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Polyhedron 24 (2005) 2933–2943

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Syntheses, crystal structures and electronic properties of a series of copper(II) complexes with 3,5-halogen-substituted Schiff base ligands and their solutions

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Received 9 March 2005; accepted 3 June 2005
Available online 3 August 2005

Abstract

We have systematically investigated the structural features, electronic properties, thermally-induced structural phase transitions and absorption spectra depending on the solvent for ten Cu(II) complexes with 3,5-halogen-substituted Schiff base ligands. Structural characterization of two new complexes, bis(*N*-*R*-1-phenylethyl- and *N*-*R*,*S*-2-butyl-5-bromosalicydenaminato-κ^2*N*,*O*)copper(II), reveals that they afford a compressed tetrahedral *trans*-[CuN_2O_2] coordination geometry with *trans*-N–Cu–N = 159.4(2)° and *trans*-O–Cu–O = 151.7(3)° for the 1-phenylethyl complex and *trans*-N–Cu–N = 157.9(3)° and *trans*-O–Cu–O = 151.0(3)° for the 2-butyl one. All the complexes exhibit a structural phase transition by heating in the solid state regardless of their structures at room temperature. The absorption spectra of a series of ten complexes exhibit a slight shift of the d–d band at 16000–20000 cm^{-1} and remarkable shift of the π–π* band at 24000–28000 cm^{-1}, which suggests that the dipole moment of the solvents presumably affects the conformation of the π-conjugated moieties of the ligands rather than the coordination environment. We have also attempted 'photochromic solute-induced solvatochromism' by a system of bis(*N*-*R*-1-phenylethyl-3,5-dichlorosalicydenaminato-κ^2*N*,*O*)copper(II) and photochromic 4-hydroxyazobenzene in chloroform solution. We successfully observed a change of the d–d and π–π* bands of the complex in the absorption spectra caused by *cis*–*trans* photoisomerization of 4-hydroxyazobenzene.

Keywords: Copper(II) complexes; Schiff base; Crystal structures; Chirality; Azobenzenes; Solvatochromism

1. Introduction

The developing interest attracted to photofunctional materials of inorganic transition metal complexes [1,2] that have azobenzenes as ligands [3,4], showing spin crossover [5,6] and exhibiting long-lived metastable states [7] is due not only to their fundamental aspects but also their potential applications, for example Fe–Co Prussian blue analogues [8] and one dimensional organometallic complexes [9]. In spite of great endeavors in this field, reliable and reasonable design of photo-switching materials has not been established at present. However, one of the promising ways to discover desirable photo-switching materials may be examining various types of chromic complexes, e.g. thermochromic [10–12], piezochromic [13,14], solvatochromic [15–17] and vapochromic [18,19], with irradiation of light. Besides merely inorganic metal complexes, organic/inorganic hybrid self-assemblies being composed of photochromic organic compounds and inorganic metal complexes may be useful for this purpose. Expected advantages of such organic/inorganic hybrid systems are as follows: (1) Reversible photoisomerization of photochromic compounds can occur even at room

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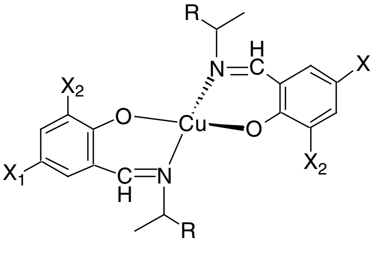
0277-5387/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2005.06.018

temperature [20]. (2) Photo-switching of characteristic properties of molecular compounds, for instance chiral molecular recognition, spin crossover and conformational conversion, can be available in contrast to other inorganic solid compounds such as Prussian blue analogues.

In this context, flexible transition metal complexes are suitable as a component of such photo-switching materials. Classically, some Cu(II) or Ni(II) complexes incorporating Schiff base ligands [21] have been known to exhibit flexibility from a square planar to a tetrahedral coordination environment by introduction of various substituents, and show structural phase transitions by heating [22–30]. Especially, Ni(II) complexes exhibit not only flexibility of the coordination environment [31–38] but also interesting magnetic behavior; diamagnetic square planar complexes change into paramagnetic tetrahedral complexes when a complex adopts such coordination geometries in the solid state, or when one is dissolved in solution, so called *solution paramagnetism* [39–41].

Herein, we report structural features, electronic properties, thermally-induced structural phase transition and absorption spectra depending on the solvent for ten Cu(II) complexes with 3,5-halogen-substituted Schiff base ligands (Scheme 1). Crystal structures of two new complexes, bis(*N*-*R*-1-phenylethyl- and *N*-*R*,*S*-2-butyl-5-bromosalicydenaminato-κ^2N,O)copper(II), are also described. Furthermore, we successfully observed a spectral change of d–d and π–π* bands of the complex caused by *cis–trans* photoisomerization of 4-hydroxyazobenzene (4HAZ) for an organic/inorganic system involving bis-(*N*-*R*-1-phenylethyl-3,5-dichlorosalicydenaminato-κ^2N,O)copper(II) and 4HAZ in chloroform solution.



	R	X_1	X_2
1	C_6H_5	Cl	Cl
2	C_6H_5	Br	Br
3	C_6H_5	H	Cl
4	C_6H_5	H	Br
5	C_2H_5	Cl	Cl
6	C_2H_5	Br	Br
7	C_2H_5	H	Cl
8	C_2H_5	H	Br
9	CH_3	H	Cl
10	CH_3	H	Br

Scheme 1. Molecular structures of **1**–**10**.

2. Experimental

2.1. Materials

Chemicals of the highest commercial grade available (Aldrich and Wako) were used as received without further purification.

2.2. Physical measurements

Elemental analyses (C, H, N) were carried out on an Elementar Vario EL analyser at Keio University. Infrared spectra were recorded using Nujol mulls on a BIORAD FTS-60A spectrophotometer in the range 4000–400 cm^{-1} at 298 K. Thermal analysis was performed on a SHIMADZU DSC-60 differential scanning calorimeter (DSC), where the heating rate was 10 K min^{-1} in the range of 313–673 K. Diffuse reflectance spectra were measured on a JASCO V-560 spectrophotometer equipped with an integrating sphere in the range 850–220 nm at 298 K. Absorption spectra were measured on a JASCO V-560 spectrophotometer in the range 900–200 nm at 298 K. Magnetic susceptibility was measured with a Sherwood Scientific magnetic susceptibility balance at 298 K. Magnetic data were corrected for the magnetization of diamagnetic contributions, which were estimated from Pascal constants. The magnetic properties were investigated with a Quantum Design MPMS-5S superconducting quantum interference device magnetometer (SQUID) at an applied field of 5000 Oe in a temperature range 5–250 K. Semi-empirical molecular orbital calculations were performed with the program ZINDO [42,43] in the CAChe software package based on the crystal structures determined.

2.3. Syntheses of complexes

2.3.1. Bis(N-R-1-phenylethyl-3,5-dichlorosalicydenaminato)copper(II) (*1*)

To a methanol solution (150 cm^3) of copper(II) acetate (0.91 g, 5.00 mmol), 3,5-dichlorosalicylaldehyde (1.91 g, 10.0 mmol), and *R*-1-phenylethylamine (1.21 g, 10.0 mmol) were added and stirred at 45 °C for 2 h. The resulting brown precipitates were collected by filtration and recrystallized from acetone/methanol. Yield 64.8%. *Anal.* Calc. for $C_{30}H_{24}N_2Cl_4CuO_2$: C, 55.44; H, 3.72; N, 2.31. Found: C, 55.37; H, 3.98; N, 4.09%. IR (KBr) $\nu_{C=N}$ 1623 cm^{-1}, ν_{Cu-N} 445 cm^{-1}, ν_{Cu-O} 419 cm^{-1}, m.p. 483 K (decomposition). Magnetic moment $\mu_{eff}/\mu_{BM} = 1.73$ at 298 K.

2.3.2. Bis(N-R,S-1-phenylethyl-3,5-dibromoosalicydenaminato)copper(II) (*2*)

The same procedure as for **1** afforded the condensation of 3,5-dibromosalicylaldehyde (2.80 g, 10.0 mmol) and *racemic* 1-phenylethylamine (1.21 g, 10.0 mmol).

Yield 74.5%. *Anal.* Calc. for $C_{30}H_{24}Br_4CuN_2O_2$: C, 43.64; H, 2.92; N, 3.38. Found: C, 43.77; H, 2.72; N, 3.25%. IR (KBr) $\nu_{C=N}$ 1617 cm^{-1}, $\nu_{Cu–N}$ 444 cm^{-1}, $\nu_{Cu–O}$ 424 cm^{-1}, m.p. 478 K (decomposition). Magnetic moment $\mu_{eff}/\mu_{BM} = 1.47$ at 298 K.

2.3.3. *Bis(N-R,S-1-phenylethyl-5-chlorosalicydenaminato)copper(II) (**3**)*

The same procedure as for **1** afforded the condensation of 5-chlorosalicylaldehyde (1.57 g, 10.0 mmol) and *racemic* 1-phenylethylamine (1.21 g, 10.0 mmol). Yield 49.6%. *Anal.* Calc. for $C_{30}H_{26}Cl_2CuN_2O_2$: C, 62.02; H, 4.51; N, 4.82. Found: C, 62.07; H, 4.29; N, 4.70%. IR (KBr) $\nu_{C=N}$ 1621 cm^{-1}, $\nu_{Cu–N}$ 465 cm^{-1}, $\nu_{Cu–O}$ 419 cm^{-1}, m.p. 474 K (decomposition). Magnetic moment $\mu_{eff}/\mu_{BM} = 1.66$ at 298 K.

2.3.4. *Bis(N-R-1-phenylethyl-5-bromosalicydenaminato)copper(II) (**4**)*

The same procedure as for **1** afforded the condensation of 5-bromosalicylaldehyde (2.01 g, 10.0 mmol) and *R*-1-phenylethylamine (1.21 g, 10.0 mmol). Yield 24.4%. *Anal.* Calc. for $C_{30}H_{26}Br_2CuN_2O_2$: C, 53.79; H, 3.91; N, 4.18. Found: C, 53.60; H, 3.69; N, 4.11%. IR (KBr) $\nu_{C=N}$ 1620 cm^{-1}, $\nu_{Cu–N}$ 463 cm^{-1}, $\nu_{Cu–O}$ 418 cm^{-1}, m.p. 469 K (decomposition). Magnetic moment $\mu_{eff}/\mu_{BM} = 1.91$ at 298 K. Brown plate-like single crystals suitable for X-ray crystallography were grown from the filtrate over a period of a few days at 298 K.

2.3.5. *Bis(N-S-2-butyl-3,5-dichlorosalicydenaminato)-copper(II) (**5**)*

The similar procedure as for **1** afforded the condensation of 3,5-dichlorosalicylaldehyde (0.96 g, 5.00 mmol) and *S*-2-butylamine (0.37 g, 5.00 mmol). Yield 25.8%. *Anal.* Calc. for $C_{22}H_{24}Cl_4CuN_2O_2$: C, 47.71; H, 4.37; N, 5.06. Found: C, 47.76; H, 3.94; N, 5.09%. IR (KBr) $\nu_{C=N}$ 1622 cm^{-1}, $\nu_{Cu–N}$ 447 cm^{-1}, $\nu_{Cu–O}$ 419 cm^{-1}, m.p. 484 K (decomposition). Magnetic moment $\mu_{eff}/\mu_{BM} = 1.53$ at 298 K.

2.3.6. *Bis(N-R,S-2-butyl-3,5-dibromosalicydenaminato)-copper(II) (**6**)*

The similar procedure as for **1** afforded the condensation of 3,5-dibromosalicylaldehyde (1.40 g, 5.00 mmol) and racemic 2-butylamine (0.37 g, 5.00 mmol). Yield 26.9%. *Anal.* Calc. for $C_{22}H_{24}Br_4CuN_2O_2$: C, 36.12; H, 3.31; N, 3.83. Found: C, 36.50; H, 2.97; N, 3.84%. IR (KBr) $\nu_{C=N}$ 1620 cm^{-1}, $\nu_{Cu–N}$ 446 cm^{-1}, $\nu_{Cu–O}$ 420 cm^{-1}, m.p. 459 K (decomposition). Magnetic moment $\mu_{eff}/\mu_{BM} = 1.48$ at 298 K.

2.3.7. *Bis(N-R,S-2-butyl-5-chlorosalicydenaminato)-copper(II) (**7**)*

The similar procedure as for **1** afforded the condensation of 5-chlorosalicylaldehyde (0.78 g, 5.00 mmol) and racemic 2-butylamine (0.37 g, 5.00 mmol). Yield 46.4%. *Anal.* Calc. for $C_{22}H_{26}Cl_2CuN_2O_2$: C, 54.49; H, 4.40; N, 5.78. Found: C, 54.46; H, 4.53; N, 5.72%. IR (KBr) $\nu_{C=N}$ 1618 cm^{-1}, $\nu_{Cu–N}$ 459 cm^{-1}, $\nu_{Cu–O}$ 436 cm^{-1}, m.p. 475 K (decomposition). Magnetic moment $\mu_{eff}/\mu_{BM} = 1.55$ at 298 K.

2.3.8. *Bis(N-R,S-2-butyl-5-bromosalicydenaminato)-copper(II) (**8**)*

The similar procedure as for **1** afforded the condensation of 5-bromosalicylaldehyde (1.01 g, 5.00 mmol) and racemic 2-butylamine (0.37 g, 5.00 mmol). Yield 49.7%. *Anal.* Calc. for $C_{22}H_{26}Br_2CuN_2O_2$: C, 46.05; H, 4.57; N, 4.88. Found: C, 46.10; H, 4.84; N, 4.81%. IR (KBr) $\nu_{C=N}$ 1616 cm^{-1}, $\nu_{Cu–N}$ 459 cm^{-1}, $\nu_{Cu–O}$ 426 cm^{-1}, m.p. 473 K (decomposition). Magnetic moment $\mu_{eff}/\mu_{BM} = 1.69$ at 298 K. Brown plate-like single crystals suitable for X-ray crystallography were grown from the filtrate over a period of a few days at 298 K.

2.3.9. *Bis(N-2-propyl-5-chlorosalicydenaminato) copper(II) (**9**)*

The same procedure as for **1** afforded the condensation of 5-chlorosalicylaldehyde (1.57 g, 10.0 mmol) and 2-propylamine (0.59 g, 10.0 mmol). Yield 50.9%. *Anal.* Calc. for $C_{20}H_{22}Cl_2CuN_2O_2$: C, 52.58; H, 4.85; N, 6.13. Found: C, 52.39; H, 5.16; N, 6.21%. IR (KBr) $\nu_{C=N}$ 1626 cm^{-1},

Table 1
Crystallographic data for **4** and **8**

	4	**8**
Formula	$C_{30}H_{26}Br_2CuN_2O_2$	$C_{22}H_{26}Br_2CuN_2O_2$
Molecular weight	669.88	573.80
Crystal system	monoclinic	monoclinic
Space group	*C*2 (#5)	*C*2/*c* (#15)
a (Å)	17.662(5)	21.816(9)
b (Å)	8.557(3)	10.577(3)
c (Å)	9.522(2)	10.362(2)
β (°)	102.28(2)	96.61(3)
V (Å^3)	1406.2(7)	2375.1(13)
Z	2	4
D_{calc} (g cm^{-3})	1.582	1.605
F(0 0 0)	670.0	730.0
μ (mm^{-1})	3.647	4.304
Crystal size (mm)	0.50 × 0.30 × 0.20	0.68 × 0.68 × 0.30
Total unique reflections	1724	2733
Observed reflections ($I > 2\sigma(I)$)	1230	1171
No. of refined parameters	169	132
R,[a] R_w,[b] *S*	0.0294, 0.0826, 1.028	0.0498, 0.2062, 1.100
Frack parameter	−0.03(2)	
Minimum and maximum residual densities (e/Å^3)	0.37, −0.37	−0.47, 0.48

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$.

[b] $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, $w = 1/(\sigma^2(F_o) + (0.0286P)^2 + 1.2163P)$ for **4**, $w = 1/(\sigma^2(F_o) + (0.1P)^2)$ for **8**, where $P = (F_o^2 + 2F_c^2)/3$.

$\nu_{\text{Cu–N}}$ 453 cm^{-1}, $\nu_{\text{Cu–O}}$ 432 cm^{-1}, m.p. 469 K (decomposition). Magnetic moment $\mu_{\text{eff}}/\mu_{\text{BM}} = 1.55$ at 298 K.

*2.3.10. Bis(N-2-propyl-5-bromosalicydenaminato) copper(II) (**10**)*

The same procedure as for **1** afforded the condensation of 5-bromosalicylaldehyde (2.01 g, 10.0 mmol) and 2-propylamine (0.59 g, 10.0 mmol). Yield 54.1%. *Anal.* Calc. for $C_{20}H_{22}Br_2CuN_2O_2$: C, 44.01; H, 4.06; N, 5.13. Found: C, 44.01; H, 4.28; N, 5.05%. IR (KBr) $\nu_{\text{C=N}}$ 1624 cm^{-1}, $\nu_{\text{Cu–N}}$ 451 cm^{-1}, $\nu_{\text{Cu–O}}$ 429 cm^{-1}, m.p. 481 K (decomposition). Magnetic moment $\mu_{\text{eff}}/\mu_{\text{BM}} = 1.54$ at 298 K.

2.4. X-ray crystallography

Intensity data of **4** and **8** were collected on a Rigaku AFC-7R four-circle diffractometer at 297 K using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SIR92 [44] and expanded by Fourier techniques. The structures were refined on F^2 anisotropically for non-hydrogen atoms by full-matrix least-squares methods with SHLEXL97 [45] on a teXsan program package [46]. Empirical absorption corrections were applied based on ψ scans. No significant decay in the intensity of three standard reflections was observed throughout the data collection. The hydrogen atoms were located at geometrically calculated position with C–H = 0.950 Å and refined isotropically. All the non-hydrogen atoms were refined anisotropically. Crystallographic data for **4** and **8** are summarized in Table 1. The crystal structures of **1** [30] and **5** [29] have been already reported elsewhere.

3. Results and discussion

*3.1. Description of the structure of **4***

The molecular structure of **4** is depicted in Fig. 1, and selected bond distances and angles of **4** are given in Table 2. Complex **4** adopts a compressed tetrahedral *trans*-[CuN_2O_2] coordination environment, which is ascribed to bulky 1-phenylethyl moieties of the ligands.

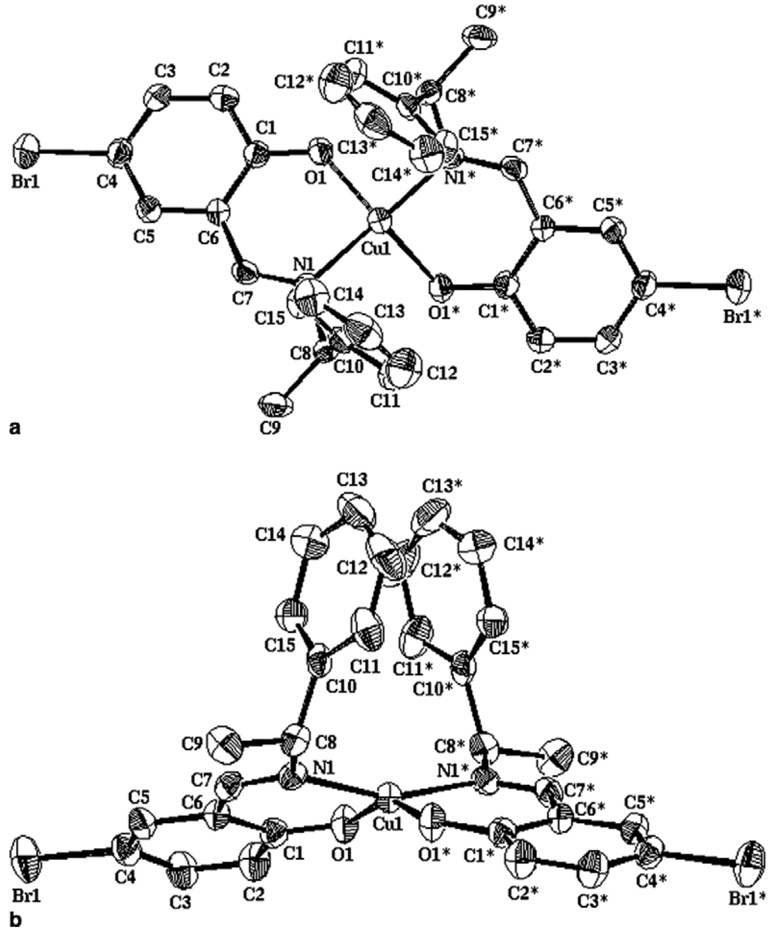


Fig. 1. The molecular structure of **4** showing the atom-labelling scheme (a) top view and (b) side view. Displacement ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity.

Table 2
Selected geometric parameters (Å, °) for **4**

Cu1–O1	1.890(4)
Cu1–N1	1.972(4)
N1–C7	1.296(6)
C6–C7	1.423(8)
O1–C1	1.319(1)
N1–C8	1.449(7)
C8–C9	1.511(9)
C8–C10	1.514(9)
O1–Cu1–O1*	151.7(3)
N1–Cu1–N1*	159.4(2)
O1–Cu1–N1*	92.0(2)
O1–Cu1–N1	93.0(2)
Cu1–O1–C1	129.2(4)
Cu1–N1–C7	124.0(4)
Cu1–N1–C8	116.5(3)
C7–N1–C8	119.4(4)
O1–C1–C2	119.0(5)
O1–C1–C6	122.7(5)
N1–C7–C6	127.0(5)
N1–C8–C9	115.2(4)
N1–C8–C10	108.6(4)
C9–C8–C10	111.0(5)

Atoms marked with *'s are expanded by the symmetry operation ($-x-1$, y, $-z-2$).

The *trans*-N1–Cu1–N1* and *trans*-O1–Cu1–O1* bond angles are 159.4(2)° and 151.7(3)°, respectively, whereas the *cis*-N1–Cu1–O1 and *cis*-N1*–Cu1–O1 bond angles are 93.0(2)° and 92.0(2)°, respectively. The Cu1–N1 and Cu1–O1 bond distances are 1.890(4) and 1.972(4) Å, respectively, and the C7=N1 imine bond length is 1.296(6) Å. There are no remarkable bond distances and angles for analogous compressed tetrahedral complexes [27,30]. The central Cu(II) ion is located at the center of symmetry along the C_2 axis. Since only *R*-enantiomers of 1-phenylethylamine were used for the preparations, the absolute configuration was found to be Δ(*R*,*R*) for the examined crystal of **4**. As for the related bis[(*N*-*R*-1-phenylethyl)(3- or 5-halogen-)salicylideneaminato]M(II) complexes, 3,5-Cl-substituted Cu(II) complex (**1**) of Δ(*R*,*R*) absolute configuration was reported with Cu–N = 1.984(4) Å, Cu–O = 1.890(3) Å, *trans*-N–Cu–N = 144.7(2)° and *trans*-O–Cu–O = 150.9 (1)° [30]. Unsubstituted Cu(II) [27], 3-EtO Cu(II) [30] and 3-Cl Zn(II) complexes [47] were reported to be Λ(*R*,*R*) absolute configuration. The pendant *R*-1-phenylethylamine groups of the ligands are on the same side of the salicydenaminato plane, and the dihedral angle between the C1/C2/C3/C4/C5/C6 mean plane and the C10/C11/C12/C13/C14 mean planes is 89.5(3)°. Intramolecular and intermolecular hydrogen bonds could not be detectable within van der Waals radii [48], crystal packing as well as chiral molecular recognition of **4** are dominated only by weak van der Waals forces during preparation or crystallization.

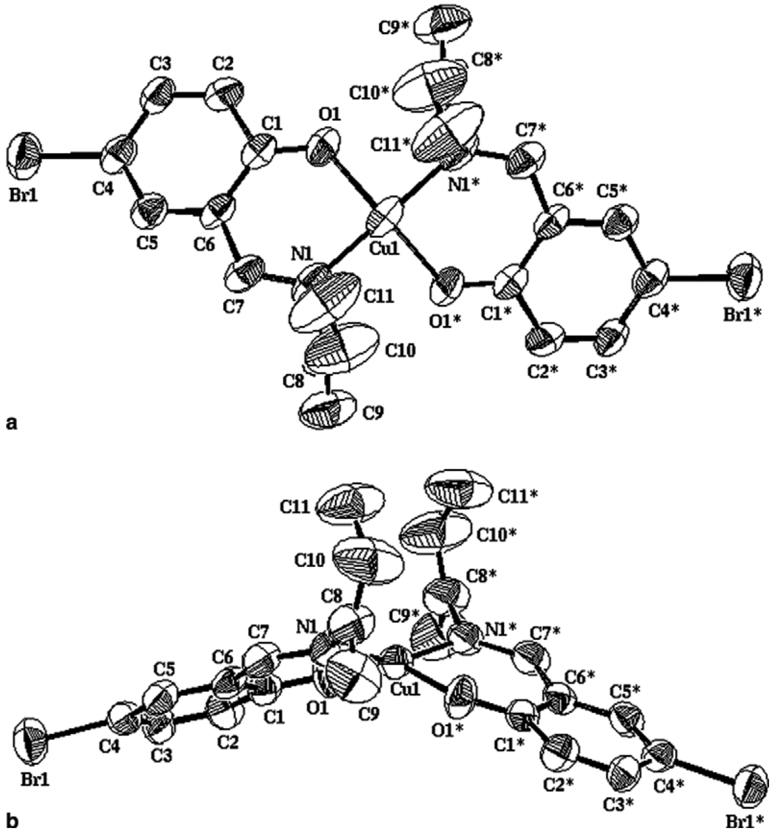


Fig. 2. The molecular structure of **8** showing the atom-labelling scheme (a) top view and (b) side view. Displacement ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity.

3.2. Description of structure of **8**

The molecular structure of **8** is depicted in Fig. 2, and selected bond distances and angles of **8** are given in Table 3. Complex **8** adopts a compressed tetrahedral *trans*-[CuN$_2$O$_2$] coordination geometry similar to **4**. This structural feature suggests that steric hindrance of the ethyl groups is sufficiently effective for distortion of the coordination environment when electron-withdrawing Br-groups are introduced. The central Cu(II) ion is on the center of symmetry. The *trans*-N1–Cu1–N1* and *trans*-O1–Cu1–O1* bond angles are 157.9(3)° and 151.0(3)°, respectively, whereas the *cis*-N1–Cu1–O1 and *cis*-N1*–Cu1–O1 bond angles are 93.3(2)° and 92.2(2)°, respectively. The Cu1–N1 and Cu1–O1 bond distances are 1.966(6) and 1.865(4) Å, respectively, and the C7=N1 imine bond length is 1.339(9) Å. The degree of distortion from square planar towards tetrahedral environment of **8** is larger than that of **4**, which leads to elongate both Cu–N and Cu–O coordination bonds of **8**. The other geometric parameters in the Schiff base ligands do not deviate significantly from the corresponding common values. Selected geometrical parameters of **5** were reported to be Cu–N = 1.969(4) and 1.971(4) Å, Cu–O = 1.886(3) and 1.892(3) Å, *trans*-N–Cu–N = 158.4(2)° and *trans*-O–Cu–O = 158.7(1)° [29]. Both sides of the 2-butyl pendant groups are on the apical side of the umbrella molecular plane. Intramolecular and intermolecular hydrogen bonds are not detectable within van der Waals radii [48] for **8**.

Table 3
Selected geometric parameters (Å, °) for **8**

Cu1–O1	1.865(4)
Cu1–N1	1.966(6)
N1–C7	1.339(9)
C6–C7	1.447(7)
O1–C1	1.284(8)
N1–C8	1.506(9)
C8–C9	1.43(1)
C8–C11	1.29(2)
O1–Cu1–O1*	151.0(3)
N1–Cu1–N1*	157.9(3)
O1–Cu1–N1*	92.2(2)
O1–Cu1–N1	93.3(2)
Cu1–O1–C1	129.1(4)
Cu1–N1–C7	124.1(4)
u1–N1–C8	120.6(6)
C7–N1–C8	115.2(7)
O1–C1–C2	120.3(6)
O1–C1–C6	123.9(5)
N1–C7–C6	124.1(6)
N1–C8–C9	115.0(8)
N1–C8–C10	114.4(8)
C9–C8–C10	130.5(9)

Atoms marked with *'s are expanded by the symmetry operation ($-x-1$, y, $-z-1/2$).

3.3. IR spectroscopy

In general, the IR spectra of the analogous free protonated ligands show an imine C=N band around 1635 cm^{-1}, and the disappearance of a C=O peak around 1700 cm^{-1} is indicative of a condensation reaction giving Schiff base ligands [49]. The IR spectra of all the complexes **1**–**10** show the imine C=N bands around 1620 cm^{-1}, and it is found that the C=N bands of the Cu(II) complexes are shifted by about 10 cm^{-1} to the lower energy regions compared to the free protonated ligands [50]. In addition, the Cu–N and Cu–O vibrations are found around 450 and 420 cm^{-1}, respectively. These spectral characteristics are due to the coordination of the imine nitrogens to the metal ions [51]. These peaks are in agreement with related complexes, regardless of the degree of distortion of the *trans*-[CuN$_2$O$_2$] coordination environment. The IR spectra are not sensitive to distortion of coordination environment for the present complexes.

3.4. Diffuse reflectance electronic spectroscopy and magnetic properties

The diffuse reflectance electronic spectra of **1**–**10** were recorded at room temperature, and the overall spectral features are similar to that of analogous complexes. The small differences of the spectral features can be classified into five patterns: (i) **1** and **2**, with 1-phenylethylamine moieties and 3,5-substituents, show a broad d–d band in the region 17000–19000 cm^{-1} and a strong continuous band in the higher energy region over 22000 cm^{-1}; (ii) **3** and **4**, with 1-phenylethylamine moieties and 5-substituents, show a broad d–d band in the region 16000–19000 cm^{-1} and a strong continuous band in the higher energy region over 23000 cm^{-1}; (iii) **5** and **6**, with 2-butylamine moieties and 3,5-substituents, show a strong d–d band around 15000 cm^{-1} and a strong continuous band in the higher energy region over 23000 cm^{-1}; (iv) **7** and **8**, with 2-butylamine moieties and 5-substituents, show a broad d–d band in the region 16000–19000 cm^{-1} and a strong continuous band in the higher energy region over 22000 cm^{-1}; (v) **9** and **10**, with 2-propylamine moieties and 3,5-substituents, show a strong d–d band around 14000 cm^{-1} and a continuous band in the higher energy region over 22000 cm^{-1}. In this way, d–d bands are more sensitive to coordination geometries and electron-withdrawing groups of the ligands than π–π* bands in the case of solid state spectra. Generally, tetrahedral complexes show a d–d band at lower energies, which shift to higher energies on moving from tetrahedral to square planar environments [52]. Apparently, the number of halogen substituents (only 5- or both 3- and 5-) is more effective than the kind of halogen (Cl or Br) substituents. The absence of pendant π-conjugated phenyl groups in the Schiff base ligands results in the π–π* region.

Theoretically, for Cu(II) complexes (effective symmetry C_{2v} point group) of the ^{2}D state three transitions, ${}^2A_1(d_{z^2}) \leftarrow {}^2A_1(d_{x^2-y^2})$, ${}^2B_1(d_{zx}) \leftarrow {}^2A_1(d_{x^2-y^2})$ and ${}^2B_2(d_{yz}) \leftarrow {}^2A_1(d_{x^2-y^2})$, are allowed, and a broad d–d band is their convolution. A strong band in the UV region is due to an overlap of the π–π* transition [47,53] and phenolate O atoms of the ligand to Cu(II) metal charge transfer transition. These transitions are related not only to *trans*-[CuN_2O_2] coordination geometries but also the net atomic charge on the coordinating atoms (O and N) of the ligands.

The effective magnetic moments (μ_{eff}) of mononuclear Cu(II) complexes **1**–**10** at 298 K are in the range from ca. 1.4 to 1.9 B.M., which is reasonable compared to the theoretical spin-only value of 1.73 B.M. for $S = 1/2$ systems with a single unpaired electron sited in an essentially $d_{x^2-y^2}$ orbital, the ^{2}D state. In contrast to the electronic spectra, the effective magnetic moment is not sensitive to distortion of the *trans*-[CuN_2O_2] coordination environment for the present complexes. In order to confirm that there is little or no intermolecular antiferromagnetic coupling, we also investigated variable-temperature (5–250 K) magnetic susceptibility behavior for **1**, whose crystal structure has been determined. Complex **1** obeys the Curie–Weiss law approximately, that is the χ_M^{-1} versus T plot is a linear graph. Thus, in the absence of X-ray structural proof, except for **1**, **4**, **5** and **8**, the effective magnetic moments demonstrate the nature of the mononuclear complexes.

Table 4
Temperature (K) of the phase transition and decomposition by DSC for **1**–**10**

	Phase transition	Decomposition
1	419	556
2	484	547
3	474	547
4	412	542
5	396	557
6	410	532
7	412	548
8	400	544
9	444	542
10	446	554

3.5. Structural phase transition

It has been investigated that the analogous Cu(II) and Ni(II) complexes exhibit a thermally-induced structural phase transition by heating regardless of the coordination geometries (square planar or tetrahedral) at room temperature [21,37]. The temperature of the structural phase transition (endothermic peaks) and decomposition (exothermic peaks) in the DSC curves for **1**–**10** are summarized in Table 4. In analogy with the related Cu(II) complexes [21], the structural phase transition may be ascribed to a transformation from a low temperature phase (compressed tetrahedral) into a high temperature phase (close to right tetrahedral). The relationship between the transition temperature and chemical structures is unclear still. Because of the lability of the compounds, we could not carry out quantitative measurements. The structural phase transition seems to be irreversible for **1**–**10**.

Furthermore, we have examined the possibility of a photo-induced structural phase transition of microcrystalline samples for **1**–**10** with IR spectroscopy in the solid state at room temperature. After irradiation of UV or visible light for 5 min at room temperature, no spectral changes could be detected for **1**–**10**. On the other hand, certain thermochromic Cu(II) complexes also exhibited photochromism in the solid state at low temperature [7,10]. Thus, at least, the present experimental facts support the stability of the Cu(II) complexes against UV or visible light at room temperature.

3.6. Calculation

A summary of the results of ZINDO calculations for **1**, **4**, **5** and **8**, whose crystal structures are known, is listed in Table 5. The dipole moment of the overall molecules were evaluated to be 6.029, 5.033, 4.166 and 4.215 D for **1**, **4**, **5** and **8**, respectively. It can be expected that both introduction of 3,5-halogen substituents and deviation from square molecules as well as breaking

Table 5
Summary of the results of ZINDO calculations for **1**, **4**, **5** and **8**

	1	4	5	8
Heat of formation (kJ mol^{-1})	325.2	295.9	255.4	251.8
Dipole moment (D)	6.029	5.033	4.166	4.215
HOMO–LUMO gap (eV)	8.20	8.09	7.88	7.77
Formal charge Cu	0.196	0.250	0.204	0.200
N	−0.129	−0.084	−0.143	−0.156
O	−0.456	−0.433	−0.483	−0.463
Calculated predominant π–π* transitions (cm^{-1})	32700	33100	31200	29700
	45700	36100	34400	32900
	51300	48300	45700	44400

molecular symmetry lead to an increase of the magnitude of dipole moment. The numbers and kinds of 3,5-halogen substituents are invariable factors for a given molecule, whereas distortion of the overall molecular structure can induce polarity depending on the molecular conformation. Thus, the dipole moment can interact between the complexes and the surrounding species in solution.

The formal charges on the Cu(II) ions are 0.196, 0.250, 0.204 and 0.200 for **1**, **4**, **5** and **8**, respectively. On the other hand, the averaged values on the coordination N atoms are −0.129, −0.084, −0.143 and −0.156, and O atoms are −0.456, −0.433, −0.483 and −0.463 for **1**, **4**, **5**, and **8**, respectively. As indicated for these values, tetrahedral distortion of the coordination environment plays a role in distribution of charge from the coordination atoms to the metal ions through coordination bonds. Although these electronic features are advantageous for charge transfer transitions, it is difficult to estimate their contribution in electronic spectra. Further, π–π* bands consist of several components in the UV regions as calculations exhibit even for the X-ray structures.

3.7. Electronic absorption spectroscopy in various solvents

Fig. 3 shows the electronic absorption spectra and CD spectra of **1** in 0.1 mmol dm^{-3} chloroform solution at 298 K. The reason why **1** is employed for the following investigation and discussion is that **1** displays the largest dipole moment in the solid state and incorporates chiral ligands whose CD spectrum is detectable. Additionally, bulky 1-phenylethyl moieties and electron-withdrawing 3,5-Cl-substituents may enhance the flexibility of **1**. The absorption spectrum of **1** exhibits a broad d–d band in the region 16000–20000 cm^{-1} and a strong π–π* band in the region 24000–28000 cm^{-1}. The corresponding CD spectrum of **1** shows a positive peak around 15000 cm^{-1} and a negative peak around 18000 cm^{-1} in the d–d region, and a negative peak around 23000 cm^{-1} and a positive peak around 25000 cm^{-1} in the π–π* region. The d–d band can be ascribed to convolution of three allowed transitions, ${}^2A_1(d_{x^2-y^2}) \rightarrow {}^2A_1(d_{z^2})$, ${}^2A_1(d_{x^2-y^2}) \rightarrow {}^2B_1(d_{xz})$, ${}^2A_1(d_{x^2-y^2}) \rightarrow {}^2B_2(d_{yz})$, in C_{2v} symmetry. The sign of the CD peaks seems to be reasonable with respect to the Δ(*R*,*R*) absolute configuration of **1**. The change of coordination geometry of **1** and conformation of its ligands in solution may attribute to the difference between absorption spectra and diffuse reflectance spectra.

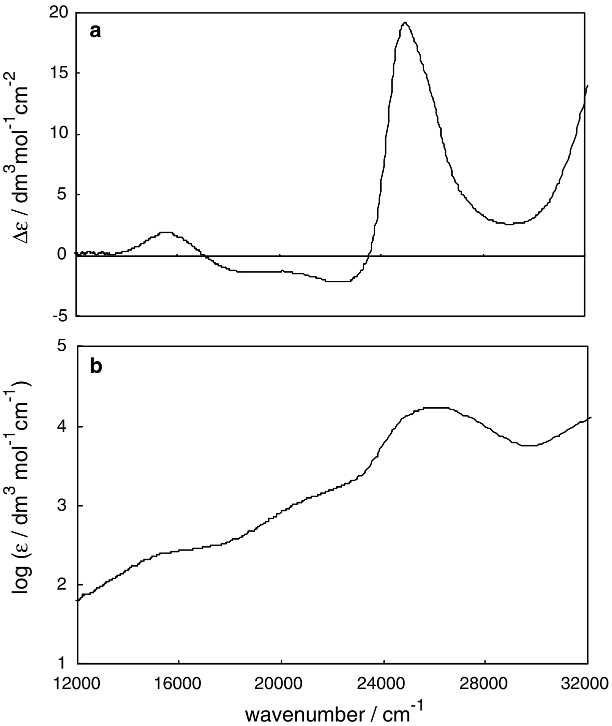


Fig. 3. The electronic (a) CD and (b) absorption spectra of **1** in 0.1 mmol^{-1} dm^3 $CHCl_3$ solution at 298 K.

The electronic absorption spectra were also recorded for **1**–**10** in various solvents, *N*,*N*′-dimethylformamide (DMF) ($\mu = 3.82$; $\varepsilon = 36.710$; $n_D^{20} = 1.428$), acetone ($\mu = 3.11$; $\varepsilon = 20.700$; $n_D^{20} = 1.356$), methanol ($\mu = 2.97$; $\varepsilon = 32.630$; $n_D^{20} = 1.326$), chloroform ($\mu = 1.11$; $\varepsilon = 4.806$; $n_D^{20} = 1.444$) and toluene ($\mu = 0.37$; $\varepsilon = 2.438$; $n_D^{20} = 1.494$) (the figures in parentheses denote dipole moment, μ(D), dielectric constant, ε, and refractive index, n_D^{20}) [15]. The predominant peaks of π–π* bands (v cm^{-1} and log ε dm^3 mol^{-1} cm^{-1}) are shown in Table 6. The results show that the π–π* bands are sensitive to the physical properties of the solvents for **1**–**10**. However, the shifts of the d–d band, depending on solvents or concentrations (1, 0.1, and 0.01 mmol dm^{-3}), are relatively small for **1**–**10**. Therefore, we can conclude that the changes of polarity of the solvent lead to structural changes of the complexes associated with conformation of the π-conjugated pendant groups of the Schiff base ligands.

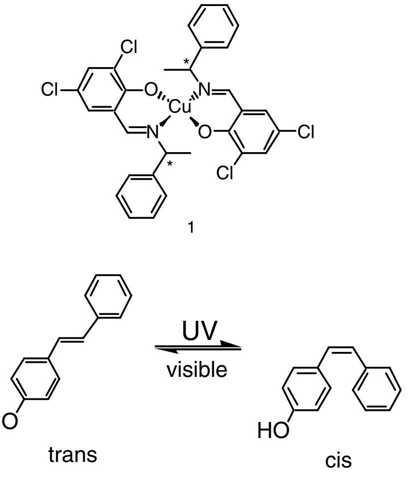
In an attempt to produce *solvatochromism induced by a photochromic solute*, we have measured the absorption spectra of a 0.1 mmol dm^{-3} chloroform solution of **1** containing equimolar 4-hydroxyazobenzene (4HAZ) (Scheme 2). It is well known that irradiation with UV and visible light results in reversible photoisomerization of 4HAZ to the *cis* forms (μ = ca. 3 D) and the *trans* forms (μ = almost 0 D). For a solution of only 4HAZ (Fig. 4(a)), irradiation with UV and visible light for 5 min, which is enough time to saturate the photoisomerization reaction, to the solution results in reversible spectral changes of the π–π* band of 4HAZ around 29000 cm^{-1}. On the other hand, for a solution containing 4HAZ and **1**, very slight and relatively large spectral changes could be observed at ca. 23000 cm^{-1} and ca. 31000 cm^{-1}. Taking into account the absorption spectrum

Table 6
Predominant π–π* peaks (ν(cm^{-1}); log ε (dm^3 mol^{-1} cm^{-1})) of the absorption spectra 0.1 mmol dm^{-3} in various solvents at 298 K for **1**–**10**

	DMF	Acetone	Methanol	Chloroform	Toluene
1	26530(4.10)	26460(4.05)	26460(4.04) 33220(3.96)	26180(4.23) 33000(4.20)^{sh}	26110(4.12)
2	26530(4.00)	26460(4.06)	26390(3.70) 33220(3.64)^{sh}	26180(3.84) 33000(3.82)^{sh}	26110(4.22)
3	26390(4.05)	26390(4.25)	26460(4.03) 32680(3.93)	26180(4.12) 32570(4.06)	26040(4.21)
4	26460(4.03)	26390(4.05)	26460(3.95) 32680(3.89)	26180(4.10) 32570(4.08)	26110(4.23)
5	26670(4.24)	26600(4.28)	26530(4.17) 33000(4.13)^{sh}	26320(4.10) 33220(4.09)	26250(4.10)
6	26600(3.65)	26600(4.00)	26600(3.96) 33220(3.97)^{sh}	26320(4.09) 32260(4.06)	26250(4.11)
7	26600(4.23) 32150(4.18)	26530(4.25)	26670(4.06) 32260(4.01)	26320(4.09) 32260(4.06)	26520(4.11)
8	26600(4.08) 32150(4.05)	26600(4.12)	26670(4.09) 32360(4.08)	26320(3.94) 32260(3.95)	26110(4.45)
9	26670(4.18)	26670(3.91)	26740(4.10) 32570(4.08)	26390(4.00) 32360(4.00)	26300(4.17)
10	26740(4.09)	26670(3.93)	26810(4.11) 32790(4.17)^{sh}	26460(4.00) 32360(4.04)	26250(4.12)

The figures marked with ^{sh} denotes a shoulder, and the remaining ones are bands.

of only **1** (Fig. 3(b)), the former band and the latter band are ascribed to d–d and π–π* bands of **1**. The spectral change caused by the photoisomerization of 4HAZ may be ascribed mainly to a conformational change of the pendant 1-phenylethylamine moiety of the ligands (Fig. 4(b)). The possibility of supramolecular helical structures of 4HAZ induced by **1** as chiral dopants in the solution can be denied, because the spectral changes are detected not by CD spectra but by absorption spectra. The fact that solvatochromic behavior mainly affects the π–π* bands, as indicated in Table 6, and the magnitude of the difference of dipole moment photoisomerization of 4HAZ may support this interpretation. Although the other complexes also exhibit spectral shifts depending on the solvent, we could not observe photoisomerization caused by 4HAZ. The appropriate pendant 1-phenylethylamine moiety and molecular flexibility enhanced by electron-withdrawing substituents are necessary for the complex served for this experiment.



Scheme 2. Molecular structure of **1** and *cis–trans* photoisomerization of 4HAZ.

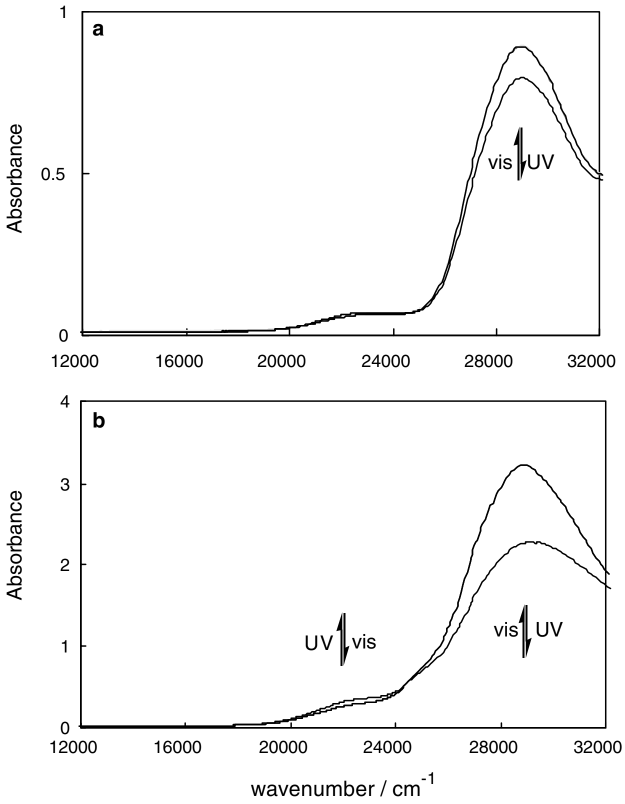


Fig. 4. The absorption spectra of (a) only 4HAZ and (b) 4HAZ and **1** in 0.1 mmol^{-1} dm^3 $CHCl_3$ solution at 298 K before and after UV or visible light irradiation for 5 min.

4. Concluding remarks

Crystal structures of two new Cu(II) complexes and systematical comparisons of structural features, thermodynamical behavior and electronic or optical properties have been reported for a series of ten related Cu(II) complexes incorporating 3,5-halogen-substituted Schiff base ligands. The pronounced solvatochromic behavior of the absorption spectra can be detected in the π–π* bands rather than the d–d bands for **1**–**10**. As for a chloroform solution of **1**, which has the largest dipole moment in the solid state among **1**–**10** and chiral ligands, and containing equimolar 4HAZ, we have examined solvatochromism of **1** induced by the photochromic solute. Irradiation of light resulted in spectral changes in the π–π* regions and little difference in the d–d regions. Further studies to apply to other nano-structured supramolecular systems of complexes and homogeneous chiral catalysts of transition metal complexes [54] without photochromic functional groups in ligands are underway.

5. Supplementary materials

Crystallographic data for the structural analyses are deposited with the Cambridge Crystallographic Data Centre, CCDC with deposition numbers 265611 and 265612 for **4** and **8**, respectively. Copies of this information can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by Grant-in-Aid for the 21st Century COE program 'KEIO Life Conjugate Chemistry' from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The authors thank Professor Yohru Yamada and Dr. Taketo Ikeno (Keio University) for the use of the DSC apparatus, Professor Hidenari Inoue (keio University) for the use of the CD spectrometer and Professor Katsuya Inoue (Institute for Molecular Science) for the use of the SQUID instrument.

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