Tetra- and Di-Nuclear Copper(II) Complexes with Stereoisomers of Sulfinylcalix[4]arene Arising from the Disposition of Four S=O Groups

Nobuhiko Iki,[*1] **Yusuke Yamane,**[1] **Naoya Morohashi,**[1] **Takashi Kajiwara,**[*2] **Tasuku Ito,**[3] and **Sotaro Miyano**[1]

[1]Department of Biomolecular Engineering, Graduate School of Engineering, Tohoku University, Aoba-ku, Sendai 980-8579
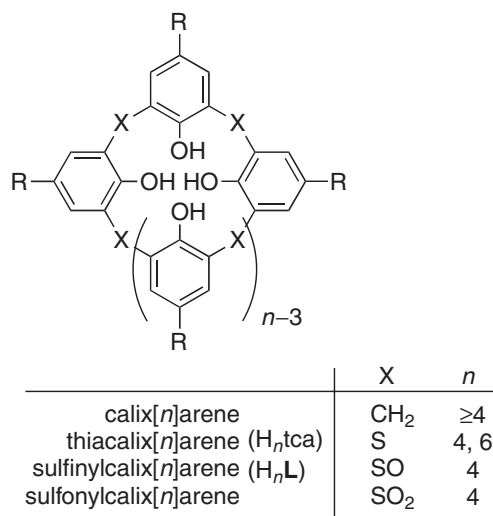
[2]Department of Chemistry, Graduate School of Science, Tohoku University and CREST, Japan Science and Technology Agency (JST), Aoba-ku, Sendai 980-8578

[3]Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578

Received September 21, 2006; E-mail: iki@orgsynth.che.tohoku.ac.jp

A systematic investigation was conducted on the structures of tetra- and di-nuclear copper(II) complexes with three stereoisomers of sulfinylcalix[4]arenes (H_4L), the isomerism of which is determined by the disposition of the sulfinyl oxygen with respect to a reference oxygen from the mean plane containing four sulfur atoms. The sulfinylcalix[4]arene with a *trans–cis–trans* S=O orientation (H_4L^{rtct}) reacted with $Cu(OAc)_2$ to form $[Cu^{II}_4(L^{rtct})(OAc)_3(\mu\text{-MeO})(MeOH)]$ (**1**), in which L^{rtct4-} adopts a cone conformation to afford tetrakis *fac*-tridentate coordination through four phenoxo oxygens and four sulfinyl groups giving a square Cu^{II}_4 core. Ligands H_4L^{rccc} and H_4L^{rctt} having *cis–cis–cis* and *cis–trans–trans* configurations formed $[Cu^{II}_4(L^{rccc})(OAc)_3(\mu\text{-OH})]$ (**2**) and $[Cu^{II}_4(L^{rctt})(OAc)_3(\mu\text{-OH})]$ (**3**), respectively, which have common features, such as a cone-type conformation of L^{4-}, tetrakis *fac*-tridentate coordination fashion, and tetracopper(II) core in a square-pyramidal geometry. The similarities among **1**–**3** clearly show that sulfinylcalix[4]arenes can coordinate to Cu^{II} in a *fac*-tridentate fashion via a donor atom X (O or S) from a sulfinyl group and two flanking phenoxo O^-s and that X is simply determined by the X–Cu distance. Using $[Cu(acac)_2]$ as a copper(II) source, H_4L^{rctt} formed $[Cu^{II}_2(H_2L^{rctt})_2]$ (**4**), suggesting the significance of auxiliary ligand for bridging copper(II) centers to assemble the core, that is, the acetato ligands in complexes **1**–**3** are needed to form the core structure. Metal–metal interactions were investigated by means of magnetic susceptibility, and it was found that both ferro- and antiferromagnetic interactions occur in tetracopper(II) complex **3**. In contrast, antiferromagnetic interaction is present in dicopper(II) complex **4**.

Over the past several decades, calix[*n*]arene has served as a versatile platform for constructing ligands for separation and sensing of metal ions because it is easily chemically modified at the phenol moiety, on which a wide variety of pendent ligating groups have been covalently attached.[1] Having sulfide in place of methylene at the bridging moiety (Scheme 1), thiacalix[4]arene has brought about a new era in calixarene chemistry, freeing ligand design from the introduction of metal-binding groups.[2] Soon after we had found a one-step protocol to synthesize thiacalix[4]arene,[3] we became aware of the fact that thiacalix[4]arene, *per se*, can extract metal ions, which are classified as soft to intermediate under "hard and soft acids and bases" theory,[4] in a *fac*-tridentate fashion with its sulfide S and the two adjacent phonoxo O^-s.[5] Furthermore, the extraction selectivity can be controlled by the oxidation state of the bridging sulfur; sulfonylcalix[4]arene having four sulfone moieties extracts hard metal ions, whereas sulfinylcalix[4]arene with four sulfoxide moieties extracts metal ions irrespective of the hardness and softness.[6] Thus, sulfur-bridged calix[4]-arenes, including sulfonyl- and sulfinylcalix[4]arenes, have been shown to be new molecular platforms that have an inherent ability for binding metal ions without modification at the
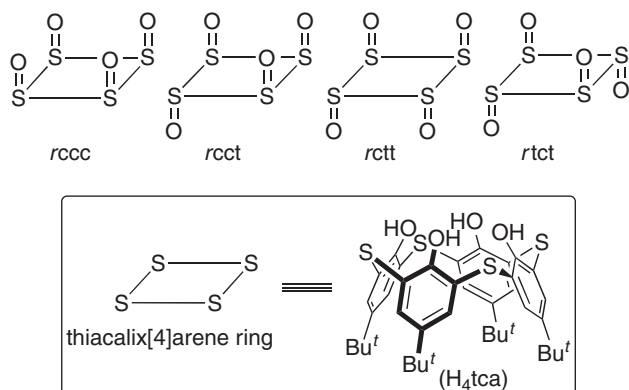

	X	*n*
calix[*n*]arene	CH_2	≥4
thiacalix[*n*]arene ($H_n$tca)	S	4, 6
sulfinylcalix[*n*]arene (H_n**L**)	SO	4
sulfonylcalix[*n*]arene	SO_2	4

Scheme 1. Calix[*n*]arenes.

phenol moiety.

Recently, coordination manners of sulfur-bridged calix-[*n*]arenes via a donor atom from the bridging group and the

adjacent phenoxo oxygen(s) have been evidenced by X-ray crystallography, which in turn has shown their ability to form multi-nuclear cluster complexes.[7–17] For instance, thiacalix[4]arene has been shown to form cluster complexes having Zn^{II}_4,[8] Cu^{II}_4,[9] Zn^{III}_3,[10] Co^{II}_3,[10] Hg^{II}_4,[11] Fe^{II}_4,[12] Mn^{II}_4,[13] and Nd^{III}_4 cores.[14] Moreover, thiacalix[6]arene can form penta-nuclear complexes with Cu^{II}_5, Co^{II}_5, and mixed-metal $M^{II}Ni^{II}_4$ (M = Mn, Co, and Cu) cores as well as decacopper(II) complex.[15] On the other hand, sulfonylcalix[4]arene has been reported to form octalanthanide(III) wheel complexes with Gd^{III}_8, Sm^{III}_8, Nd^{III}_8, and Pr^{III}_8 cores,[16] highly symmetrical tetranuclear complex with Mn^{II}_4, Co^{II}_4, and Ni^{II}_4 cores,[17] dinuclear and cubane-type tetranuclear complexes with Ln^{III}_2 and Ln^{III}_4 cores (Ln = Eu and Tb),[18] respectively, and dodecalanthanide(III) wheel with a Ho^{III}_{12} core.[19] As compared to thia- and sulfonyl-calix[4]arenes, however, only a little is known about crystal structure of metal complex with sulfinylcalix[4]arene; a dipalladium(II) complex, $[Pd_2(H_2\mathbf{L^{rtct}})(H_3\mathbf{L^{rtct}})_2]$,[20] and tetramanganese(II) complex, $[Mn^{II}_4(\mathbf{L^{rccc}})_2]$,[13] with sulfinylcalix[4]-arene having a *r*tct and *r*ccc configuration ($H_4\mathbf{L^{rtct}}$ and $H_4\mathbf{L^{rccc}}$), respectively (Scheme 2). As can be seen, one distinctive feature of sulfinylcalix[4]arene among sulfur-bridged calixarenes is its ability to undergo stereoisomerization arising from the disposition of the S=O group from the mean plane of the four sulfur bridges to give four configurational isomers: *r*tct, *r*ccc, *r*ctt, and *r*cct (Scheme 2).[21] Because of the configurational isomerism of $H_4\mathbf{L}$, the question of how does the S=O direction of the sulfinyl ligand affect the structure of complex arises. To determine systematically the effect of the S=O configuration, we determined the structures of multi-nuclear copper(II) complexes of sulfinylcalix[4]arene having *r*tct, *r*ccc, and *r*ctt configurations and report them here.

Results and Discussion

Synthesis.   Since *p-tert*-butyl- ($H_4\mathbf{L^{rtct}}$) and *p-tert*-octyl-sulfinylcalix[4]arenes with *r*tct configuration are readily available by direct oxidation of the corresponding thiacalix[4]arene, the properties and solvent extraction behavior have been the most intensively studied among the isomers.[6,21,22] As mentioned above, $H_4\mathbf{L^{rtct}}$ is able to switch the coordinating atom between S and O depending on the softness or hardness of the coordinated metal ion.[6] Because of this ability, we used copper(II) ion for preparing complexes, expecting that it would help determine the essential factor that controls which atom (O or S) of the sulfinyl moiety coordinates to metal ion. Reaction of $H_4\mathbf{L}$, having *r*tct, *r*ccc, and *r*ctt configurations, and copper(II) acetate monohydrate in a 1:4 ratio in $CHCl_3$/EtOH, followed by crystallization from the appropriate solvent systems (see experimental), gave single crystals of $[Cu_4L(OAc)_3$-$L']$-type complex (**1–3**) with a tetra-copper(II) core, where L' equals auxilliary ligands, such as (μ-MeO$^-$)(MeOH) and (μ-OH$^-$) (Scheme 3). In the case of $H_4\mathbf{L^{rcct}}$, the color of the reaction mixture turned from greenish to pale-yellow, suggesting that a species consisting of the ligand and Cu formed in the solution. However, various attempts, including changing the solvent system for crystallization, did not give any single crystals suitable for X-ray diffraction. In addition to copper(II) acetate, bis(acetylacetonato)copper(II) was also employed as a copper(II) source in the case of the *r*ctt isomer; reaction of $H_4\mathbf{L^{rctt}}$ with $[Cu(acac)_2]$ in a 1:6 ratio in CH_2Cl_2, followed by crystallization, afforded dicopper(II) complex, $[Cu_2$-$(H_2\mathbf{L^{rctt}})_2]$ (**4**). In each reaction system, acetate and acetylacetonate behaved as a base to remove protons from $H_4\mathbf{L}$ upon coordination to the copper(II) ion.

$[Cu^{II}_4(\mathbf{L^{rtct}})(OAc)_3(\mu\text{-MeO})(MeOH)]$ (1).   In the solid state, $H_4\mathbf{L^{rtct}}$ adopts a 1,3-alternate conformation having apparent S_4 symmetry due to four sets of hydrogen bonding, S=O⋯HO, causing the phenol OH groups to align in alternating directions with respect to the mean plane containing the four sulfur bridges (S_4).[22] Upon reacting with copper(II), the ligand adopted a cone conformation to support tetracopper(II) core on one side above S_4 plane with the aid of three acetates, μ-MeO$^-$, and MeOH ligands (Fig. 1). On the other side of S_4 plane, one $CHCl_3$ molecule was included in the cone-shaped cavity of $\mathbf{L^{rtct4-}}$, while the other two molecules were in the crystal lattice (not shown in Fig. 1a). Measures describing ligand conformations, such as inter-planer angles between opposite phenyl rings and inclination angles of a phenyl ring from
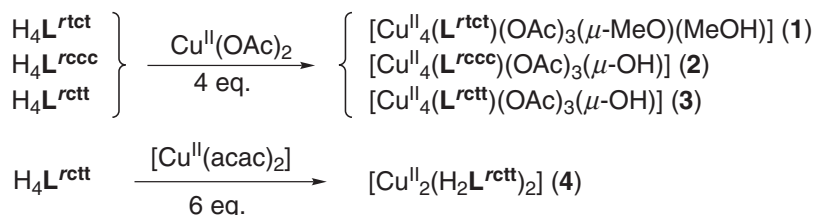

Scheme 2. *p-tert*-Butylthiacalix[4]arene ring and four stereoisomers of *p-tert*-butylsulfinylcalix[4]arene, $H_4\mathbf{L}$. Herein, we use the term *cis* (c) or *trans* (t) to denote the disposition of sulfoxide oxygen with respect to reference oxygen from the mean plane containing four sulfur atoms. The isomer notation proceeds around the system from reference oxygen, which should be chosen to maximize the number of *cis* arrangements, and *cis* is preferable to *trans*.

Scheme 3. Complex formation reaction.

S_4 plane, are tabulated in Table 1. Using un-coordinated thiacalix[4]arene (H$_4$tca), which adopts an ideal cone conformation with exact C_{4v} symmetry[23] as a reference, the angles of $\mathbf{L}^{rtct4-}$ in complex **1** shows only a slight deviation, and thus, the conformation can be regarded as cone.

Figure 1b shows top view of coordination environment of tetracopper(II) core. As can be seen, $\mathbf{L}^{rtct4-}$ acts as a tetrakis *fac*-tridentate ligand through four phenoxo (O1, O3, O5, and O7), two sulfinyl oxygens (O2 and O6), and two sulfinyl sulfurs (S2 and S4). Each phenoxo oxygen bridges adjacent
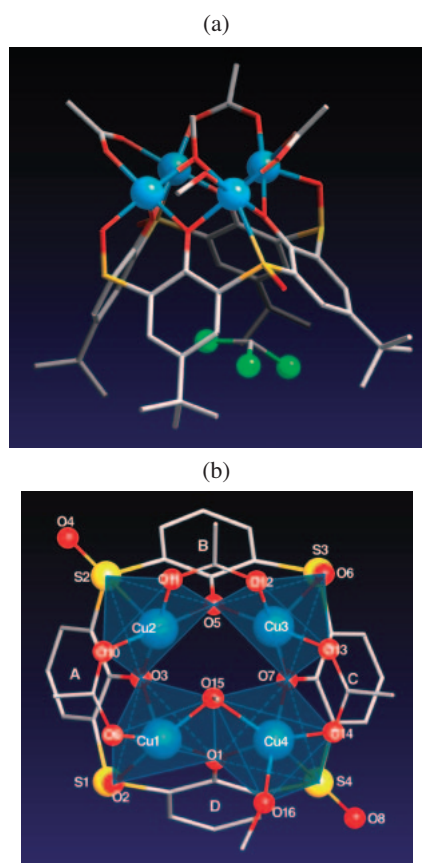
(a)

(b)

Fig. 1.   Crystal structure of [Cu^{II}$_4$($\mathbf{L}^{rtct}$)(OAc)$_3$(μ-MeO)-(MeOH)] (**1**). (a) Side view and (b) top view showing the copper(II) coordination polyhedra. *tert*-Butyl groups are omitted in (b).
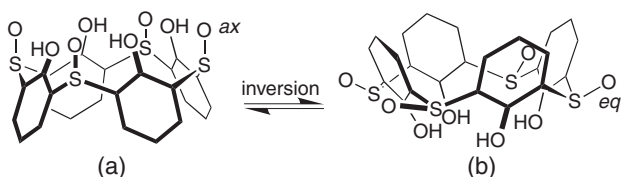
copper(II) pairs to form square arrangement of four Cu^{II} ions. Furthermore, Cu1 and Cu4 are connected by μ-methoxo O15. The coordination environments, which includes ligation atoms, bond distances from copper(II), and angles subtended at copper(II) centers, are listed in Table 1S. As can be seen, Cu1, Cu2, and Cu3 have a square-pyramidal geometry, whereas Cu4 have an octahedral geometry. As mentioned above, selection of coordinating atom at the bridging group is peculiar to sulfinylcalix[4]arene among sulfur-bridged calix[4]arenes. Complex **1** shows that the sulfur atoms (S2 and S4) of the sulfinyl groups that are equatorial with respect to an axis passing through the center of $\mathbf{L}^{rtct4-}$ coordinate to the copper(II) ion and oxygen atoms (O2 and O6) of the sulfinyl groups that are axial coordinate to copper(II). It is reasonable to think that this coordination manner is brought about to facilitate O,X,O facial coordination with a suitable Cu–X bond length, where X represents the donor atom from the bridging group. In summary, copper(II) center seemingly requires O,X,O coordination from $\mathbf{L}^{rtct4-}$ to cause the two adjacent phenols to align in a *syn* rather than an *anti* fashion, resulting in cone conformation of $\mathbf{L}^{rtct4-}$, which can accommodate four copper(II) centers on one side of S_4 plane. Since the S=O configuration with respect to the S_4 plane is not dependent on the calix[4]-arene conformation, determined by the rotation of phenyl rings along the axis connecting bridging sulfur atoms, selection of X between S and O is solely determined by the ability of $\mathbf{L}^{rtct4-}$ to provide the Cu^{II} ion an O,X,O *fac* coordination environment, not the preference of Cu^{II} ion to the donor atoms. In fact, not only the soft sulfur atom but also hard oxygen donor atom of from sulfinyl groups have been shown to coordinate to a soft Pd^{II} ion in [Pd^{II}$_2$(H$_3$$\mathbf{L}^{rtct}$)$_2$(H$_2$$\mathbf{L}^{rtct}$)],[20] which supports that the selection between S and O is not governed by the metal-donor affinity but by stereochemistry.

[Cu^{II}$_4$($\mathbf{L}^{rccc}$)(OAc)$_3$(μ-OH)] (2).   Having all S=O groups directed *cis* with respect to a reference S=O group, H$_4$$\mathbf{L}^{rccc}$ can arranged into two cone-shaped isomers with C_{4v} symmetry by ring inversion (Scheme 4). On the basis of spectroscopic evidence, the structure of H$_4$$\mathbf{L}^{rccc}$ in solution has been tentatively assigned to the one depicted in Scheme 4a, because of hydrogen bonding between OH groups and sulfinyl oxygens.[21b] In tetracopper(II) complex **2** (Fig. 2), $\mathbf{L}^{rccc4-}$ adopts a cone conformation to provide four O,O,O *fac*-tridentate coordination environments to the Cu^{II}$_4$ core. The cavity of $\mathbf{L}^{rccc4-}$ is large enough to include one acetonitrile molecule.

Table 1.   Interplanar Dihedral Angles (°) of H$_{4-n}$$\mathbf{L}^{n-}$ in Complexes **1–4**[a]

| | **1** | **2** | **3** | **4** (H$_2$$\mathbf{L}^{rctt2-}$) | | H$_4$tca[c] |
	($\mathbf{L}^{rtct4-}$)	($\mathbf{L}^{rccc4-}$)	($\mathbf{L}^{rctt4-}$)	upper	lower[b]	
A/C	71.75	77.22	43.65	82.88	86.28	74.4
B/D	64.58	42.89	92.19	54.54	59.84	
S_4/A	57.94	52.98	70.72	45.90	40.56	58.8[d]
S_4/B	55.06	69.87	42.94	56.32	52.18	
S_4/C	50.33	49.86	65.69	51.36	53.43	
S_4/D	60.36	67.28	49.30	69.14	68.00	

a) A–D denotes aromatic planes as shown in Figures 1b–3b and 5b. S_4 denotes average plane of four sulfur atoms in H$_{4-n}$$\mathbf{L}^{n-}$. b) In this row, A should read E, B should read F, and so on. c) *p*-*tert*-Butylthiacalix[4]arene including one CHCl$_3$ molecule having exact C_4 symmetry. Cited from Ref. 23. d) Instead of S_4 plane, average plane of four phenol oxygen is used. Ref. 23.

Scheme 4. Ring inversion of H_4L^{rccc} between cone-shaped isomers having (a) axial and (b) equatorial sulfinyl oxygen. Double bonds and *tert*-butyl groups are omitted for clarity.
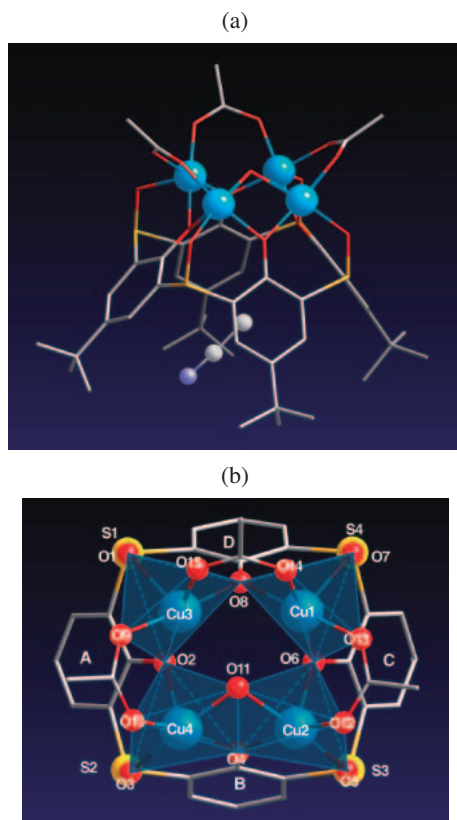
(a)

(b)

Fig. 2. Crystal structure of $[Cu^{II}_4(L^{rccc})(OAc)_3(\mu\text{-}OH)]$ (**2**). (a) Side view and (b) top view showing the copper(II) coordination polyhedra. *tert*-Butyl groups are omitted in (b).

Judging from the angles between phenyl rings and S_4 plane (Table 1), the conformation is not an ideal cone but intermediate between cone and pinched cone, the latter of which is defined by an acute inter-planar angle between a pair of distal phenyl rings. The complex does not have C_4 symmetry because of the conformation of L^{rccc4-} as well as the additional ligands (three acetates and $\mu\text{-}OH^-$) attached to the upper side of the Cu^{II}_4 core; however, it apparently has a pseudo-mirror plane containing O15, O8, and O6 atoms to divide the complex into two sides (Fig. 2b).

As can be seen in Fig. 2b (and also from Table 2S), all four copper(II) ions have a square-pyramidal coordination geometry. There are two kinds of coordination environments: Cu1 and Cu3 have four basal oxygen atoms from two phenols and two acetates and one axial oxygen from sulfinyl group, and Cu2 and Cu4 have four basal oxygen atoms from phenol,
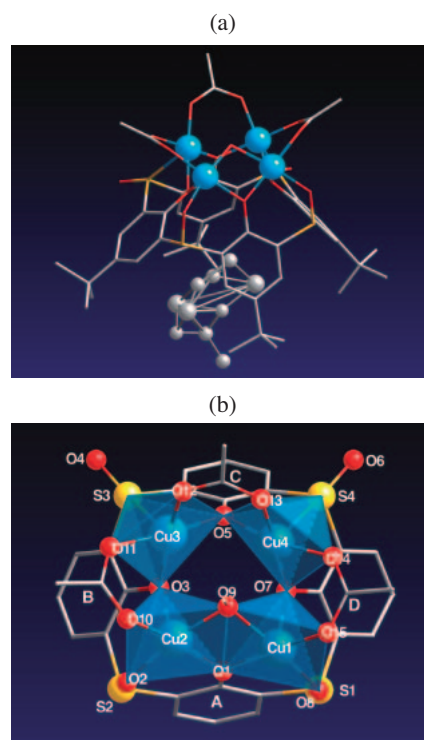
(a)

(b)

Fig. 3. Crystal structure of $[Cu^{II}_4(L^{rctt})(OAc)_3(\mu\text{-}OH)]$ (**3**). (a) Side view and (b) top view showing the copper(II) coordination polyhedra. *tert*-Butyl groups are omitted in (b).

sulfinyl, acetate and $\mu\text{-}OH^-$ and one axial oxygen from phenol moiety. It has been reported that thiacalix[4]arene (H_4tca) formed a tetracopper(II) complex, $[Cu^{II}_4(tca)_2]$, in which tca^{4-} adopts a cone conformation to provide O,S,O *fac*-tridentate donor sets.[9] Considering another stereoisomer of L^{rccc4-}, depicted as Scheme 4b, which also has sulfur bridges flanked by two phenol units, one can expect that L^{rccc4-} will coordinate via O,S,O to the Cu^{II} ions like tca^{4-} does in $[Cu^{II}_4(tca)_2]$. However, L^{rccc4-} coordinated via O,O,O sets, instead of O,S,O. This suggests that oxygen on a sulfinyl group has higher coordination ability than the sulfinyl S does, which can be attributed to a resonance effect[24] between the phenol O^- and the sulfinyl group at the *ortho* position that delocalize the anionic charge on the sulfinyl oxygen.

$[Cu^{II}_4(L^{rctt})(OAc)_3(\mu\text{-}OH)]$ (**3**). Sulfinylcalix[4]arene H_4L^{rctt} is distinguished from H_4L^{rccc} by its two adjoining S=O groups that are equatorial, while the two remaining S=O groups are axial (Scheme 2). From discussion above, L^{rccc4-} can in principle facilitate both O,O,O and O,S,O coordination fashion, which in fact can be seen in tetracopper(II) complex **3** (Fig. 3, Table 3S). However, complex **3** has many features common to complex **2**. First, L^{rctt4-} acts as a tetrakis *fac*-tridentate ligand for Cu^{II}_4 core. Second, the upper side of the Cu^{II}_4 core is coordinated by three acetates and one $\mu\text{-}OH^-$. Third, L^{rctt4-} adopts a conformation intermediate between a cone and a pinched-cone conformation (see Table 1) including one solvent molecule (disordered as a superimposition of $0.5CH_2Cl_2$ and $0.5AcOEt$ molecules shown as gray spheres in Fig. 3a). Fourth, it has a pseudo-mirror plane containing O1, O5, and O9. Fifth, all of the copper(II) ions have
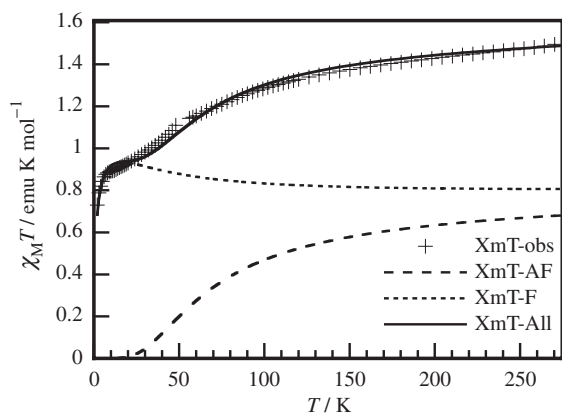
Fig. 4.   Temperature dependence of the product of the molar magnetic susceptibility (χ_M) and temperature (T) for complex **3**. The solid line (annotated as "All") is the theoretical curve, which consists of ferromagnetic (F, dotted line) and antiferromagnetic (AF, broken line) parts. The best-fit parameters; $g = 2.0$ (fixed), $J_1 = -43(1)\,\mathrm{cm}^{-1}$, $J_2 = 17(2)\,\mathrm{cm}^{-1}$, $\theta = -0.9(1)\,\mathrm{K}$.

a square-pyramidal coordination geometry. Therefore, it is reasonable to think that, because of the similarity between **2** and **3**, the selection between S and O of the sulfinyl group for coordination is predominantly determined by the bond length between X and a Cu^{II} ion to afford O,X,O *fac*-coordination.

Interactions between copper(II) ions in complex **3** were investigated by measuring the dc-magnetic susceptibilities in the range of 2–300 K. The $\chi_M T$ versus T plot showed a continuous decrease in $\chi_M T$ as the temperature decreased (Fig. 4). Since each copper(II) ion has a square-pyramidal coordination environment, each magnetic orbital, i.e., $d_{x^2-y^2}$, lies in the basal plane. Accordingly, the temperature dependence was analyzed on the basis of the Hamiltonian:[25]

$$\boldsymbol{H} = -2J_1 S_{\mathrm{Cu1}} \cdot S_{\mathrm{Cu2}} - 2J_2 S_{\mathrm{Cu3}} \cdot S_{\mathrm{Cu4}}, \qquad (1)$$

where J_1 denotes the interaction between Cu1 and Cu2 and J_2 is for Cu3 and Cu4.[26] The best-fit parameters were obtained by summing the weak antiferro- and ferromagnetic interactions with J values of $-43(1)$ and $17(2)\,\mathrm{cm}^{-1}$, respectively (Fig. 4). In general, a dicopper(II) core having a μ-phenoxo/μ-hydroxo double bridge shows strong antiferromagnetic interaction. For instance, dicopper(II) complexes with 2,6-di(iminomethyl)phenol and μ-hydroxo ligands, in which Cu–O$_{\mathrm{phenoxo}}$–Cu and Cu–O$_{\mathrm{hydroxo}}$–Cu angles are 98 and 99–101°, respectively, show strong antiferromagnetic exchange with $-J$ values of several hundred wavenumbers.[27] The structural resemblance in the coordination geometry of these to that of the Cu1–Cu2 core in complex **3** (having Cu–O$_{\mathrm{phenoxo}}$–Cu $= 98.04°$ and Cu–O$_{\mathrm{hydroxo}}$–Cu $= 99.08°$) suggests that an antiferromagnetic interaction operates between the two Cu^{II} ions and $J_1 = -43(1)\,\mathrm{cm}^{-1}$. Accordingly, a ferromagnetic interaction occurs between Cu3 and Cu4 with $J_2 = 17(2)\,\mathrm{cm}^{-1}$. This is different from the general trend normally observed for dicopper(II) cores bridged with μ-phenoxo ligand, that is, μ-phenoxo-bridged dicopper(II) core with bridging angle larger than 99° exhibit strong antiferromagnetic interactions with $2J$ value of several hundred wavenumbers,[28] and Cu–O$_{\mathrm{phenoxo}}$–
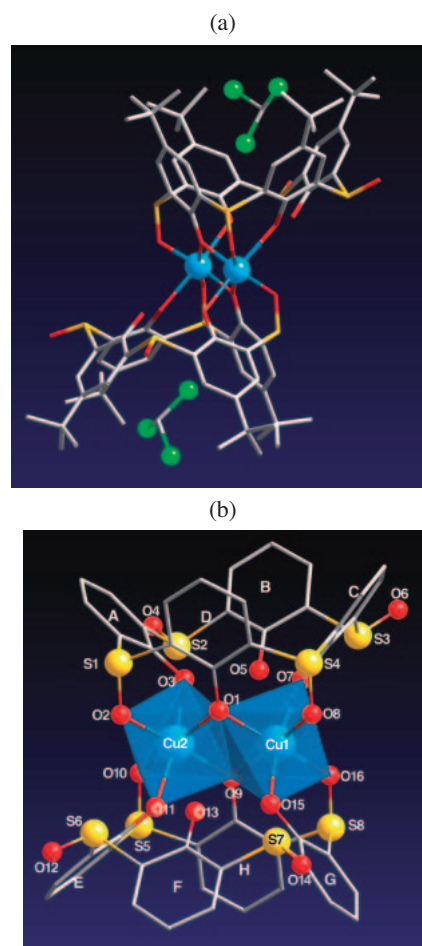

Fig. 5.   Crystal structure of [Cu$^{II}_2$(H$_2$**L**^{rtt})$_2$] (**4**). (a) Side view and (b) top view showing the copper(II) coordination polyhedra. *tert*-Butyl groups are omitted in (b).

Cu $= 102.8°$ in complex **3**. The ferromagnetic coupling between Cu3–Cu4 may be attributed to a small or negligible overlap between each $d_{x^2-y^2}$, because the basal plane involving the Cu3 and Cu4 centers are not co-planar with an interplanar angle of 114.85°.

[Cu$^{II}_2$(H$_2$L^{rtt})$_2$] (4).   Using [Cu^{II}(acac)$_2$] in place of Cu^{II}(OAc)$_2$ as a copper(II) source, the reaction with H$_4$**L**^{rtt} unexpectedly resulted in a 2:2-type complex, [Cu$^{II}_2$(H$_2$**L**^{rtt})$_2$] (**4**) (Fig. 5), rather than a 1:4-type complex, like **3**. Even a large excess of [Cu^{II}(acac)$_2$] was used. It should be noted that in contrast to tetracopper(II) complexes **1**–**3**, acac$^-$ is not found in complex **4** as an additional ligand, indicating that the ability of acac$^-$ to bridge copper(II) cores is rather low. In other words, a suitable bridging ligand, such as acetate, is essential to stabilize Cu$^{II}_4$ core as exemplified in complexes **1**–**3**. In this sense, one H$_2$**L**$^{rtt2-}$ in **4** can be regarded as a bridging ligand for the dicopper(II) core, but cannot bridge tetracopper(II) core in [Cu$^{II}_4$(**L**^{rtt})]$^{4+}$. The complex has pseudo C_{2h} symmetry, the axis of which passes through two copper(II) centers and the pseudo symmetry plane contains O1, O5, O9, and O13. Each H$_2$**L**$^{rtt2-}$ adopts a cone conformation to act as a bis O,O,O-*fac*-tridentate ligand to copper(II) centers as well as to include a CHCl$_3$ molecule. Comparison of the interplanar angles in Table 1 indicates that the conformation of H$_2$**L**$^{rtt2-}$ slightly

Table 2. Crystallographic Data and Structural Refinement for Complexes **1–4**

	1·3CHCl₃	**2·2CH₃CN·2H₂O**	**3·0.5CH₂Cl₂·1.5AcOEt**	**4·6CHCl₃**
Empirical formula	$C_{51}H_{63}Cl_9Cu_4O_{16}S_4$	$C_{50}H_{64}Cu_4N_2O_{17}S_4$	$C_{52.5}H_{67}ClCu_4O_{18}S_4$	$C_{86}H_{98}Cl_{18}Cu_2O_{16}S_8$
Formula weight	1633.46	1347.43	1403.91	2409.30
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$C2/c$	$P2_1/c$
$a/\text{Å}$	11.050(2)	11.189(5)	47.042(6)	22.5229(14)
$b/\text{Å}$	17.543(4)	46.81(2)	15.0532(19)	24.4488(15)
$c/\text{Å}$	18.063(4)	11.523(5)	17.264(2)	22.5927(15)
$\alpha/°$	82.112(5)	90	90	90
$\beta/°$	73.418(5)	102.580(8)	102.349(3)	116.168(2)
$\gamma/°$	85.745(5)	90	90	90
$V/\text{Å}^3$	3322.1(12)	5891(5)	11943(3)	11165.7(12)
Z	2	4	8	4
Crystal size/mm³	$0.1 \times 0.18 \times 0.25$	$0.02 \times 0.2 \times 0.3$	$0.35 \times 0.3 \times 0.08$	$0.15 \times 0.2 \times 0.38$
$F(000)$	1660	2776	5784	4936
T/K	223(2)	293(2)	200(2)	293(2)
$\rho_{calc}/\text{g cm}^{-3}$	1.633	1.519	1.562	1.433
Reflections collected	34104	20770	49418	96771
Independent reflections	15289 [$R_{int} = 0.0440$]	8052 [$R_{int} = 0.0664$]	16995 [$R_{int} = 0.0296$]	25680 [$R_{int} = 0.0684$]
$\mu(\text{Mo K}\alpha)/\text{mm}^{-1}$	1.812	1.633	1.658	1.017
Data/restraints/parameters	15289/0/802	8052/0/715	16995/0/850	25671/0/1258
R_1, wR_2 ($I > 2\sigma(I)$)	0.0478, 0.1048	0.1097, 0.2768	0.0371, 0.0978	0.0774, 0.2055
R_1, wR_2 (all data)	0.0948, 0.1150	0.1540, 0.2650	0.0554, 0.1018	0.1382, 0.2373
Goodness-of-fit on F^2	0.887	1.448	0.939	0.960
Largest diff. peak and hole/eÅ⁻³	0.923 and −0.709	3.569 and −1.046	0.803 and −0.511	2.479 and −1.230

deviates from ideal cone to pinched cone. Each copper core is in a typical distorted octahedral coordination geometry with an elongated axis (Fig. 5b and Table 4S). For example, Cu1 has four basal oxygens from two phenoxo O1, O9 and two sulfinyl O8, O16 and two axial oxygens from two phenoxo O7, O15. Bond distances and angles describing the coordination environment for copper(II) center (Table 4S) show that Cu1 and Cu2 are in an almost identical environments.

Magnetic susceptibility for complex **4** was too small to be measured, suggesting that antiferromagnetic coupling operates between copper(II) centers. This can be rationalized by the large Cu–O–Cu angles (99.83 and 100.23°) involving bridging phenoxo O1 and O9, respectively. The ¹H NMR spectrum of **4** was aquired in CDCl₃ and showed a noisy baseline and high δ values for the ArH signal (Fig. 1S), suggesting that complex is slightly paramagnetic and/or that part of complex **4** dissociates in the CDCl₃ solution to give a paramagnetic copper(II) species. The *tert*-butyl moiety showed three singlet peaks with a 1:2:1 intensity, meaning that complex **4** has genuine C_{2h} symmetry in solution.

Conclusion

In conclusion, sulfinylcalix[4]arenes with *rtct*, *rccc*, and *rctt* configurations reacted with Cuᴵᴵ(OAc)₂ to form tetracopper(II) cluster complexes with tetrakis O,X,O-*fac*-tridentate coordination, which was realized by adopting cone-type conformation to assemble all phenoxo O⁻ to one side of calix[4]arene ring. The selection of ligating atom X between O and S of the sulfinyl moiety simply depends on the stereochemistry; if sulfinyl group is in axial direction, then O coordinates. If equatorial, S does. The formation of dicopper(II) complex by reacting H₄**L**ʳᶜᵗᵗ with [Cuᴵᴵ(acac)₂] suggests that the ability of the aux-

iliary ligand to bridge copper(II) ions plays a significant role in assembling the cores. In other words, the clustering ability of H₄**L**ʳᶜᵗᵗ can be controlled by choosing metal ion source. In addition to studying the effect of auxiliary ligand, controlling the complex structure of the stereoisomers of sulfinylcalix[4]-arene by using a metal ion having extremely hard or soft character to select O or S at the sulfinyl moiety is one of next challenges.

Experimental

Synthesis of Copper(II) Complex with H₄Lʳᶜᶜᵗ. A mixture of H₄**L**ʳᶜᶜᵗ (50.0 mg, 6.37×10^{-5} mol) in CHCl₃ (10 mL) and Cu(OAc)₂·H₂O (52.0 mg, 2.55×10^{-4} mol) in EtOH (10 mL) was heated at reflux for 6 h and evaporated to dryness, and the residue was washed with EtOH. After dissolving the solid residue in a small amount of CHCl₃, the undissolved residue was filtered off. Small pale-yellow crystals were obtained by vapor diffusion of hexane into the solution; X-ray analysis was not successful. Mp > 350 °C (decomp.).

Synthesis of Complex 1. A mixture of H₄**L**ʳᶜᵗ (50.1 mg, 6.37×10^{-5} mol) in CHCl₃ (10 mL) and Cu(OAc)₂·H₂O (52.0 mg, 2.55×10^{-4} mol) in EtOH (10 mL) was heated at reflux for 6 h and then evaporated to dryness, and the residue was washed with EtOH. After dissolving the solid residue in CHCl₃, the undissolved residue was filtered off. The CHCl₃ solution was concen-

trated by evaporation, into which methanol vapor was slowly diffused to afford brownish single crystals of the complex (37.5 mg, 36% yield). Mp > 350 °C (decomp.); IR (KBr) 2962, 1566, 1481, 1446, 1261, 1053, 1000 cm^{-1}. Anal. Calcd for $C_{48}H_{60}Cu_4O_{16}S_4$: C, 45.20; H, 4.74%. Found: C, 44.82; H, 4.58%.

Synthesis of Complex 2. A mixture of H_4L^{rccc} (50.1 mg, 6.37×10^{-5} mol) in CHCl$_3$ (10 mL) and of Cu(OAc)$_2 \cdot$H$_2$O (52.0 mg, 2.55×10^{-4} mol) in MeOH (10 mL) was heated at reflux for 6 h and then evaporated to dryness, and the residue was washed with MeOH. After dissolving into CHCl$_3$ (10 mL), the undissolved impurities were filtered off. Evaporation of the filtrate to dryness afforded a green powder of the complex. Single crystals were obtained by slow diffusion of MeCN into a 1,2-dichloroethane solution of the complex (24.9 mg, 29% yield). Mp > 350 °C (decomp.), IR (KBr) 3425, 2959, 1578, 1485, 1447, 1265, 1022, 991 cm^{-1}. Anal. Calcd for $C_{46}H_{54}Cu_4O_{15}S_4$: C, 44.94; H, 4.43%. Found: C, 44.62; H, 4.56%.

Synthesis of Complex 3. A mixture of H_4L^{rctt} (50.1 mg, 6.37×10^{-5} mol) in CHCl$_3$ (10 mL) and Cu(OAc)$_2 \cdot$H$_2$O (52.0 mg, 2.55×10^{-4} mol) in EtOH (10 mL) was heated at reflux for 6 h and then evaporated to dryness, and the residue was washed with EtOH. After dissolving the solid into CHCl$_3$ (10 mL), the undissolved impurities were filtered off. Evaporation of the filtrate afforded a brown powder of the complex. Single crystals were obtained by slow diffusion of MeOH into a CHCl$_3$ solution of the complex (16.1 mg, 18% yield). Mp > 320 °C (decomp.); IR (KBr) 3441, 2959, 1562, 1477, 1447, 1265, 1049, 988 cm^{-1}. Anal. Calcd for $C_{46}H_{54}Cu_4O_{15}S_4$: C, 44.94; H, 4.43%. Found. C, 44.72; H, 4.67%.

Synthesis of Complex 4. A mixture of H_4L^{rctt} (50.0 mg, 6.37×10^{-5} mol) and [Cu^{II}(acac)$_2$] (100.0 mg, 3.82×10^{-4} mol) in CH$_2$Cl$_2$ (20 mL) was heated at reflux for 24 h and then evaporated to dryness, and the residue was washed with benzene and acetone to afford a greenish-white powder of the complex. Single crystals were obtained by slow diffusion MeOH into a CHCl$_3$ solution of the complex (23.0 mg, 15% yield). IR (KBr) 2963, 1481, 1443, 1265, 1042, 1003 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.77 (18H, s, Bu^t), 1.24 (36H, s, Bu^t), 1.88 (18H, s, Bu^t), 6.77 (4H, br, ArH), 8.90 (4H, s, ArH), 9.36 (4H, s, ArH), 11.13 (4H, br, ArH). Anal. Calcd for $C_{80}H_{92}Cu_2O_{16}S_8 \cdot 1.5H_2O$: C, 55.86; H, 5.56%. Found: C, 55.50; H, 5.48%.

X-ray Crystallography. Data for all of the compounds were collected on a Bruker SMART CCD diffractometer employing graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data integration and reduction were undertaken with SAINT and XPREP.[29] The structures were solved by the direct method using SHELXS-97[30] and refined using least-squares methods on F^2 with SHELXL-97.[31] Non-hydrogen atoms were modeled with anisotropic displacement parameters, and hydrogen atoms were placed by the differential Fourier syntheses and refined isotropically (Table 2). Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-606249 to 606252 for compounds **1** to **4**, respectively. Copies of the data can be obtained free of charge via http://www.ccdc. cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting Information

Coordination environments of Cu^{II} core in complexes **1–4** (Tables 1S–4S, respectively) and ^{1}H NMR spectra for complex **4** in CDCl$_3$ (Fig. 1S). This material is available on the web at http://www.csj.jp/journals/bcsj/.

References

1   a) *Calixarenes for Separations, ACS Symposium Series 757*, ed. by G. J. Lumetta, R. D. Rogers, A. S. Gopalan, American Chemical Society, Washington DC, **2000**. b) *Calixarenes in Action*, ed. by L. Mandolini, R. Ungaro, Imperial College Press, London, **2000**. c) R. Ludwig, *Fresenius' J. Anal. Chem.* **2001**, *367*, 103.

2   a) N. Iki, S. Miyano, *Nippon Kagaku Kaishi* **2001**, 609; *Chem. Abstr.* **2001**, *136*, 216664. b) N. Iki, S. Miyano, *J. Inclusion Phenom. Macrocyclic Chem.* **2001**, *41*, 99. c) N. Morohashi, N. Iki, S. Miyano, *J. Synth. Org. Chem. Jpn.* **2002**, *60*, 550. d) M. W. Hosseini, in *Calixarenes 2001*, ed. by M. Asfari, V. Böhmer, J. Harrowfield, J. Vicens, Kluwer Academic Publishers, Dordrecht, **2001**. e) P. Lhoták, *Eur. J. Org. Chem.* **2004**, 1675. f) N. Morohashi, F. Narumi, N. Iki, T. Hattori, S. Miyano, *Chem. Rev.* **2006**, *106*, 5291.

3   a) H. Kumagai, M. Hasegawa, S. Miyanari, Y. Sugawa, Y. Sato, T. Hori, S. Ueda, H. Kamiyama, S. Miyano, *Tetrahedron Lett.* **1997**, *38*, 3971. b) N. Iki, C. Kabuto, T. Fukushima, H. Kumagai, H. Takeya, S. Miyanari, T. Miyashi, S. Miyano, *Tetrahedron* **2000**, *56*, 1437.

4   a) R. G. Pearson, *J. Am. Chem. Soc.* **1963**, *85*, 3533. b) R. G. Pearson, *J. Chem. Educ.* **1968**, *45*, 581.

5   N. Iki, N. Morohashi, F. Narumi, S. Miyano, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1597.

6   a) N. Iki, H. Kumagai, N. Morohashi, K. Ejima, M. Hasegawa, S. Miyanari, S. Miyano, *Tetrahedron Lett.* **1998**, *39*, 7559. b) N. Morohashi, N. Iki, A. Sugawara, S. Miyano, *Tetrahedron* **2001**, *57*, 5557.

7   T. Kajiwara, N. Iki, M. Yamashita, *Coord. Chem. Rev.*, in press.

8   N. Iki, N. Morohashi, C. Kabuto, S. Miyano, *Chem. Lett.* **1999**, 219.

9   G. Mislin, E. Graf, M. W. Hosseini, A. Bilyk, A. K. Hall, J. M. Harrowfield, B. W. Skelton, A. H. White, *Chem. Commun.* **1999**, 373.

10   A. Bilyk, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, G. Mislin, B. W. Skelton, C. Taylor, A. H. White, *Eur. J. Inorg. Chem.* **2000**, 823.

11   H. Akdas, E. Graf, M. W. Hosseini, A. De Cian, A. Bilyk, B. W. Skelton, G. A. Koutsantonis, I. Murray, J. M. Harrowfield, A. H. White, *Chem. Commun.* **2002**, 1042.

12   C. Desroches, G. Pilet, P. Á. Szilágyi, G. Molnár, S. A. Borshch, A. Bousseksou, S. Parola, D. Luneau, *Eur. J. Inorg. Chem.* **2006**, 357.

13   C. Desroches, G. Pilet, S. A. Borshch, S. Parola, D. Luneau, *Inorg. Chem.* **2005**, *44*, 9112.

14   A. Bilyk, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, B. W. Skelton, A. H. White, *Aust. J. Chem.* **2000**, *53*, 895.

15   a) T. Kajiwara, N. Kon, S. Yokozawa, T. Ito, N. Iki, S. Miyano, *J. Am. Chem. Soc.* **2002**, *124*, 11274. b) T. Kajiwara, R. Shinagawa, T. Ito, N. Kon, N. Iki, S. Miyano, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 2267.

16   T. Kajiwara, H. Wu, T. Ito, N. Iki, S. Miyano, *Angew.*

Chem., Int. Ed. **2004**, *43*, 1832.

17   T. Kajiwara, T. Kobashi, R. Shinagawa, T. Ito, S. Takaishi, M. Yamashita, N. Iki, *Eur. J. Inorg. Chem.* **2006**, 1765.

18   T. Kajiwara, K. Katagiri, M. Hasegawa, A. Ishii, M. Ferbinteanu, S. Takaishi, T. Ito, M. Yamashita, N. Iki, *Inorg. Chem.* **2006**, *45*, 4880.

19   T. Kajiwara, K. Katagiri, S. Takaishi, M. Yamashita, N. Iki, *Chem. Asian J.* **2006**, *1*, 349.

20   N. Morohashi, N. Iki, S. Miyano, T. Kajiwara, T. Ito, *Chem. Lett.* **2001**, 66.

21   a) N. Morohashi, N. Iki, C. Kabuto, S. Miyano, *Tetrahedron Lett.* **2000**, *41*, 2933. b) N. Morohashi, H. Katagiri, N. Iki, Y. Yamane, C. Kabuto, T. Hattori, S. Miyano, *J. Org. Chem.* **2003**, *68*, 2324.

22   G. Mislin, E. Graf, M. W. Hosseini, A. D. Cian, J. Fisher, *Tetrahedron Lett.* **1999**, *40*, 1129.

23   A. Bilyk, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, B. W. Skelton, A. H. White, *Inorg. Chem.* **2001**, *40*, 672.

24   S. Oae, M. Yoshihara, W. Tagaki, *Bull. Chem. Soc. Jpn.* **1967**, *40*, 951.

25   O. Kahn, *Molecular Magnetism*, VCH Publishers, Weinheim, **1993**.

26   In the analysis, weak interaction between dicopper(II) cores, Cu1–Cu2 and Cu3–Cu4, was treated with the Weiss constant θ.

27   a) N. A. Bailey, D. E. Fenton, J. Lay, P. B. Roberts, J.-M. Latour, D. Limosin, *J. Chem. Soc., Dalton Trans.* **1986**, 2681. b) P. Guerriero, U. Casellato, D. Ajo, S. Sitran, P. A. Vigato, R. Graziani, *Inorg. Chim. Acta* **1988**, *142*, 305.

28   L. K. Thompson, S. K. Mandal, S. S. Tandon, J. N. Bridson, M. K. Park, *Inorg. Chem.* **1996**, *35*, 3117.

29   *SMART, SAINT, and XPREP, Area Detector Control and Data Integration and Reduction Software*, Bruker Analytical X-ray Instruments Inc., Madison, WI, **1995**.

30   G. M. Sheldrick, SADABS, Empirical Absorption Correction Program for Area Detector Data, University of Göttingen, Germany, **1996**.

31   G. M. Sheldrick, *SHELX97, Programs for Crystal Structure Analysis*, University of Göttingen, Germany, **1998**.