structures and packings were determined by using single-crystal X-ray diffraction methods. **1** is composed of infinite stacks of alternating metal-free phz molecules and the dicopper complex cations $[Cu_2(phz)_3(MeOH)_2]^{2+}$ and gives a CT band from the latter to the former at 710 nm indicative of a donor-acceptor complex. One phz in **2** and an opposite phz in another molecule alternatively stacked to give infinite columns. The copper of **3** is coordinated to NO_3^- and phz in a tetrahedral geometry. The molecular packing of **4** is composed of infinite linear chains of -Ag-phz-Ag-phz- along the a axis and a π-π interaction of the phz molecules between the chains along the c axis. The 3D complex **5** is made of a 2D framework of six-membered rings of silvers, a weak Ag-O bonding, and a π-π interaction of phz molecules between the 2D sheets. Solvent and counteranion as well as metal ion have been shown to play an important role in the molecular packing of metal complexes with phz because they are coordinated to metal ion to change the complex structure. Crystal data: **1**, triclinic $P\bar{1}$, a = 13.008(2) Å, b = 13.694(2) Å, c = 7.789(1) Å, α = 102.50(1)°, β = 105.02(1)°, γ = 72.81(1)°, V = 1256.4(3) Å^3, Z = 2, 3568 reflections, R = 0.069; **2**, triclinic $P\bar{1}$, a = 10.811(4) Å, b = 12.576(3) Å, c = 8.992(1) Å, α = 105.20(1)°, β = 92.59(2)°, γ = 110.90(5)°, V = 1089.0(5) Å^3, Z = 2, 3579 reflections, R = 0.045; **3**, monoclinic $P2_1/n$, a = 10.686(2) Å, b = 26.937(1) Å, c = 7.219(2) Å, β = 102.18(1)°, V = 2031(1) Å^3, Z = 4, 2256 reflections, R = 0.035; **4**, triclinic $P\bar{1}$, a = 7.2044(6) Å, b = 12.943(2) Å, c = 7.138(2) Å, α = 98.64(2)°, β = 98.70(1)°, γ = 89.92°, V = 650.3(2) Å^3, Z = 2, 2275 reflections, R = 0.034; **5**, monoclinic $P2_1/n$, a = 5.007(3) Å, b = 19.454(2) Å, c = 7.248(6) Å, β = 102.18(1)°, V = 685.0(7) Å^3, Z = 4, 2256 reflections, R = 0.035.

Introduction

Donor-acceptor complexes of aromatic-electron systems often possess interesting physical properties such as low-energy optically allowed intermolecular electronic transitions (charge-transfer bands), which in special cases even occur thermally to the extent that they may lead to metallic like conductivities.[1] Such properties not only are dependent on specific molecular properties of the individual components such as ionization energy of the donor and electron affinity of the acceptor but are also strongly influenced by details of relative arrangement and interactions in the crystal lattice. Therefore the synthetic method controlling the orientation of molecules in the crystals should be developed. The crystal packings of the donor-acceptor complexes are divided into the following five types: (1) infinite stacks of alternating donor and acceptor[1a,2-8] -D-A-D-A-, (2) infinite stacks of alternating two donors and two acceptors[9] -D-D-A-A-, (3) infinite segregated stack of donors and acceptors[10,11] -D-D-D-D- and -A-A-A-A-, (4) infinite stacks of only donors[12] -D-D-D-D-, and (5) discrete sandwiches[13,14] D-A-D. Organic molecules such as phenazine, acridine, carbazole, phenothiazine, and peryrene have been used as donors. Acceptors have included organic molecules such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), pyromellitic dianhydride (PMDA), 1,4-substituted pyridinum cations and chloranile, and a few inorganic metal complexes, $M(tfd)_2$ ($M = Ni^{2+}$, Pd^{2+}; tfd = trifluoromethylene-1,2-dithiolate)[3,9,15] and $M(mnt)_2$ ($M = Co^{2+}$, Ni^{2+}, Cu^{2+}, Zn^{2+}; mnt = maleonitriledithiolate).[16,17]

Phenazine (phz) is structurally related to and isoelectronic with acridine and anthracene, but differs in ionization energy of which values are 5.75, ~6.2, and 6.9 eV, respectively.[18] Crystal structures of 1:1 phenazine compounds with PMDA[8] and TCNQ[5] have been determined. Phenazine and PMDA are alternatively stacked, and the crystal structure is isomorphous with those of the donor-acceptor complexes between anthracene[19] and PMDA and between acridine and PMDA.[7,14]

Phenazine is of interest in the connection of construction of molecular assembly of the metal complexes because it acts as monodentate and bridging ligand as well as an electron donor. We have synthesized both a novel donor-acceptor complex

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Table I. Crystal Data for $[Cu_2(phz)_3(MeOH)_2](phz)(PF_6)_2$ (**1**), $[Cu(phz)_2(H_2O)]ClO_4$ (**2**), $[Cu(phz)_2(NO_3)]$ (**3**), $\{[Ag(phz)]ClO_4\}_\infty$ (**4**), and $[Ag_2(phz)(NO_3)_2]_\infty$ (**5**)

	1	2	3	4	5
formula	$CuC_{25}H_{20}N_4OPF_6$	$CuC_{24}H_{16}N_4O_5Cl$	$CuC_{24}H_{16}N_5O_3$	$AgC_{12}H_8N_2O_4Cl$	$AgC_6H_4N_2O_3$
fw	600.97	539.41	485.97	387.53	259.98
cryst size, mm	0.30 × 0.40 × 0.30	0.30 × 0.40 × 0.30	0.20 × 0.25 × 0.20	0.25 × 0.25 × 0.40	0.20 × 0.30 × 0.20
cryst system	triclinic	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a, Å	13.008(2)	10.811(4)	10.686(2)	7.2044(6)	5.007(3)
b, Å	13.694(2)	12.576(3)	26.937(1)	12.943(2)	19.454(2)
c, Å	7.789(1)	8.992(1)	7.219(2)	7.138(2)	7.248(6)
α, deg	102.50(1)	105.20(1)	90.00	98.64(2)	90.00
β, deg	105.02(1)	92.59(2)	102.18(1)	98.70(1)	104.02(7)
γ, deg	72.81(1)	110.90(5)	90.00	89.92(1)	90.00
V, Å^3	1265.4(3)	1089.0(5)	2031(1)	650.3(2)	685.0(7)
Z	2	2	4	2	4
ρ_c, g cm^{-3}	1.574	1.645	1.589	1.979	2.521
λ, Å	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Cu Kα (1.541 78)	Mo Kα (0.710 69)	Mo Kα (0.710 69)
μ cm^{-1}	9.946	11.72	18.07	17.54	28.73
no. of unique data used ($\lvert F\rvert > 3\sigma\lvert F_o\rvert$)	3568	3579	2256	2275	1230
R,[a] R_w[b]	0.069, 0.098	0.044, 0.053	0.035, 0.044	0.034, 0.043	0.055, 0.064

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

between a phenazine molecule and a dicopper(I) complex with phenazines which shows a charge-transfer band at ca. 710 nm and a huge polynuclear silver(I) complex with phenazines which has a three-dimensional network.

Experimental Section

General Methods. All operations were carried out under argon and ethylene by using the standard Schlenk or vacuum line technique. Tetrakis(acetonitrile)copper(I) hexafluorophosphate was prepared according to literature procedures.[20] Acetone treated with potassium permanganate was dried over potassium carbonate from 4-Å molecular sieves. Acetonitrile was purified according to a literature procedure.[21] NMR spectra were obtained in acetone-d_6 with a JEOL GX-270 NMR spectrometer. All reported peak positions are relative to tetramethylsilane. Electronic spectra were recorded on a Hitachi spectrometer. Reagent grade phenazine and silver(I) perchlorate were obtained from Wako Pure Chemical, Inc. All other chemicals were of reagent grade and were used without further purification.

Safety Note. *Perchlorate salts of metal complexes with organic ligands are potentially explosive*! Only small amounts of materials should be prepared, and these should be handled with great caution.

Synthesis of $[Cu_2(phz)_3(MeOH)_2](phz)(PF_6)_2$ (1). Tetrakis(acetonitrile)copper(I) hexafluorophosphate (2.0 mM, 745 mg) and phenazine (3.0 mM, 541 mg) were stirred in methanol (10 mL) for 10 min under argon atmosphere. After standing for 1 day at ambient temperature, the mixture was filtered under argon pressure and deep red crystals (1.8 mM, 108 mg) were obtained. Anal. Calcd for $Cu_2C_{50}H_{40}N_8O_2P_2F_{12}$: C, 49.97; H, 3.35; N, 9.32; F, 18.97. Found: C, 49.87; H, 3.39; N, 9.26; F, 18.94. The single crystals were synthesized as follows. Tetrakis(acetonitrile)copper(I) hexafluorophosphate (0.20 mM, 74.5 mg) and phenazine (0.30 mM, 54.1 mg) were stirred in methanol (10 mL) for 10 min under an argon atmosphere. The yellow mixture was filtered under argon pressure. The filtrate was sealed in a glass tube under an argon atmosphere. After standing for 3 days at ambient temperature, deep red plate crystals were obtained.

Synthesis of $[Cu(phz)_2(H_2O)]ClO_4$ (2). Copper(II) perchlorate hexahydrate (0.025 mM, 9.25 mg) and copper plates (3 × 3 × 1 mm, five pieces) were stirred in methanol (5 mL) for 0.5 h under an ethylene atmosphere, and an acetone solution (5 mL) of phenazine (0.05 mM, 9.01 mg) was added. The mixture was stirred and filtered under argon pressure. The filtrate was sealed in a glass tube under argon atmosphere. After standing for 3 days at 5 °C, red brown plate crystals were obtained. Anal. Calcd for $CuC_{24}H_{18}N_4O_5Cl$: C, 53.24; H, 3.34; N, 10.36. Found: C, 53.34; H, 3.46; N, 10.49.

Synthesis of $[Cu(phz)_2(NO_3)]$ (3). Copper(II) nitrate trihydrate (0.05 mM, 12.1 mg) and copper plates (3 × 3 × 1 mm, five pieces) were stirred in methanol (4 mL) for 0.5 h under an ethylene atmosphere, and a methanol solution (6 mL) of phenazine (0.2 mM, 36 mg) was added. The mixture was stirred for 1 h under argon atmosphere and then filtered. The filtrate was sealed under an argon atmosphere. After standing for 3 days at 0 °C, yellow crystals were obtained. Anal. Calcd for $CuC_{24}H_{18}N_5O_3$: C, 59.31; H, 3.33; N, 14.41. Found: C, 59.25; H, 3.26; N, 14.46.

Synthesis of $\{[Ag(phz)]ClO_4\}_\infty$ (4). A methanol solution (10 ml) of silver(I) perchlorate (0.1 mM, 20.7 mg) was added to a methanol solution (10 mL) of phenazine (0.1 mM, 18 mg) under an argon atmosphere. The yellow solution was quickly filtered, and the filtrate was sealed in a glass tube under argon atmosphere. After standing for 3 days at 5 °C in a dark room, yellow plate crystals were obtained.

Synthesis of $[Ag_2(phz)(NO_3)_2]_\infty$ (5). Silver(I) nitrate (0.08 mM, 13.6 mg) was added to a solution (10 mL) of phenazine (0.08 mM, 14.4 mg) under an argon atmosphere. The yellow solution was quickly filtered, and the filtrate was sealed in a glass tube under an argon atmosphere. After standing for 3 days at 5 °C in a dark room, yellow needle crystals were obtained.

X-ray Data Collection, Structure Solution, and Refinement. Three crystals of copper(I) complexes were coated with paraffin to avoid decomposition in the air. Diffraction data were obtained on a Rigaku AFC-5R four-circle diffractometer at ambient temperature. Crystal data and details of measurements for the copper(I) and silver(I) complexes with phenazine, $[Cu_2(phz)_3(MeOH)_2](phz)(PF_6)_2$ (**1**), $[Cu(phz)_2(H_2O)]ClO_4$ (**2**), $[Cu(phz)_2(NO_3)]$ (**3**), $\{[Ag(phz)]ClO_4\}_\infty$ (**4**), and $[Ag_2(phz)(NO_3)_2]_\infty$ (**5**), are summarized in Table I. The standard reflections were monitored every 50 measurements, and the decay of their intensities was within 5%. Reflection data were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied.

The structures were solved by direct methods[22] and refined anisotropically for non-hydrogen atoms by block-diagonal least-squares calculations. Reliability factors are defined as $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[23] Hydrogen atoms were included as a fixed contribution in the last cycle; their temperature factors were assumed to be isotropic. The calculations were performed on the VAX computer by using the program system TEXAN.[24] The final R and R_w values were 0.069 and 0.098 for **1**, 0.044 and 0.053 for **2**, 0.035 and 0.044 for **3**, 0.034 and 0.043 for **4**, and 0.055 and 0.064 for **5**, respectively. The final parameters for non-hydrogen atoms and selected bond distances and angles for **1**–**5** are given in Tables II–VII, respectively.

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Table II. Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for the Non-Hydrogen Atoms of $[Cu_2(phz)_3(MeOH)_2](phz)(PF_6)_2$[a]

atom	*x*	*y*	*z*	*B*(eq)[b]
Cu(1)	0.20258(7)	0.28156(6)	0.9788(1)	3.24(4)
P(1)	0.4916(4)	0.4101(4)	0.6913(6)	5.2(2)
P(2)	0	0	1.0000	3.2(1)
F(1)	0.401(1)	0.513(1)	0.676(2)	11.5(9)
F(2)	0.408(1)	0.359(1)	0.698(2)	12(1)
F(3)	0.579(1)	0.467(1)	0.687(2)	13(1)
F(4)	0.577(1)	0.320(1)	0.691(3)	15(1)
F(5)	0.514(1)	0.424(2)	0.885(2)	16(1)
F(6)	−0.0411(5)	0.0754(4)	0.8542(7)	6.5(3)
F(7)	−0.0704(7)	0.0769(5)	1.124(1)	11.5(5)
F(8)	0.0909(7)	0.0550(6)	1.087(1)	11.6(5)
F(9)	0.467(1)	0.387(1)	0.496(2)	13(1)
O(1)	0.2272(4)	0.2712(4)	1.2521(7)	4.5(3)
N(1)	0.3195(4)	0.1736(4)	0.8913(7)	2.8(2)
N(2)	0.4920(5)	0.0213(5)	0.7518(8)	3.6(3)
N(3)	0.0805(4)	0.4064(4)	0.9710(7)	2.6(2)
N(4)	0.0849(5)	0.4197(4)	0.4419(8)	3.4(3)
C(1)	0.6468(6)	0.1764(7)	1.096(1)	4.7(4)
C(2)	0.5621(7)	0.2527(7)	1.168(1)	4.6(4)
C(3)	0.4558(6)	0.2524(6)	1.099(1)	4.0(3)
C(4)	0.1887(6)	0.0875(6)	0.685(1)	4.0(4)
C(5)	0.1696(6)	0.0088(7)	0.546(1)	4.6(4)
C(6)	0.2550(7)	−0.0640(6)	0.475(1)	4.3(4)
C(7)	0.3590(7)	−0.0601(6)	0.542(1)	4.4(4)
C(8)	0.4264(5)	0.1749(5)	0.957(1)	3.0(3)
C(9)	0.2987(5)	0.0953(5)	0.7588(9)	2.9(3)
C(10)	0.3862(6)	0.0192(5)	0.687(1)	3.3(3)
C(11)	0.5133(5)	0.0977(5)	0.887(1)	3.2(3)
C(12)	0.6232(6)	0.1008(6)	0.962(1)	4.0(4)
C(13)	−0.0419(6)	0.3121(5)	0.991(1)	3.4(3)
C(14)	−0.0173(5)	0.4072(5)	0.9985(9)	2.5(3)
C(15)	0.0989(5)	0.4981(5)	0.9720(9)	2.7(3)
C(16)	0.2007(5)	0.5011(5)	0.941(1)	3.4(3)
C(17)	0.2209(6)	0.5922(6)	0.946(1)	4.1(4)
C(18)	0.1418(6)	0.6862(6)	0.981(1)	4.0(4)
C(19)	−0.0069(7)	0.2955(6)	0.456(1)	4.4(4)
C(20)	0.0003(6)	0.3997(5)	0.479(1)	3.2(3)
C(21)	0.0882(6)	0.5185(6)	0.4637(9)	3.3(3)
C(22)	0.1791(6)	0.5444(6)	0.429(1)	3.9(4)
C(23)	0.1815(7)	0.6436(7)	0.447(1)	4.6(4)
C(24)	0.0935(7)	0.7251(6)	0.503(1)	5.0(4)
C(25)	0.2942(7)	0.1905(7)	1.349(1)	5.3(4)

[a] Numbers in parentheses are estimated standard deviation in the least significant digits. [b] *E*(eq) is the isotropic equivalent of the anisotropic thermal parameter.

Table III. Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for the Non-Hydrogen Atoms of $[Cu(phz)_2(H_2O)](ClO_4)$[a]

atom	*x*	*y*	*z*	*B*(eq)[b]
Cu(1)	0.26277(5)	0.02656(4)	0.84023(5)	2.95(2)
Cl(1)	0.7329(1)	0.4262(1)	0.1616(1)	4.93(4)
O(1)	0.4835(3)	0.0910(3)	0.9194(3)	5.7(1)
O(2)	0.6774(5)	0.3036(3)	0.1467(5)	8.1(2)
O(3)	0.726(2)	0.493(1)	0.304(1)	10.5(5)
O(4)	0.639(1)	0.430(1)	0.046(1)	14.9(7)
O(5)	0.851(1)	0.4612(8)	0.112(2)	14.1(6)
O(6)	0.868(2)	0.439(2)	0.240(3)	13(1)
O(7)	0.761(3)	0.463(1)	0.042(2)	8.5(9)
O(8)	0.690(4)	0.501(4)	0.266(4)	15(2)
N(1)	0.1962(3)	0.0496(3)	1.0389(3)	2.37(9)
N(2)	0.0851(3)	0.0889(3)	1.3185(3)	2.7(1)
N(3)	0.2758(3)	−0.0049(3)	0.6184(3)	2.42(9)
N(4)	0.3699(3)	−0.0473(3)	0.3287(3)	2.8(1)
C(1)	0.2187(4)	0.1615(3)	1.1302(4)	2.5(1)
C(2)	0.3007(4)	0.2616(3)	1.0884(4)	3.5(1)
C(3)	0.1621(4)	−0.2168(4)	0.5675(4)	3.6(1)
C(4)	0.1298(4)	−0.3300(4)	0.4704(5)	4.3(2)
C(5)	0.1770(4)	−0.3497(4)	0.3268(5)	4.1(1)
C(6)	0.2583(4)	−0.2576(4)	0.2819(4)	3.4(1)
C(7)	0.2931(3)	−0.1380(3)	0.3776(4)	2.7(1)
C(8)	0.3938(3)	0.0637(3)	0.4180(4)	2.6(1)
C(9)	0.4706(4)	0.1624(4)	0.3666(4)	3.4(1)
C(10)	0.4932(4)	0.2749(4)	0.4531(5)	3.8(1)
C(11)	0.4411(4)	0.2978(4)	0.5949(5)	3.8(1)
C(12)	0.3705(4)	0.2058(3)	0.6492(4)	3.2(1)
C(13)	0.3447(3)	0.0860(3)	0.5636(4)	2.4(1)
C(14)	0.2447(3)	−0.1175(3)	0.5238(4)	2.5(1)
C(15)	0.0642(3)	−0.0213(3)	1.2297(4)	2.4(1)
C(16)	0.1211(3)	−0.0428(3)	1.0888(3)	2.3(1)
C(17)	0.0974(4)	−0.1622(3)	1.0035(4)	2.9(1)
C(18)	0.0180(4)	−0.2546(3)	1.0519(4)	3.4(1)
C(19)	−0.0403(4)	−0.2324(4)	1.1886(5)	3.5(1)
C(20)	−0.0169(4)	−0.1212(3)	1.2760(4)	3.0(1)
C(21)	0.3213(4)	0.3739(4)	1.1788(5)	4.2(1)
C(22)	0.2641(4)	0.3923(4)	1.3167(5)	4.0(1)
C(23)	0.1875(4)	0.2982(3)	1.3626(4)	3.4(1)
C(24)	0.1615(3)	0.1799(3)	1.2700(4)	2.6(1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] *B*(eq) is the isotropic equivalent of the anisotropic thermal parameter.

Results

Structure of $[Cu_2(phz)_3(MeOH)_2](phz)(PF_6)_2$ (1). Compound **1** consists of a dicopper(I) complex cation, PF_6^- anion, and metal-free phz molecule as shown in Figure 1. Each copper in the cation is coordinated to methanol and terminal and bridging phz molecules to form a T-shaped three-coordinate geometry,[25] of which one bond angle N(1)–Cu–N(3) is remarkably larger than two bond angles N(1)–Cu–O(1) and N(3)–Cu–O(1). The Cu–N distance is longer for bridging phz than for terminal phz. Two methanols are related through a center of symmetry, therefore facing on opposite sides Cu(1) and Cu(1′). There is one report of a T-shaped three-coordinate copper(I) complex with alcohol.[26] The Cu–O distance of 2.099(3) Å is shorter than 2.262(7) Å in $[Cu_2(tc)_2](ClO_4)_2$ (tc = thiochrome) since the angle N(1)–Cu–N(3) of 156.1(2)° is smaller than the angle N–Cu–N of 165.8(3)° in $[Cu_2(tc)_2](ClO_4)_2$.[26] The disordered PF_6^- is not coordinated to the copper, the nearest Cu–F distance being 4.11 Å. The dihedral angle between bridging and terminal phz planes is 46.9°. The molecular packing of compound **1** is illustrated in Figure 2. Metal-free phz and the dicopper complex cation are alternately stacked along the *c*-axis. Figure 3 illustrates the overlap (π–π interaction) between the metal-free phz molecule and phz bridged to two coppers in the complex, where the terminal phz molecules are omitted. This is a first example of infinite stacks of alternating metal-free ligand and the ligand coordinated to metal. The dihedral angle between the metal-free and bridging phz molecule planes is 7.6°, and the nearest separation between the planes is 3.42 Å. This separation is essentially the same or slightly longer than 3.33 and 3.38 Å for 1:1 donor–acceptor complexes of phz with PMDA[8] and TCNQ,[5] respectively.

Structure of $[Cu(phz)_2(H_2O)]ClO_4$ (2). The copper atom in compound **2** is coordinated to two terminal phz molecules and a water in a distorted trigonal geometry as shown in Figure 4. The Cu–N distances of 1.949(3) Å (average) are essentially the same as those of 1.946(5) Å in compound **1**. On the other hand, the Cu–O distance of 2.241(3) Å is longer than 2.099(5) Å in **1** and shorter than 2.262(7) Å in $[Cu_2(tc)_2](ClO_4)_2$[26] because the N(1)–Cu–N(3) angle of 163.2(1)° in **2** is between 156.1(2)° in **1** and 165.8(3)° in $[Cu_2(tc)_2](ClO_4)_2$. ClO_4^- is not coordinated to the copper, the nearest Cu–O distance being 4.45 Å. Figure 5 illustrates the molecular packing of compound **2**, which shows infinite stacks of alternating one phz in **2** and the opposite phz in another one. The nearest intermolecular distance and the dihedral angle between the phz planes are 3.46 Å (Figure 5) and 3.8°, respectively, indicating the existence of a π–π interaction.

Structure of $[Cu(phz)_2(NO_3)]$ (3). The copper atom in compound **3** is coordinated to two terminal phz molecules and a nitrate in a distorted tetrahedral geometry as shown in Figure 6. The bond angle O(1)–Cu–O(3) of 53.5(1)° is remarkably smaller

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(25) Munakata, M.; Maekawa, M.; Kitagawa, S.; Matsuyama, S.; Masuda, H. *Inorg. Chem.* **1989**, *28*, 4300 and therein references.

(26) Kitagawa, S.; Matsuyama, S.; Munakata, M.; Osawa, N.; Masuda, H. *J. Chem. Soc., Dalton Trans.* **1991**, 1717.

Table IV. Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for the Non-Hydrogen Atoms of [Cu(phz)$_2$(NO$_3$)][a]

atom	*x*	*y*	*z*	*B*(eq)[b]
Cu(1)	0.27381(5)	0.10088(2)	0.81655(8)	3.57(2)
O(1)	0.1503(2)	0.1019(1)	1.0414(4)	5.2(1)
O(2)	−0.0402(3)	0.1331(1)	0.9936(4)	5.2(1)
O(3)	0.0409(3)	0.1096(1)	0.7582(4)	4.9(1)
N(1)	0.3532(3)	0.0394(1)	0.7640(4)	2.8(1)
N(2)	0.4783(3)	−0.0511(1)	0.7173(4)	3.3(1)
N(3)	0.2911(2)	0.1740(1)	0.8207(4)	2.7(1)
N(4)	0.2958(3)	0.2786(1)	0.8434(4)	3.1(1)
N(5)	0.0478(3)	0.1149(1)	0.9323(5)	3.6(1)
C(1)	0.2874(3)	−0.0038(1)	0.7329(5)	2.8(1)
C(2)	0.1543(3)	−0.0049(1)	0.7230(6)	3.7(2)
C(3)	0.0884(3)	−0.0483(1)	0.6915(6)	4.1(2)
C(4)	0.1528(4)	−0.0932(1)	0.6690(5)	3.9(2)
C(5)	0.2789(4)	−0.0937(1)	0.6776(5)	3.8(2)
C(6)	0.3524(3)	−0.0494(1)	0.7102(4)	2.9(1)
C(7)	0.5432(3)	−0.0077(1)	0.7435(5)	3.1(1)
C(8)	0.6763(3)	−0.0077(1)	0.7493(5)	3.9(2)
C(9)	0.7438(4)	0.0347(2)	0.7748(6)	4.5(2)
C(10)	0.6823(4)	0.0800(2)	0.7966(6)	4.4(2)
C(11)	0.5554(4)	0.0818(1)	0.7921(5)	3.8(2)
C(12)	0.4804(3)	0.0379(1)	0.7676(4)	2.9(1)
C(13)	0.3459(3)	0.1977(1)	0.9838(5)	2.7(1)
C(14)	0.4024(3)	0.1699(1)	1.1472(5)	3.3(1)
C(15)	0.4565(4)	0.1940(1)	1.3088(5)	4.0(2)
C(16)	0.4577(4)	0.2465(1)	1.3177(5)	4.1(2)
C(17)	0.4042(3)	0.2740(1)	1.1661(5)	3.6(2)
C(18)	0.3466(3)	0.2506(1)	0.9930(5)	2.9(1)
C(19)	0.2432(3)	0.2550(1)	0.6822(5)	2.9(1)
C(20)	0.1880(4)	0.2834(1)	0.5204(5)	3.8(2)
C(21)	0.1318(4)	0.2606(2)	0.3581(6)	4.4(2)
C(22)	0.1278(4)	0.2083(2)	0.3449(5)	4.2(2)
C(23)	0.1811(3)	0.1799(1)	0.4949(5)	3.4(2)
C(24)	0.2402(3)	0.2022(1)	0.6686(5)	2.8(1)

[a] Numbers in parentheses are extimated standard deviations in the least significant digits. [b] *B*(eq) is the isotropic equivalent of the anisotropic thermal parameter.

Table V. Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for the Non-Hydrogen Atoms of {[Ag(phz)](ClO$_4$)}$_\infty$[a]

atom	*x*	*y*	*z*	*B*(eq)[b]
Ag(1)	0.46214(4)	0.22789(3)	0.24819(5)	3.41(1)
Cl(1)	0.5354(2)	0.2685(1)	0.7389(2)	3.85(4)
O(1)	0.4984(7)	0.3478(4)	0.6149(6)	6.5(2)
O(2)	0.5013(7)	0.1681(3)	0.6251(7)	6.5(2)
O(3)	0.4186(7)	0.2860(4)	0.8830(6)	6.9(2)
O(4)	0.7287(6)	0.2779(3)	0.8204(7)	6.3(2)
N(1)	0.1551(4)	0.2247(3)	0.2385(5)	2.7(1)
N(2)	0.7685(4)	0.2272(3)	0.2599(5)	2.7(1)
C(1)	−0.2315(6)	0.0419(4)	0.2576(7)	3.6(2)
C(2)	−0.1369(7)	−0.0488(4)	0.2513(8)	4.2(2)
C(3)	0.0571(7)	−0.0507(4)	0.2443(8)	4.1(2)
C(4)	0.1542(6)	0.0401(4)	0.2415(7)	3.4(2)
C(5)	0.1533(6)	0.4091(4)	0.2329(7)	3.6(2)
C(6)	0.0582(7)	0.4999(4)	0.2369(8)	4.2(2)
C(7)	−0.1352(7)	0.5017(4)	0.2548(8)	4.1(2)
C(8)	−0.2279(6)	0.4132(4)	0.2633(7)	3.8(2)
C(9)	0.0599(5)	0.1362(3)	0.2458(6)	2.7(1)
C(10)	0.8634(5)	0.1374(3)	0.2548(6)	2.6(1)
C(11)	0.8641(5)	0.3163(3)	0.2564(6)	2.7(1)
C(12)	0.0599(5)	0.3143(3)	0.2424(6)	2.7(1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] *B*(eq) is the isotropic equivalent of the anisotropic thermal parameter.

than the 109.28° regular tetrahedral geometry. N(1)–Cu–N(3) of **1** is 44.3(1)°. The Cu–N distances of 1.956(3) Å (average) are slightly longer than or essentially the same as that of 1.933(5) Å for the terminal phz's of compound **1** and 1.949(3) Å in compound **2**. The Cu–O distances of 2.298(3) and 2.446(3) Å are remarkably long compared with 2.099(5) Å of **1** and 2.241(3) Å of **2**. There is no π–π interaction between the phz molecules, because NO$_3^-$ is coordinated to copper to give a tetrahedral complex.

Table VI. Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for the Non-Hydrogen Atoms of [Ag$_2$(phz)(NO$_3$)$_2$]$_\infty$ [a]

atom	*x*	*y*	*z*	*B*(eq)[b]
Ag(1)	−0.2607(1)	0.66577(3)	−0.2227(1)	4.34(3)
O(1)	−0.568(1)	0.7272(3)	−0.4813(9)	4.8(2)
O(2)	−0.828(1)	0.6576(3)	−0.376(1)	4.9(3)
O(3)	−1.002(1)	0.7418(3)	−0.561(1)	6.2(3)
N(1)	−0.102(1)	0.5630(3)	−0.0862(7)	2.7(2)
N(2)	−0.802(1)	0.7088(3)	−0.4730(8)	2.8(2)
C(1)	−0.545(1)	0.3819(3)	−0.226(1)	3.4(3)
C(2)	−0.297(1)	0.3794(3)	−0.095(1)	3.2(2)
C(3)	−0.140(1)	0.4402(3)	−0.0430(8)	2.5(2)
C(4)	−0.246(1)	0.5041(3)	−0.1327(9)	2.4(2)
C(5)	−0.505(1)	0.5043(3)	−0.264(1)	3.1(2)
C(6)	−0.646(1)	0.4449(4)	−0.311(1)	3.4(3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] *B*(eq) is the isotropic equivalent of the anisotropic thermal parameter.

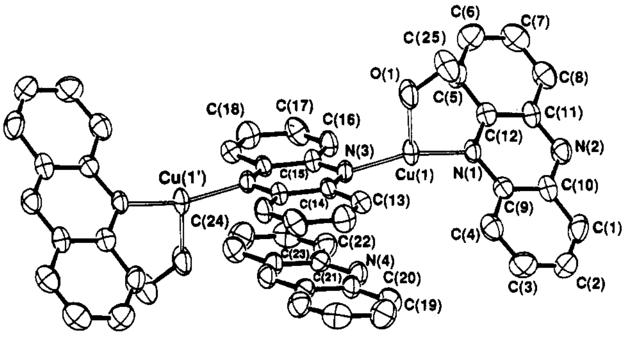

Figure 1. Molecular structure of [Cu$_2$(phz)$_3$(MeOH)$_2$](phz)(PF$_6$)$_2$ (**1**).

Table VII. Selected Bond Distances (Å) and Angles (deg) for **1**–**5**

	1	**2**	**3**	**4**	**5**
M–N(1)	1.933(5)	1.946(3)	1.933(3)	2.203(3)	2.286(5)
M–N(2)			1.978(3)	2.196(3)	
M–N(3)	1.959(5)	1.951(3)			
M–O(1)	2.099(5)	2.241(3)	2.298(3)		2.432(6)
M–O(3)			2.446(3)		2.597(7) (O(3′))
N(1)–M–N(3)	156.1(2)	163.2(1)	144.3(1)		
N(1)–M–N(2)				178.6(1)	
N(1)–M–O(1)	105.4(2)	101.3(1)			148.4(2)
N(1)–M–O(3)			121.4(1)		124.1(2) (O(3′))
N(3)–M–O(1)	97.8(2)	95.2(1)	92.5(1)		
O(1)–M–O(3)			53.7(9)		74.3(2) (O(3′))

Structure of {[Ag(phz)]ClO$_4$}$_\infty$ (4). The molecular structure of {[Ag(phz)]ClO$_4$}$_\infty$ is shown in Figure 7. Silver is coordinated to two nitrogen atoms of different phz's which act as bridging ligands. The perchlorates are not coordinated, the nearest Ag–O(ClO$_4^-$) distance being 2.793(4) Å. The bond angle N(1)–Ag–N(2′) is 178.6(1)°, and subsequently **4** forms an infinite linear chain. The Ag–N distances of 2.202 and 2.196 Å fall into the region of 2.12–2.21 Å reported for two-coordinate silver(I) complexes.[27] The packing arrangement of **4** is shown in Figure 8, which indicates the overlap of the phz molecules between the infinite linear chains. The shortest intermolecular distance of 3.36 Å between two phz is comparable to 3.35 Å of graphite and indicates the existence of a π–π interaction. The complex forms a two-dimensional structure composed of infinite linear chains along the *a* axis and a π–π interaction along the *c* axis.

Structure of [Ag$_2$(phz)(NO$_3$)$_2$]$_\infty$ (5). Figure 9 depicts a segment of the two-dimension structure in [Ag$_2$(phz)(NO$_3$)$_2$]$_\infty$. The asymmetric unit consist of a Ag atom, a nitrate group, and half of a phz molecule. Crystallographic centers of inversion are

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[27] Munakata, M.; Maekawa, M.; Kitagawa, S.; Adachi, M. *Inorg. Chim. Acta* **1990**, *167*, 181 and therein references.

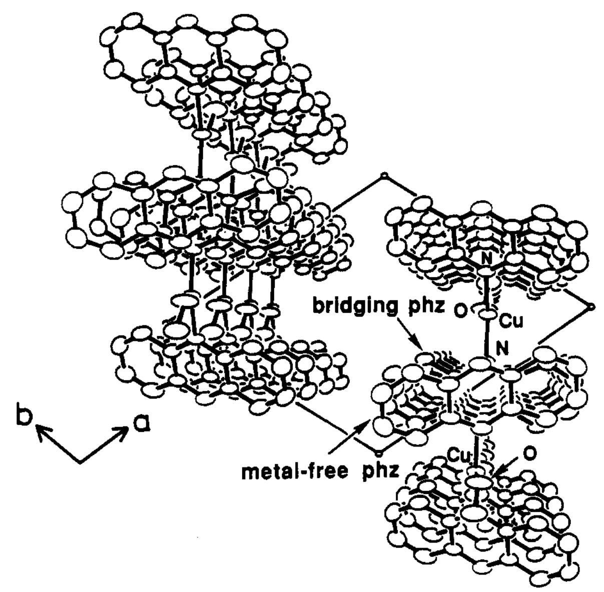

Figure 2. Perspective view of stacks of alternating metal-free phz and the dicopper complex in **1**.

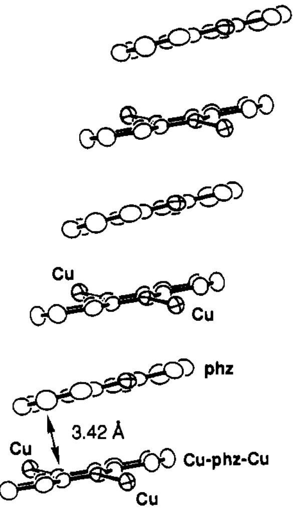

Figure 3. Side view of stacks of alternting metal-free phz and the bridging phz in **1**, where the terminal phz molecules are omitted.

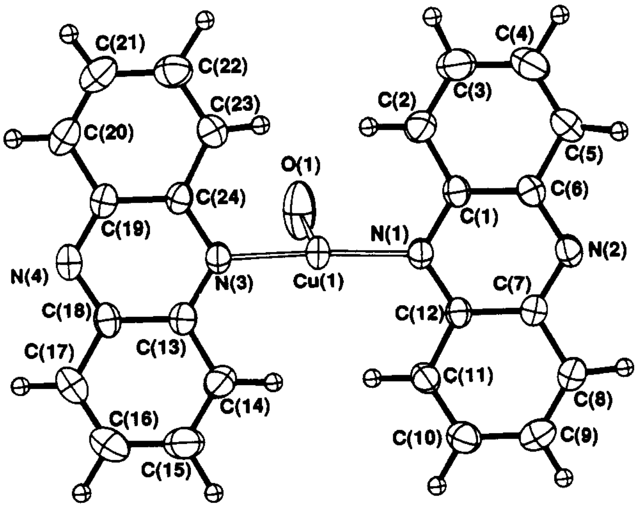

Figure 4. Molecular structure of [Cu(phz)$_2$(H$_2$O)]ClO$_4$ (**2**).

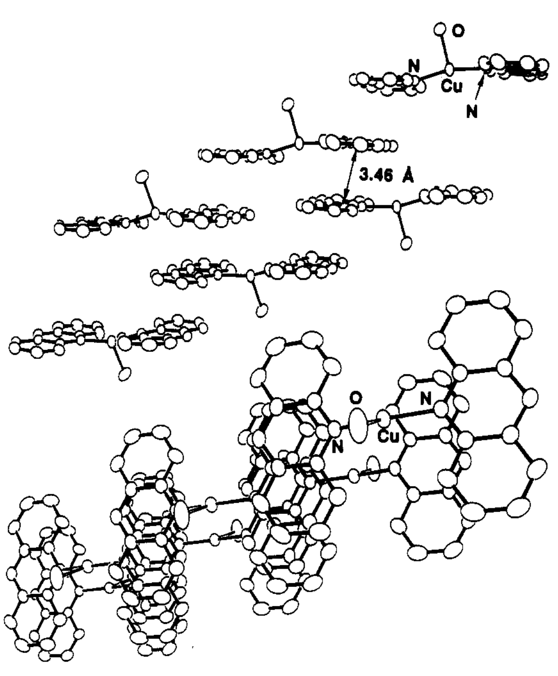

Figure 5. Perspective (bottom) and side (top) views of the packing arrangement of **2**.

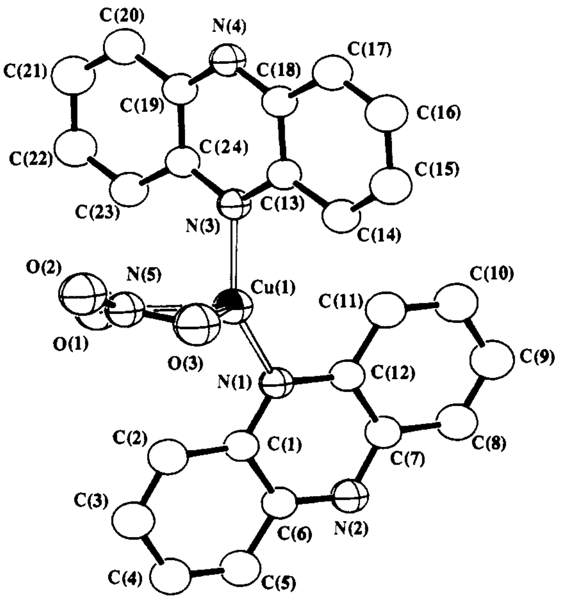

Figure 6. Molecular structure of [Cu(phz)$_2$(NO$_3$)] (**3**).

located at the center of the phz molecule. The Ag–N(1) distance of 2.286(5) Å is a little longer than those of 2.207(3)–2.225 Å for silver(I) complexes with nitrogen and oxygen atoms.[28] The O(1) and O(3′) atoms are also coordinated to the Ag atom, because the distances of 2.432(6) and 2.569(7) Å are in the range 2.367–2.689 Å for Ag(I) complexes with nitrate.[28b,29] The packing arrangement of [Ag$_2$(phz)(NO$_3$)$_2$]$_\infty$ in Figure 10 shows a huge polynuclear complex of which the sheet with a framework of six-membered rings of silvers extends in the direction of the *b* and *c* axes. The Ag–Ag distances bridged with phz and NO$_3^-$ are different, being 7.400(2) and 5.074(3) Å, respectively, but the two-dimensional silver sheet approximately lies on the same plane. Each sheet is weakly linked by the interaction between Ag and O(2), the Ag–O(2) intermolecular distance being 2.669(7) Å. The deviation distance (0.435 Å) of Ag atom from the plane defined by O(1), O(3′), and N(1) toward O(2) of the neighboring sheet therefore arises through the interaction. In addition, there is the π–π interaction of the phz molecules between the network sheets of the shortest intermolecular distance of 3.34 Å (Figure

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(28) (a) Deloume, J.-P.; Faure, R.; Loiseleur, H. *Acta Crystallogr.* **1977**, *B33*, 2709. (b) Guay, F.; Beauchamp, A. L. *J. Am. Chem. Soc.* **1979**, *101*, 6260. (c) Vranka, R. G.; Amma, E. L. *Inorg. Chem.* **1966**, *5*, 1020.

(29) Ho, D. M.; Bau, R. *Inorg. Chem.* **1983**, *22*, 4073. Meiners, J. H.; Clardy, J. C.; Verkade, J. G. *Inorg. Chem.* **1975**, *14*, 632.

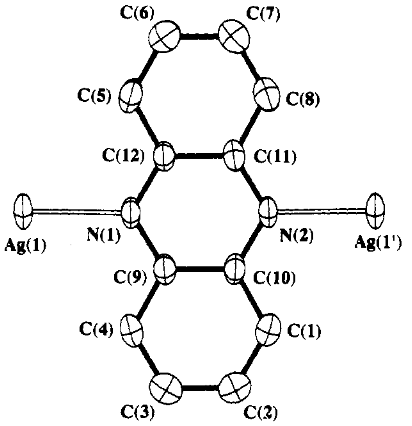

Figure 7. Molecular structure of $\{[Ag(phz)]ClO_4\}_\infty$ (4).

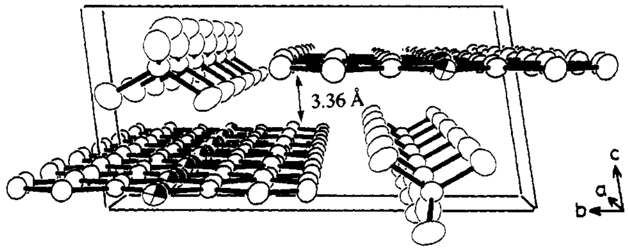

Figure 8. Perspective view of the packing arrangement of 4.

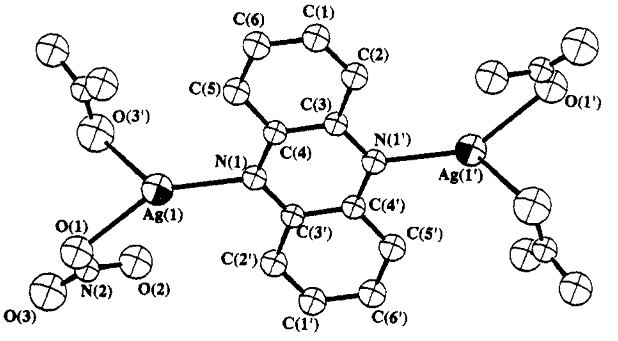

Figure 9. Molecular structure of $[Ag_2(phz)(NO_3)_2]_\infty$ (5).

10). The complex forms a three-dimensional structure composed of the two-dimensional sheets connected by chemical bonds, the weak $Ag-O(NO_3)$ bonding, and the $\pi-\pi$ interactions between the sheets.

^{1}H NMR Spectra of Metal-phz Complexes. An acetone-d_6 solution of 2 indicates ^{1}H NMR resonances at 8.05 and 8.43 ppm assigned to 2-, 3-, 7-, and 8-H and 1-, 4-, 6-, and 9-H of phz, respectively, where the chemical shifts of 2-, 3-, 7-, and 8-H and 1-, 4-, 6- and 9-H of metal-free phz are 7.96 and 8.26 ppm, respectively. In methanol-d_4 solution of 1 the resonances of 2-, 3-, 7-, and 8-H and 1-, 4-, 6-, and 9-H of phz were observed at 8.07 and 8.49 ppm, respectively, indicating rapid exchange between the coordinating and metal-free phz molecules. On the other hand, the ^{1}H NMR resonances of methanol-OH of 1 in acetone-d_6 solution were observed at 3.10 and 3.32 ppm assigned to coordinated and dissociated methanols, respectively, indicating slow exchange between the coordinating and metal-free methanols compared with that of the phz molecules. The upfield shift of methanol upon the coordination to copper is of interest.

Discussion

Regulation by Solvent. Dicopper(I) complex with phz and methanol, 1, is formed in methanol from tetrakis(acetonitrile)copper(I) ion and phz and crystallizes as infinite stacks of alternating dicopper(I) complex cation and metal-free phz, $-[Cu_2(phz)_3(MeOH)_2]-phz-$. On the other hand, in acetone mononuclear copper(I) complex with phz and water, 2, is formed and crystallizes as infinite stacks of only the copper(I) complex cations, $-[Cu(phz)_2(H_2O)]-[Cu(phz)_2(H_2O)]-$. Methanol can be coordinated to copper because of its relatively large coordination power.[30] Water contained as an impurity in acetone is preferentially coordinated to copper rather than acetone because the coordination power of acetone is very small compared to that of water.[30] Attempts to synthesize single crystals of a Cu-phz complex in dried thf were unsuccessful. The solvent effect on the molecular packing is of interest in connection with design in the molecular assembly of metal complexes.

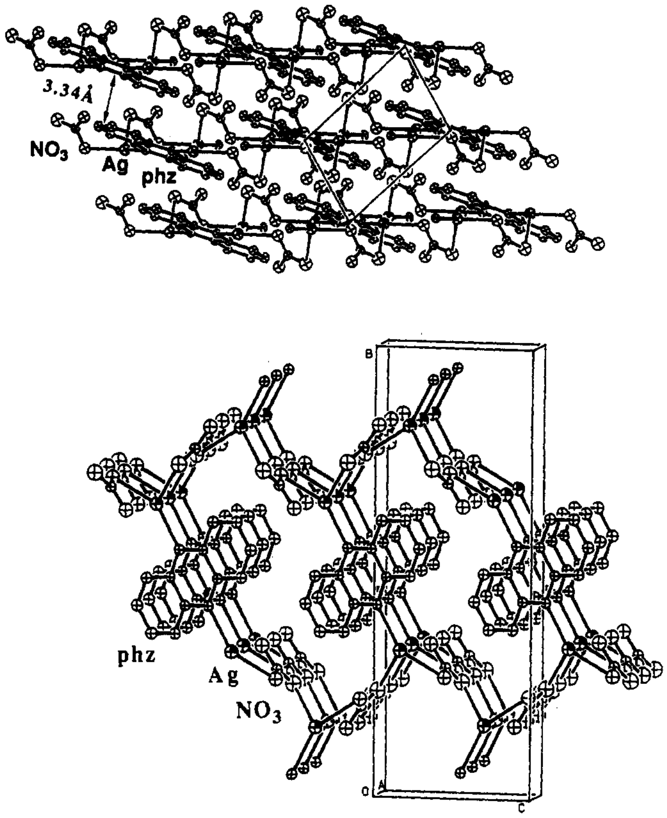

Figure 10. Perspective (bottom) and side (top) views of the packing arrangement of 5.

Regulation by Counteranions. It is well-known that nitrate ion can be more strongly coordinated to metal ions than perchlorate and hexafluorophosphate ions. The counteranion NO_3^- is coordinated to copper to form a mononuclear complex with phz and NO_3^- (3) in methanol, but PF_6^- is not coordinated to copper to form a dinuclear copper complex with phz's and methanols which is crystallized as infinite stacks of alternating complex and free phz, 1. The mononuclear copper complex of tetrahedral geometry 3 has no intermolecular overlap between the phz molecules in the packing, whereas the mononuclear copper cation having ClO_4^- as the counteranion, 2, exhibits an intermolecular $\pi-\pi$ interaction between the phz molecules in the crystal structure. In the case of the Ag-phz complex, the counteranion ClO_4^- is not coordinated to the copper(I) to give infinite linear chains bridged by phz, 4. On the other hand, the NO_3^- in 5 takes part in the formation of a two-dimensional network with six-member rings of silvers as a bridging ligand. Thus the counteranion plays an important role in the molecular packing of metal-phz complexes because the complex structures are changed on coordination of the counteranions.

Regulation by Metal Ions. Silver (I) shows a pronounced tendency to exhibit linear coordination, whereas copper(I) prefers

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three-coordination rather than two-coordination.[31] Good examples of three-coordinate copper(I), **1**, and two-coordinate silver(I), **4**, are presented in the metal–phz–ClO_4^- system: The crystal structure of **1** remarkably differs from that of **4**. In metal–phz–NO_3^- system copper gives a mononuclear complex with phz and NO_3^-, **3**, whereas silver(I) gives a two-dimensional complex with phz and NO_3^-, **5**. The selection of metal ion is also very important in the synthesis of the molecular assembly of metal complexes.

Electronic Spectra of Metal–phz Complexes. Copper(I) complexes with unsaturated compounds such as pyridine and 2,2′-bipyridine exhibit charge-transfer bands from metal to the ligand.[32] The copper(I) complexes with phz, **2** and **3**, also show Cu → phz CT band at ca. 420 nm (shoulder). Compound **1** having an infinite stack of alternating dinuclear copper cations and metal-free phz's shows new bands at 560 and 710 nm in addition to ca. 400 nm in the KBr pellet (Figure 11). A methanol solution of **1** also shows the corresponding bands with low intensity at 610 and 740 nm, indicating that the alternating stack is partly maintained even in solution. The bands may be assigned to a CT band from the metal-free phz molecule to the bridging phz of the dinuclear copper complex, because bridging phz acts as an electron acceptor owing to the coordination to copper. The 710 and 740 nm bands for **1** are comparable to 740 nm for a typical donor–acceptor complex, perylene–chloranyl 1:1 complex,[2,33] indicating a strong donor–acceptor interaction in **1**.

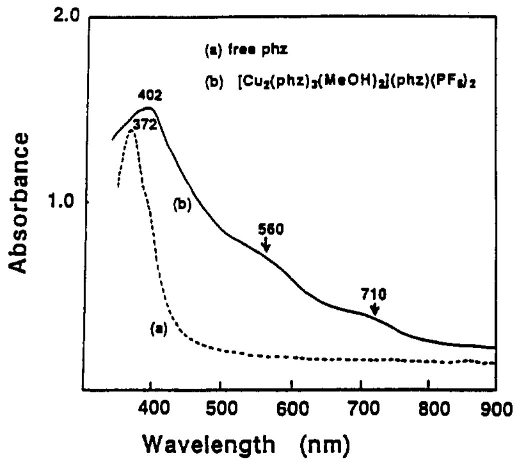

Figure 11. Electronic spectra of **1** and phz (KBr pellet).

Acknowledgment. This work was supported in part by a Grant-in Aid for Science Research (No. 04225102 and No. 04453049) from the Ministry of Education, Science, and Culture. We thank the Japan Private School Promotion Foundation for financial support.

Supplementary Material Available: Tables S1–S20, giving atom coordinates, bond angles, bond distances, anisotropic thermal parameters, and hydrogen atom locations (46 pages). Ordering information is given on any current masthead page.

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