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Copper(II) Clusters of Two Pairs of 2,3-Dihydroxybutanedioyl Dihydrazones: Synthesis, Structure, and Magnetic Properties

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Condensation reactions of (2*R*,3*R*)- and (2*S*,3*S*)-2,3-dihydroxybutanedihydrazide with salicylaldehyde and 3-methoxysalicylaldehyde gave two enantiomeric pairs, (2*R*,3*R*)/(2*S*,3*S*)-2,3-dihydroxybutanedioylbis(salicylaldehydehydrazone) [(2*R*,3*R*)-BSH and (2*S*,3*S*)-BSH] and (2*R*,3*R*)/(2*S*,3*S*)-2,3-dihydroxybutanedioyl bis(3-methoxysalicylaldehydehydrazone) [(2*R*,3*R*)-MBSH and (2*S*,3*S*)-MBSH]. Their reactions with Cu^{II} salts provided two chiral hexanuclear clusters $[Cu_6L_2(C_5H_5N)_{10}]_2[C_5H_6N]_3(ClO_4)_7\cdot(CH_3OH)\cdot(C_5H_5N)$ [L = (2*R*,3*R*)-BSH; (2*S*,3*S*)-BSH] and four chiral tridecanuclear clusters $[Cu_{13}L_3(OH)_2(CH_3COO)_6(C_5H_5N)_6(DMF)_3]\cdot6DMF\cdot3H_2O$ [L = (2*R*,3*R*)-BSH; (2*S*,3*S*)-BSH] and $[Cu_{13}X_3(OH)_2(CH_3COO)_6(C_5H_5N)_2(DMF)_8]\cdot6H_2O$ [X = (2*R*,3*R*)-MBSH, (2*S*,3*S*)-MBSH]. Their structures were determined by single-crystal X-ray diffraction analysis. All six compounds are enantiomers of each other. The two hexanuclear clusters exhibit two orthogonal linear trinuclear units. The two pairs of tridecanuclear clusters display esthetic structures with different symmetries; they feature rare heptanuclear vertex-sharing dicubane cores and their six unshared Cu^{II} vertexes are linked to another six Cu^{II} ions. These represent the first examples of chiral clusters bearing dicubane cores. Magnetic studies revealed the presence of overall antiferromagnetic interactions in these compounds.

Introduction

The development of multifunctional materials in which compounds combine different physical properties and functions is appealing, and as such, chiral magnets have received significant attention in recent years owing to the potential synergy between structural chirality and magnetic properties in these compounds and the thus-derived novel functionalities.[1] As demonstrated in recent studies, the introduction of chirality into magnetic systems can result in interesting properties such as magneto-optical properties, ferroelectricity, and magnetochiral dichroism, all as a result of the asymmetric dipole moment.[1a,2] A few examples in which chirality was introduced in special magnetic materials such as single-molecular magnets have been successful.[3] The chirality in these chiral magnets can be induced by chiral linkers[4] as well as by achiral linkers through spontaneous resolution with or without the aid of a chirality-inducing agent.[3a,3c,5] However, most studies in this field are centered around 1D to 3D compounds,[2b,6] and discrete chiral magnetic clusters are much less reported.[3a,3b,7] Thus, we took on the challenge to develop more chiral magnetic clusters by using new chiral ligands with the aim of exploring esthetic cluster structures and their magnetic properties.

As is well known, magnetic cubane clusters have drawn significant interest in the last years for their interesting structures and their special magnetic properties. A few groups have reported some homometallic and heterometallic cubane clusters with special magnetic properties, including single-molecular magnets.[8] However, most of these studies revolve around single cubane structures and defective dicubane structures;[9] perfect dicubanes such as vertex-sharing dicubanes, face-sharing dicubanes, and edge-sharing dicubanes are much less reported.[10] To the best of our knowledge, there are only a few compounds possessing the vertex-shared dicubane core, the magnetochemical properties of which have been fully elucidated.[11] On the other hand, only a few reports pertain to chiral paramagnetic transition-metal clusters containing cubane structures.[4b,7a,12] The introduction of chirality into dicubane structures has never been documented. The selection of linking atoms is of great importance in controlling the structures and properties of dicubanes. In this study, we used alkoxo O atoms as linking atoms to consolidate metal ions to form cubane structures that show magnetic interactions. To achieve the targeted aim of obtaining discrete polynuclear compounds, we used phenyl groups to control the growth of the dimensionalities.

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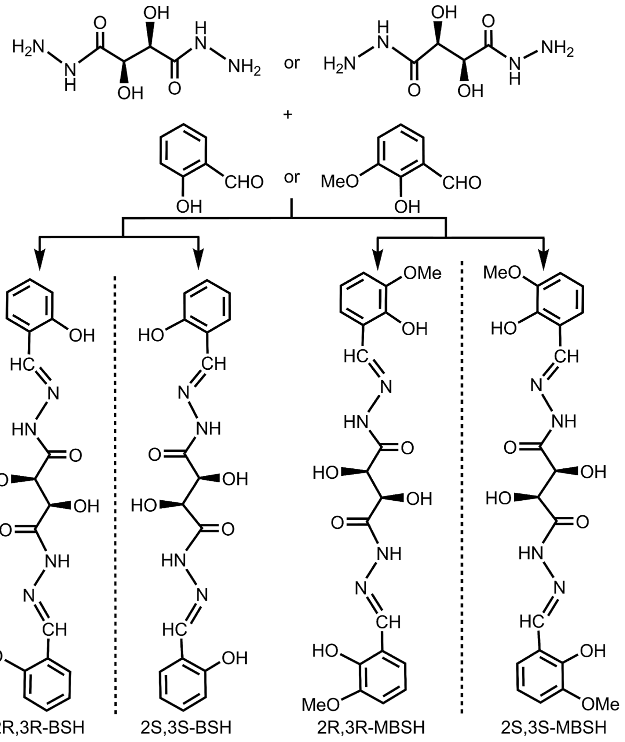
On the basis of the above considerations, we prepared two pairs of multifunctional chiral ligands and separated two chiral hexanuclear clusters and four chiral tridecanuclear clusters. The four tridecanuclear clusters feature rare heptanuclear vertex-sharing dicubane cores. They represent the first examples in which chirality is introduced into dicubanes.

Results and Discussion

Synthesis and Characterization

(2*R*,3*R*)/(2*S*,3*S*)-2,3-Dihydroxybutanedihydrazide were prepared from the reactions of diethyl (2*R*,3*R*)/(2*S*,3*S*)-2,3-dihydroxybutanedioate with hydrazine hydrate following a procedure described in the Supporting Information. Their respective reactions with salicylaldehyde and 3-methoxysalicylaldehyde gave two enantiomeric pairs (2*R*,3*R*)/(2*S*,3*S*)-2,3-dihydroxybutanedioylbis(salicylidenehydrazone) [(2*R*,3*R*)-BSH and (2*S*,3*S*)-BSH] and (2*R*,3*R*)/(2*S*,3*S*)-2,3-dihydroxybutanedioylbis(3-methoxysalicylidenehydrazone) [(2*R*,3*R*)-MBSH and (2*S*,3*S*)-MBSH] as shown in Scheme 1. Details of their synthesis and characterization can be found in the Supporting Information. Reactions of Cu^{II} salts with these chiral ligands by using similar traditional solution methods gave two chiral hexanuclear clusters $[Cu_6L_2(C_5H_5N)_{10}]_2[C_5H_6N]_3(ClO_4)_7\cdot(CH_3OH)\cdot(C_5H_5N)$ [L = (2*R*,3*R*)-BSH, **1**; (2*S*,3*S*)-BSH, **2**] and four chiral tridecanuclear clusters $[Cu_{13}L_3(OH)_2(CH_3COO)_6(C_5H_5N)_6(DMF)_3]\cdot 6DMF\cdot 3H_2O$ [L = (2*R*,3*R*)-BSH, **3**; (2*S*,3*S*)-BSH, **4**] and $[Cu_{13}X_3(OH)_2(CH_3COO)_6(C_5H_5N)_2(DMF)_8]\cdot 6H_2O$ [X = (2*R*,3*R*)-MBSH, **5**; (2*S*,3*S*)-MBSH, **6**]. Compounds **1** and **2** were separated from the mixtures by using $Cu(ClO_4)_2\cdot 6H_2O$ as the Cu^{II} salt. However, replacement of $Cu(ClO_4)_2\cdot 6H_2O$ by $[Cu_2(OAc)_4(H_2O)_2]$ in these reactions produced discrete tridecanuclear clusters **3**–**6**. Clearly, the anions of the Cu^{II} salts contribute significantly to the construction of the different types of clusters. The selection of pyridine/pyrazine as the base for **3**–**6** and only pyridine for **1** and **2** is also of importance for the construction of these compounds. All attempts to use inorganic bases or other organic bases in these reactions failed. Upon exposing crystals of **3**–**6** to air for longer than 3 h, the faces of the crystals became opaque and cracking was observed; this implies the loss of lattice solvent molecules, as well as the possible collapse of the skeleton. To further confirm this, the powder X-ray diffraction (PXRD) patterns of **3**, as an example of these compounds, were recorded at different times (Figure S1, Supporting Information). Weakened intensities and broadened peaks were observed in the PXRD patterns of **3** recorded after its exposure to air for longer than 3 h.

The chiralities of **1**–**6** were substantiated by circular dichroism (CD) spectroscopy, which was performed in the solid state at room temperature (Figure S2). The CD spectra of **1**/**2**, **3**/**4**, and **5**/**6** present Cotton effects, and the spectra of the compounds forming a pair are almost mirror images, which indicates that each compound is enantiopure and the corresponding pairs of compounds are enantiomers of each other.



Scheme 1. Synthetic routes to the chiral ligands used in this study.

As revealed by single-crystal X-ray diffraction analysis, $[Cu_6\{(2R,3R)\text{-BSH}\}_2(C_5H_5N)_{10}]_2[C_5H_6N]_3(ClO_4)_7\cdot CH_3OH\cdot C_5H_5N$ (**1**) and $[Cu_6\{(2S,3S)\text{-BSH}\}_2(C_5H_5N)_{10}]_2[C_5H_6N]_3(ClO_4)_7\cdot CH_3OH\cdot C_5H_5N$ (**2**) are enantiomers that feature discrete hexanuclear units as shown in Figure 1. All of the Cu^{II} ions in **1** and **2** have square-pyramidal coordination environments. The basal positions of Cu3–Cu6 are occupied by one pyridyl nitrogen atom, one phenolic oxygen atom, one nitrogen atom of the C=N group, and one carbonyl oxygen atom; the apex position is open for another pyridyl nitrogen atom. Cu1 and Cu2 are coordinated by one pyridyl nitrogen atom, two carbonyl amide nitrogen atoms from two BSH^{5-} ligands, and one alkoxo oxygen atom in the basal positions; another alkoxo oxygen atom from another BSH^{5-} ligand is in the apex position.

The two BSH^{5-} ligands in compounds **1** and **2** act as pentavalent μ_4,η^{10}-bridging anions, and all of the nitrogen and oxygen atoms in the ligands are involved in coordination to the Cu^{II} ions as depicted (Figure 1, c, d). Among the six Cu^{II} ions, Cu1 and Cu2 are both chelated by two BSH^{5-} ligands; however, the other Cu^{II} ions are only chelated by one BSH^{5-} ligand. Cu3, Cu1, and Cu4 are connected by two –N–N– groups from two BSH^{5-} ligands to form a linear trinuclear unit, as are Cu5, Cu2, and Cu6. Cu1 and Cu2 from the two linear trinuclear units are further bridged by two O–C–C–O moieties from two BSH^{5-} ligands, which results in the consolidation of the six Cu^{II} ions by two BSH^{5-} ligands to form hexanuclear units in **1** and **2**. The two linear Cu_3 units in the hexanuclear units are nearly normal to

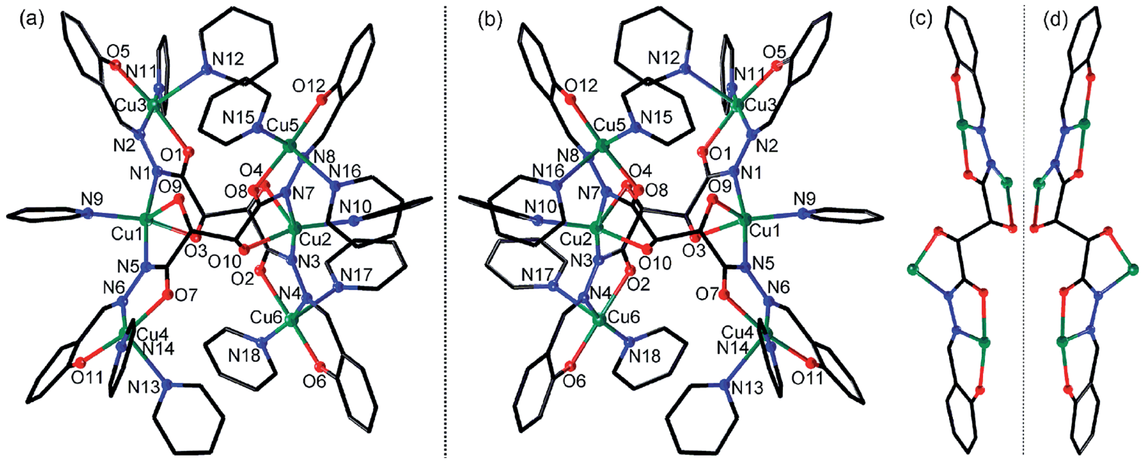


Figure 1. Molecular structures of (a) **1** and (b) **2** with selected atoms labeled and ligand coordination modes of (c) **1** and (d) **2**.

each other with an angle of 86.97(1)° for **1** and 87.07(1)° for **2**. To the best of our knowledge, this kind of hexanuclear cluster with two orthogonal linear trinuclear units is rare. Only one compound has been reported to possess this kind of skeleton.[13] The other reported hexanuclear clusters with two linear trinuclear units usually exhibit "dimer-of-trimers" structure with a ladder-like architecture.[13,14]

The single-crystal X-ray diffraction analysis results reveal that **3** and **4** have the formula of $[Cu_{13}L_3(OH)_2(CH_3COO)_6(C_5H_5N)_6(DMF)_3]\cdot 6DMF\cdot 3H_2O$ [L = (2*R*,3*R*)-BSH, **3**; (2*S*,3*S*)-BSH, **4**]; their tridecanuclear units are shown in Figure 2. The tridecanuclear units in **3** and **4** feature a dicubane core with a threefold axis passing through the O12, Cu3, and O13 atoms. The seven Cu^{II} ions in the dicubane core are connected by two hydroxy groups and six alkoxo oxygen atoms from three BSH^{6-} ligands to form a heptanuclear vertex-sharing dicubane core; the six unshared Cu^{II} ions are arranged in a nearly eclipsed fashion (Figure 2). Cu2, Cu2A, and Cu2B in one cubane are additionally connected by three carboxylato groups in turn. The other three carboxylato groups in the dicubane core chelate separately to Cu4, Cu4A, and Cu4B. The Cu^{II} ions in the dicubane core present three types of coordination geometries. Cu3 possesses a nearly ideal trigonal prismatic geometry, as demonstrated by the twist angle [2.24(1)° for **3** and 2.42(1)° for **4**] of the two triangular faces O3–O3A–O3B and O4–O4A–O4B, which was calculated as the mean of the Newman projection angles viewed along the centroids of focus. This kind of ideal trigonal prism around the Cu^{II} ion is unusual and unprecedented. The Cu2, Cu2A, and Cu2B atoms have distorted octahedral coordination environments with one acetato oxygen atom, one hydroxy oxygen atom, and one alkoxo oxygen atom and one nitrogen atom from one BSH^{6-} ligand in the equatorial positions; another alkoxo oxygen atom from another BSH ligand and another acetato oxygen atom are in the axial positions. Cu4, Cu4A, and Cu4B present coordination geometries similar to those of Cu2, Cu2A, and Cu2B. The Cu–O/N bond lengths are comparable to those reported in the literature.[15]

The unshared six Cu^{II} ions in the heptanuclear vertex-sharing dicubane cores of **3** and **4** are further linked to another six Cu^{II} ions (Cu1, Cu1A, Cu1B, Cu5, Cu5A, and Cu5B) by the three BSH^{6-} ligands to form discrete tridecanuclear units. Cu1 is coordinated by one carbonyl oxygen atom, one nitrogen atom and a phenoxyl oxygen atom from one BSH^{6-} ligand, and another pyridyl nitrogen atom to form a planar square geometry. Cu5 has a square pyramidal geometry in which the coordinating atoms in the basal positions are similar to those in Cu1. The difference between Cu5 from Cu1 is that one of the axial positions of Cu5 is coordinated by one DMF molecule. The pyridyl plane of Cu1 nearly parallels the phenyl plane of Cu5A with a dihedral angle of 2.377° for **3** and 1.068° for **4** and a center-to-center distance of 3.8304(3) Å for **3** and 3.8126(2) Å for **4**; this is indicative of the existence of $\pi\cdots\pi$ stacking interactions between the two rings. As a result, the two square planes of Cu1 and Cu5A are nearly parallel to each other with a dihedral angle of 7.183° for **3** and 7.785° for **4**.

Structural analysis revealed discrete tridecanuclear units in $[Cu_{13}X_3(OH)_2(CH_3COO)_6(C_5H_5N)_2(DMF)_8]\cdot 6H_2O$ [X = (2*R*,3*R*)-MBSH, **5**; (2*S*,3*S*)-MBSH, **6**], as depicted in Figure 3. The tridecanuclear units feature a heptanuclear vertex-sharing dicubane core with a twofold rotation axis defined by Cu1 and the center of Cu3 and Cu3A. Four Cu^{II} ions are bridged by three alkoxo oxygen atoms and one hydroxy group to form one cubane. The two cubanes in **5** and **6** share one Cu^{II} vertex to form a heptanuclear vertex-sharing dicubane core; the six unshared Cu^{II} ions are arranged in a nearly eclipsed fashion, which is similar to the arrangements in **3** and **4**. An important difference is that the dicubane cores in **5** and **6** show lower symmetry and slightly more severe distortion than those in **3** and **4**, as indicated by the corresponding Cu–O bond lengths and the O–Cu–O and Cu–O–Cu angles. Two of the Cu^{II} ions in each cubane are further connected by one carboxylato group. Cu1 is coordinated by six alkoxo oxygen atoms to form a nearly ideal trigonal prismatic geometry, as demonstrated by the twist angle [2.14(2)° for **5** and 2.01(2)° for **6**] of the two triangular

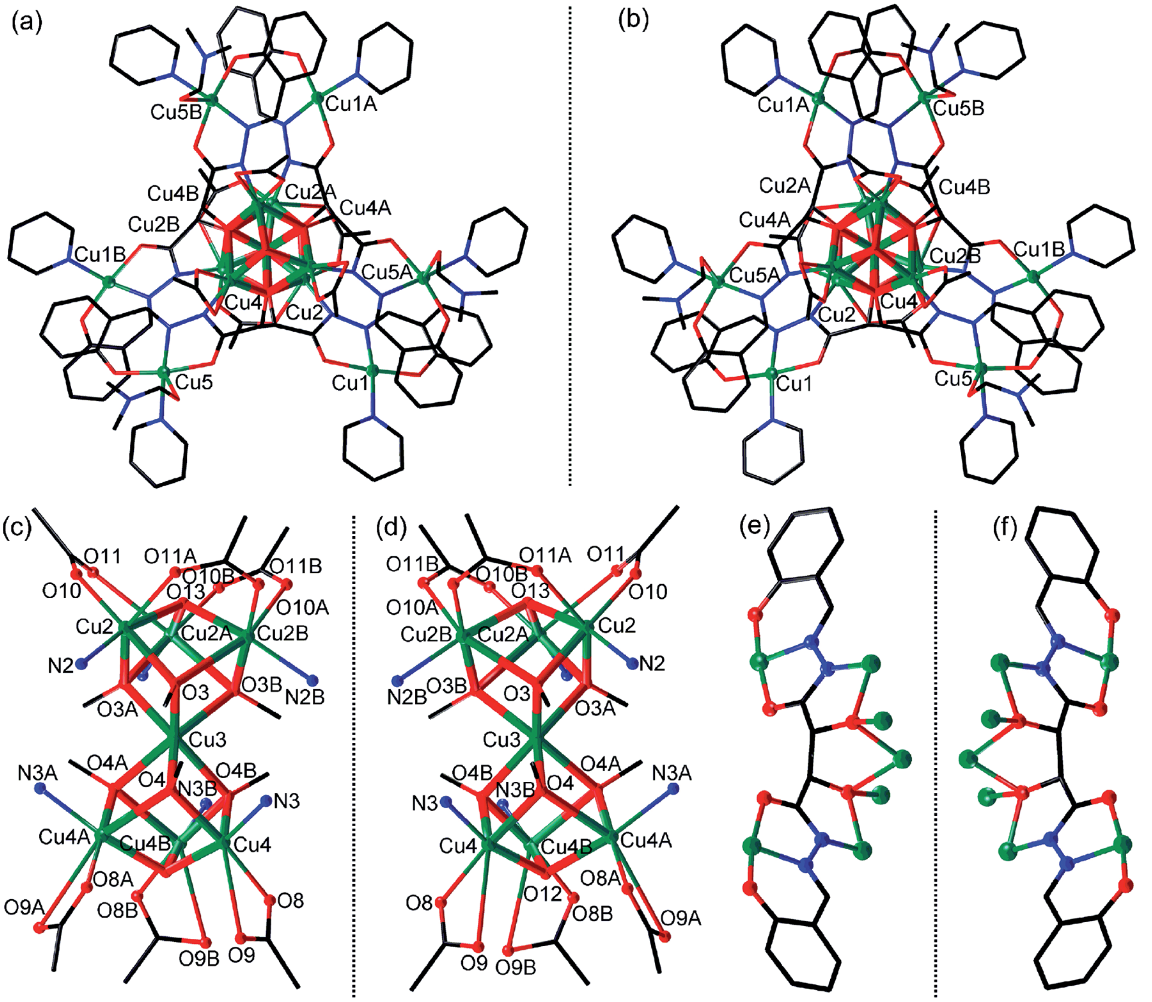


Figure 2. Molecular structures of (a) **3** and (b) **4** with selected atoms labeled. The dicubane cores in (c) **3** and (d) **4** (d). Ligand coordination modes of (e) **3** and (f) **4**. Symmetry codes for **3**: A) $-x + y, -x + 1, z$; B) $-y + 1, x - y + 1, z$. Symmetry codes for **4**: A) $-x + y + 1, -x + 1, z$; B) $-y + 1, x - y, z$.

faces O4–O5A–O12 and O4A–O5–O12A, which was calculated as the mean of the Newman projection angles viewed along the centroids of focus. This kind of ideal trigonal prism around the Cu^{II} ion is unusual and unprecedented. Cu4 presents a severely distorted octahedral geometry with one alkoxo oxygen atom and one nitrogen atom from one MBSH^{6-} ligand, one hydroxy group, and one DMF molecule in the equatorial sites; one alkoxo oxygen atom and one acetato oxygen atom sit in the axial positions. Cu2 is coordinated in a square pyramidal geometry with one hydroxy group, one alkoxo oxygen atom and one nitrogen atom from one MBSH^{6-} ligand, and one acetate oxygen atom in the basal positions; another alkoxo oxygen atom sits in the apex position. Cu5 has a severely distorted octahedral geometry with one hydroxy group, one alkoxo oxygen atom and one nitrogen atom from the MBSH^{6-} ligand, and an acetato oxygen atom in the equatorial positions; another alkoxo oxygen atom and another carboxylato oxygen atom lie in the axial positions. The Cu–O/N bond lengths are comparable to those in **3** and **4**.

The dicubane cores in **5** and **6** are further connected to another six Cu^{II} ions (Cu3, Cu3A, Cu6, Cu6A, Cu7, and Cu7A) by the three MBSH^{6-} ligands. Cu3 and Cu3A present square pyramidal geometries. Their basal positions are occupied by one carbonyl oxygen atom, one N atom and one phenolic O atom from one MBSH^{6-} ligand, and another oxygen atom from one DMF. Their apex position is occupied by another weakly bound oxygen atom from one DMF molecule with much longer Cu–O bond lengths of 3.04(4) Å for **5** and 2.866(17) Å for **6**. The two basal planes of Cu3 and Cu3A are nearly parallel to each other with dihedral angles of 1.552(2)° for **5** and 3.038(8)° for **6** and Cu···Cu distances of 4.2583(13) Å for **5** and 4.2681(14) Å for **6**. Cu6 and Cu6A present coordination geometries that are similar to those of Cu3 and Cu3A; one pyridyl N atom lies in one basal position instead of one oxygen atom from one DMF molecule. The difference in the coordination geometries of Cu7 and Cu7A from those of Cu3 and Cu3A is that there are no coordinating atoms in the axial positions. Thus, Cu7 and Cu7A show square planar geometries. The

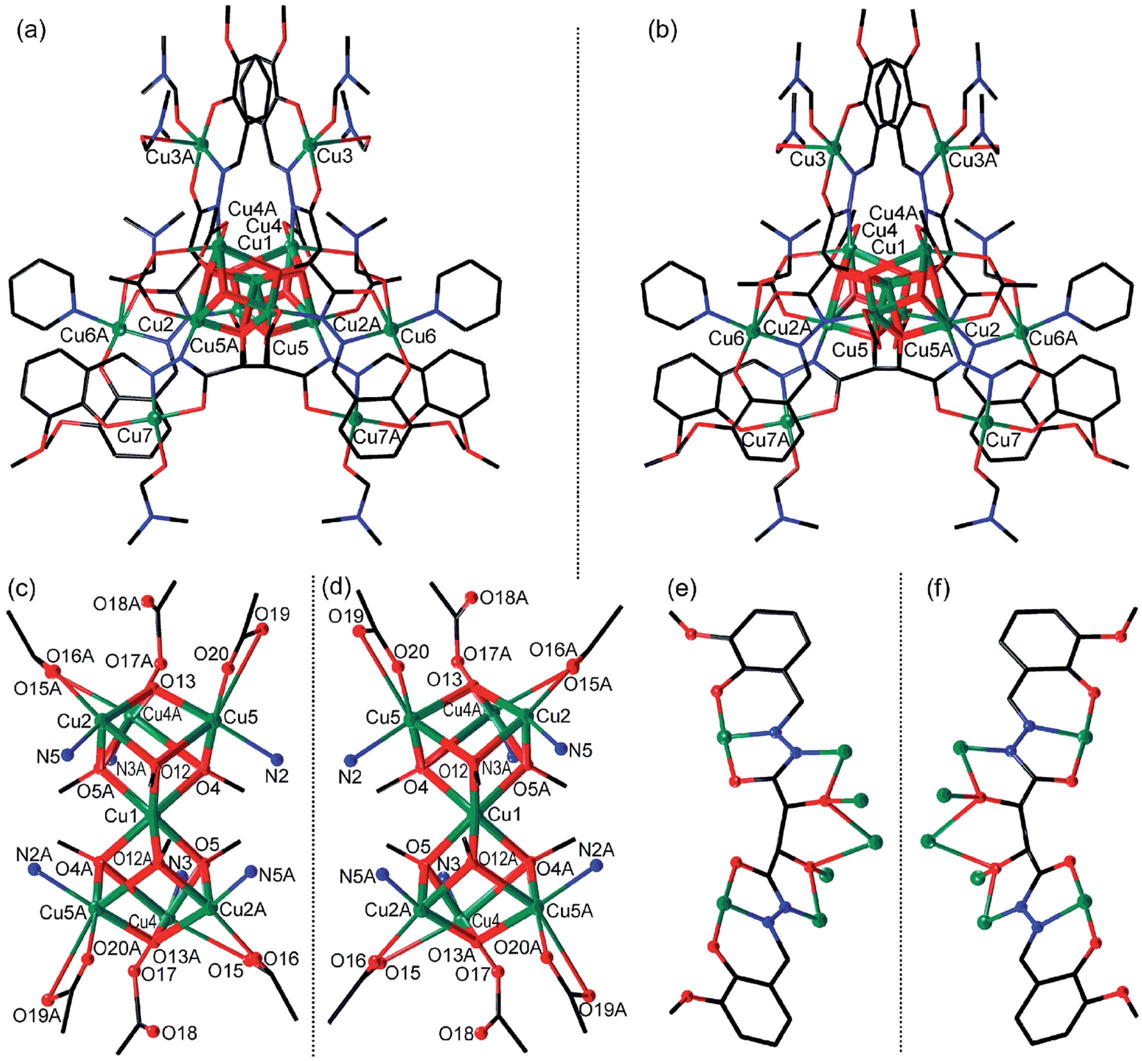
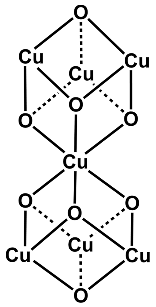


Figure 3. Molecular structures of (a) **5** and (b) **6** with selected atoms labeled. The dicubane cores of (c) **5** and (d) **6** and the ligand coordination modes of (e) **5** and (f) **6**. Symmetry codes for **5**: A) $-x + 2, y, -z + 1/2$. Symmetry codes for **6**: A) $-x, y, -z + 3/2$.

two basal planes of Cu6 and Cu7A (or Cu6A and Cu7) are nearly parallel to each other with dihedral angles of 9.952(7)° for **5** and 6.442(6)° for **6** and Cu···Cu distances of 4.3786(11) Å for **5** and 4.4037(13) Å for **6**. The pyridyl ring of Cu6 is nearly parallel to the phenyl ring of Cu7A with a dihedral angle of 8.238(7)° for **5** and 6.650(7)° for **6**, a center-to-center distance of 4.336(1) Å for **5** and 4.402(1) Å for **6**, and a pyridyl center-to-phenyl plane distance of 3.566(1) Å for **5** and 3.521(1) Å for **6**, which is indicative of the existence of $\pi\cdots\pi$ stacking interactions between the two rings. All MBSH^{6-} ligands in **5** and **6** behave in the same coordination modes as those shown in Figure 3.

The BSH ligand in **1** and **2** presents a μ_4,η^{10}-bridging mode, which is much different from the μ_7,η^{14}-bridging mode for the BSH ligand in **3** and **4**. It is easy to see that the coordination modes for the two hydrazone parts at the two ends of the BSH ligand in **1**–**4** are the same (Scheme S1). However, the two adjacent alkoxo O atoms in the middle part of the BSH ligand in **3** and **4** show coordination modes that are much different to those in **1** and **2** (Scheme S1). This leads to corresponding O–C–C–O torsion angles in the range of 60.5(8) to 63.5(8)° for **1** and **2**, and of 35.4(8) to 36.5(7)° for **3** and **4**. The MBSH^{6-} ligands in **5** and **6** adopt coordination modes similar to those in **3** and **4**, and the corresponding O–C–C–O torsion angles are in the range of 29.3(3) to 40(3)°. Compounds **3**–**6** show similar tridecanuclear skeletons and feature heptanuclear vertex-sharing dicubane cores (Scheme 2). However, the tridecanuclear units in **3** and **4** have threefold rotation axes, and the tridecanuclear units in **5** and **6** have only twofold rotation axes. In comparison to the BSH^{6-} ligand in **3** and **4**, the MBSH^{6-} ligand in **5** and **6** has one more methoxyl group on each phenyl group. It seems that the introduction of a methoxyl group into the ligand does not have a large influence on the structures of the thus-formed complexes, but it does reduce the symmetry of the structure. This kind of heptanuclear vertex-sharing dicubane core having six unshared metal vertexes that are connected to another six metal ions has never been documented. To the best of our knowledge, only a few paramagnetic metal compounds have been reported to show a heptanuclear vertex-sharing dicubane core.[11d–11g] Among them, only one Cu^{II} compound was reported with a heptanuclear vertex-sharing dicubane core.[11d] However, this dicubane core is $Cu_7O_6Cl_2$ not Cu_7O_8. Furthermore, only a few chiral paramagnetic clusters containing cubane structures have been reported.[4b,7a,12] For the introduction of chirality into dicubane structures, compounds **3**–**6** are the first examples.



Scheme 2. The dicubane cores in **3**–**6**.

Magnetic Properties

As revealed by single-crystal X-ray diffraction analysis, compounds **1**/**2**, **3**/**4**, and **5**/**6** are enantiomers of each other; **1** and **2** possess hexanuclear cluster skeletons, whereas **3**–**6** possess tridecanuclear cluster structures. Consequently, **1** and **2** might possess similar magnetic properties, as might compounds **3**–**6**; this was confirmed by solid-state magnetic susceptibility (χ_m) measurements in the temperature range of 2.0 to 300 K in a direct current field of 1000 Oe (see Figures 4–6).

The magnetic properties of **1** and **2** in the form of both $\chi_m T$ and χ_m versus T plots are shown in Figure 4. The $\chi_m T$ values of **1** and **2** at 300 K are 2.08 and 2.14 cm^3 K mol^{-1} per Cu_6 unit, respectively, which are close to the expected value (2.25 cm^3 K mol^{-1}) for six magnetically isolated high-spin Cu^{II} ions. Upon decreasing the temperature, the $\chi_m T$ values of **1** and **2** decrease steadily; this suggests the presence of dominant antiferromagnetic coupling in the two compounds. The plateau in the temperature range of 6 to 40 K for both compounds might be caused by the net spins of the hexanuclear units.[16] The further steep decrease in $\chi_m T$ upon lowering the temperature could result from interhexanuclear antiferromagnetic interactions in **1** and **2**. As revealed by structural analysis, the hexanuclear clusters of **1** and **2** are constructed from two orthogonal linear trinuclear units through two O–C–C–O moieties that cannot transmit magnetic interaction effectively [Equation (1)]. The Cu^{II} center in the linear trinuclear unit interacts with the other two Cu^{II} ions through the Cu–N–N–Cu linkage with nearly the same torsion angles, assuming they convey the same magnetic interactions (J). Thus, the magnetic data of **1** and **2** can be roughly estimated according to a simple model for a centrosymmetric $S = 1/2$ linear trimer with the Hamiltonian $H = -2J(S_1S_2 + S_2S_3)$,[17] in which S_2 is the spin state of the central Cu^{II} ion, by employing a molecular field approximation to estimate the intertrimer and interhexamer interaction ($2zJ'$).

$$\chi_{hexanuclear} = 2\chi_{trinuclear} = 2 \times \frac{Ng^2\beta^2}{4kT} \times \frac{1 + e^{-2J/kT} + 10e^{J/kT}}{1 + e^{-2J/kT} + 2e^{J/kT}} \qquad (1)$$

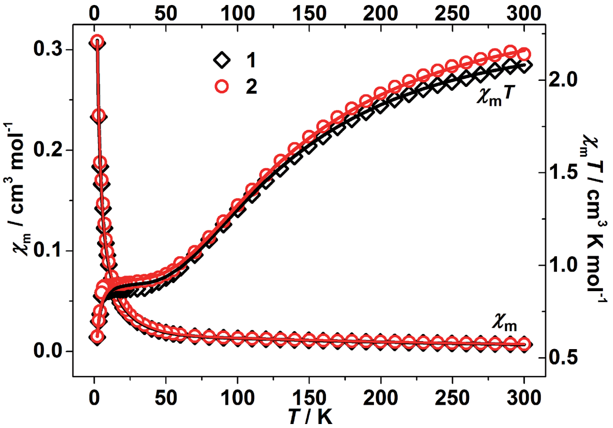


Figure 4. Plots of χ_m and $\chi_m T$ versus T for **1** and **2**. The solid lines denote the theoretical fits of the experimental data.

The magnetic susceptibility data of **1** and **2** were least-squares fit to Equation (2) to give the best-fitting parameters: J = –59.45 cm^{-1}, $2zJ'$ = –0.74 cm^{-1}, and g = 2.25 with an agreement factor $R = 1.22 \times 10^{-4}$ for **1**; and J = –61.04 cm^{-1}, $2zJ'$ = –0.81 cm^{-1}, and g = 2.28 with an agreement factor $R = 1.80 \times 10^{-4}$ for **2**. The fitting values agree well with the experimental data (Figure 4). These results indicate the presence of an overall intermetallic antiferromagnetic coupling in **1** and **2**.

$$\chi_M = \frac{\chi_{hexanuclear}}{1 - (2zJ'/Ng^2\beta^2)\chi_{hexanuclear}} \qquad (2)$$

As shown in Figures 5 and 6, the shapes of the χ_m and $\chi_m T$ versus T curves for **3**–**6** are similar. The $\chi_m T$ values of **3**–**6** at 300 K are 3.90, 3.79, 3.30, and 3.21 cm^3 K mol^{-1}, respectively, which are lower than the value expected (4.88 cm^3 K mol^{-1}) for 13 magnetically isolated high-spin Cu^{II} ions. Upon decreasing the temperature, the $\chi_m T$ values decrease slowly and reach 1.25, 1.14, 0.87, and 1.05 cm^3 K mol^{-1} at 2 K for **3**–**6**, respectively. This reveals the presence of dominant antiferromagnetic coupling in the four compounds, which might be interpreted by the structural parameters, including the Cu···Cu separations and Cu–O–Cu angles, in the four compounds. The Cu···Cu distances in the dicubane cores are in the range of 3.1211(2) to 3.1970(3) Å for **3**, 3.1189(1) to 3.2056(3) Å for **4**, 3.0645(10) to 3.3289(9) Å for **5**, and 3.0811(11) to 3.3418(10) Å for **6**, which indicates that the cubanes in these compounds can be considered as a "6+0" type in the classification proposed by Tercero et al.[18] The structures and magnetic couplings of this type of cubane have been seldom studied. Every adjacent two Cu^{II} ions in the dicubane cores of **3**–**6** are doubly bridged by alkoxido atoms with average Cu–O–Cu angles in the CuO_2Cu units in the range of 95.4 to 98.9° for **3**, 95.5 to 98.9° for **4**, 94.4 to 99.8° for **5**, and 95.2 to –100.4° for **6**, which might favor antiferromagnetic interactions rather than ferromagnetic interactions between the Cu^{II} ions, as supposed by similar cases.[11b–11d,19] Another six Cu^{II} ions in **3**–**6** interact with the dicubane cores through Cu–N–N–Cu linkages with Cu···Cu separations of 4.7170(3)–4.8057(3) Å for **3**, 4.7248(2)–4.8095(2) Å for **4**, 4.7507–4.7864 Å for **5**, and 4.7792(14)–4.8027(15) Å for **6**, which are reported to mediate antiferromagnetic interactions between Cu^{II} ions.[20]

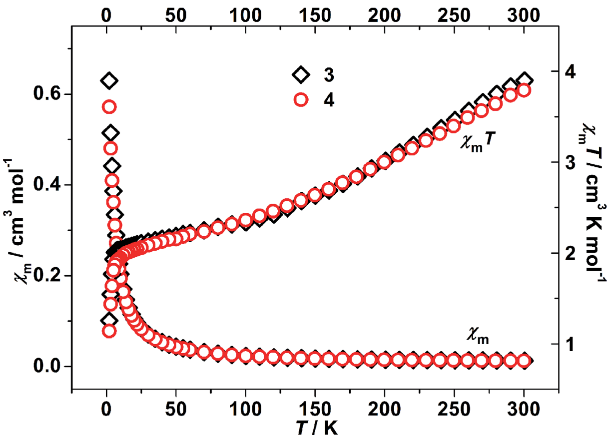


Figure 5. Plots of χ_m and $\chi_m T$ versus T for **3** and **4**.

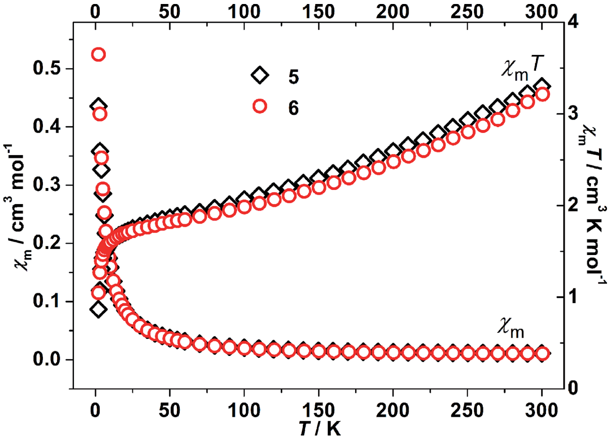


Figure 6. Plots of χ_m and $\chi_m T$ versus T for **5** and **6**.

Conclusions

In summary, two enantiomeric pairs of ligands were designed and prepared. Their reactions with cupric salts gave one enantiomeric pair of chiral hexanuclear clusters and two enantiomeric pairs of chiral tridecanuclear clusters. The selection of appropriate bases is of importance for their formation. The anions of the Cu^{II} salts contribute significantly to the construction of different types of cluster skeletons. The two hexanuclear clusters feature two nearly orthogonal linear trinuclear units that are cross-linked to each other. The four chiral tridecanuclear clusters exhibit a rare heptanuclear vertex-sharing dicubane core, and these clusters represent the first examples of chiral clusters bearing dicubane cores. The results indicate that the introduction of a methoxyl group onto the ligand does not have much of an influence on the skeletons of the thus-formed complexes, but it does reduce the symmetry of the skeleton. These results open promising perspectives towards the construction of more esthetic high-nuclear clusters from analogous ligands by adjusting the reaction parameters. The magnetic measurements revealed the presence of overall antiferromagnetic interactions between the metal ions in these complexes.

Experimental Section

Materials and General Methods: The two pairs of chiral ligands [(2*R*,3*R*)-BSH/(2*S*,3*S*)-BSH and (2*R*,3*R*)-MBSH/(2*S*,3*S*)-MBSH] used in this study, as well as the materials used in their synthesis, that is, (2*R*,3*R*)/(2*S*,3*S*)-2,3-dihydroxybutanedihydrazide, were prepared following procedures described in the Supporting Information. Other chemicals were used as obtained without further purification. Infrared spectra were recorded as KBr pellets by using a Nicolet 360 FTIR spectrometer. Mass spectra were recorded with a Bruker Esquire HCT spectrometer. Elemental analyses (C, H, and N) were performed with a Vario EL analyzer. Powder X-ray diffraction data were collected with a Rigaku D/max 2500v/pc diffractometer with Cu-K_α radiation (λ = 1.5418 Å). Magnetic susceptibilities were determined for crystalline samples at an applied magnetic field of 1000 Oe by using a Quantum Design MPMS-XL SQUID magnetometer in the range from 300 to 2 K. Data were corrected for the diamagnetic contribution calculated from Pascal constants and the diamagnetism of the sample and sample holder were taken into account. Circular dichroism spectra in the solid state were recorded at room temperature with a JASCO J-810 CD spectrometer as KBr pellets.

CAUTION! Perchlorate salts are potentially explosive. The experiments were performed in an isolated room and experimenters were equipped with safeguards. Only a small amount of the materials should be prepared and handled with great care.

Synthesis of $[Cu_6\{(2R,3R)\text{-BSH}\}_2(C_5H_5N)_{10}]_2[C_5H_6N]_3(ClO_4)_7\cdot CH_3OH\cdot C_5H_5N$ (1): (2*R*,3*R*)-BSH (0.0390 g, 0.1 mmol) was dissolved in methanol (8 mL) at room temperature with stirring. Subsequently, a methanol solution (8 mL) of $Cu(ClO_4)_2\cdot 6H_2O$ (0.1105 g, 0.3 mmol) was added dropwise. After stirring for another 3 h, pyridine (1 mL) was added. The resulting mixture was stirred for another 5 h to give a green solution that was filtered. The filtrate was allowed to evaporate at ambient temperature for four weeks to give dark green blocks of crystals of **1**, yield 75%. IR (KBr pellet): $\tilde{\nu}$ = 3438 (m), 1607 (s), 1547 (vs), 1484 (w), 1465 (w), 1449 (m), 1377 (w), 1311 (w), 1220 (w), 1200 (w), 1152 (m), 1090 (br., s), 966 (w), 908 (w), 796 (w), 757 (m), 699 (m), 623 (m), 513 (w) cm^{-1}. $C_{193}H_{179}Cl_7Cu_{12}N_{40}O_{53}$ (4917.39): calcd. C 47.14, H 3.67, N 11.39; found C 47.28, H 3.40, N 11.67.

$[Cu_6\{(2S,3S)\text{-BSH}\}_2(C_5H_5N)_{10}]_2[C_5H_6N]_3(ClO_4)_7\cdot CH_3OH\cdot C_5H_5N$ (2): Prepared in a way similar to that of **1** by using (2*S*,3*S*)-BSH instead of (2*R*,3*R*)-BSH, yield 78%. IR (KBr pellet): $\tilde{\nu}$ = 3439 (m), 1608 (s), 1546 (vs), 1486 (w), 1465 (w), 1449 (m), 1376 (w), 1317 (w), 1219 (w), 1199 (w), 1151 (m), 1121 (s), 1109 (s), 966 (w), 908 (w), 799 (w), 755 (m), 698 (m), 626 (m), 492 (w) cm^{-1}.

$C_{193}H_{179}Cl_7Cu_{12}N_{40}O_{53}$ (4917.39): calcd. C 47.14, H 3.67, N 11.39; found C 47.39, H 3.88, N 11.56.

$[Cu_{13}\{(2R,3R)\text{-BSH}\}_3(OH)_2(CH_3COO)_6(C_5H_5N)_6(DMF)_3]\cdot 6DMF\cdot 3H_2O$ (3): (2*R*,3*R*)-BSH (0.0390 g, 0.1 mmol) was dissolved in DMF (5 mL) at room temperature with stirring. Subsequently, a DMF solution (5 mL) of $[Cu_2(OAc)_4(H_2O)_2]$ (0.0596 g, 0.15 mmol) was added. After stirring for another 3 h, pyridine (1 mL) and a water solution (1 mL) of pyrazine (0.0100 g, 0.1 mmol) was added. The resulting mixture was stirred for another 5 h to give a dark green clear solution that was filtered. The filtrate was allowed to evaporate at ambient temperature for three weeks to give dark green block crystals of **3**, yield 80%. IR (KBr pellet): $\tilde{\nu}$ = 3414 (br., m), 3048 (w), 2871 (w), 1662 (m), 1603 (s), 1537 (s), 1487 (w), 1465 (w), 1448 (m), 1386 (m), 1330 (w), 1249 (w), 1221 (w), 1200 (m), 1149 (m), 1124 (w), 1095 (w), 1074 (w), 1045 (w), 1018 (w), 908 (w), 800 (w), 757 (m), 697 (m), 671 (w), 594 (w), 497 (w) cm^{-1}. $C_{123}H_{155}Cu_{13}N_{27}O_{44}$ (3541.76): calcd. C 41.71, H 4.41, N 10.68; found C 41.40, H 4.58, N 10.90.

$[Cu_{13}\{(2S,3S)\text{-BSH}\}_3(OH)_2(CH_3COO)_6(C_5H_5N)_6(DMF)_3]\cdot 6DMF\cdot 3H_2O$ (4): Prepared in a way similar to that of **3** by using (2*S*,3*S*)-BSH instead of (2*R*,3*R*)-BSH, yield 78%. IR (KBr pellet): $\tilde{\nu}$ = 3418 (br., m), 3048 (w), 2871 (w), 1663 (m), 1605 (s), 1532 (s), 1487 (w), 1466 (w), 1444 (m), 1386 (m), 1327 (w), 1249 (w), 1220 (w), 1200 (m), 1149 (m), 1124 (w), 1095 (w), 1073 (w), 1045 (w), 1018 (w), 908 (w), 800 (w), 756 (m), 698 (m), 670 (w), 592 (w), 498 (w) cm^{-1}. $C_{123}H_{155}Cu_{13}N_{27}O_{44}$ (3541.76): calcd. C 41.71, H 4.41, N 10.68; found C 41.49, H 4.29, N 10.39.

$[Cu_{13}\{(2R,3R)\text{-MBSH}\}_3(OH)_2(CH_3COO)_6(C_5H_5N)_2(DMF)_8]\cdot 6H_2O$ (5): A DMF solution (5 mL) of $[Cu_2(OAc)_4(H_2O)_2]$ (0.0596 g, 0.15 mmol) was added dropwise to a stirred mixture of (2*R*,3*R*)-MBSH (0.039 g, 0.1 mmol) and DMF (5 mL). After stirring for 3 h, pyridine (1 mL) and a water solution (1 mL) of pyrazine (0.0100 g, 0.1 mmol) were added dropwise. The resulting mixture was stirred for another 5 h to give a dark green clear solution that was filtered. The filtrate was allowed to evaporate at ambient temperature for two weeks to give dark green block crystals of **5**, yield 70%. IR (KBr pellet): $\tilde{\nu}$ = 3414 (s), 1607 (s), 1540 (vs), 1467 (w), 1439 (m), 1386 (m), 1315 (w), 1246 (m), 1218 (m), 1110 (m), 1087 (w), 1048 (w), 968 (w), 857 (w), 743 (m), 695 (w), 509 (w) cm^{-1}. $C_{106}H_{146}Cu_{13}N_{22}O_{52}$ (3386.47): calcd. C 37.59, H 4.35, N 9.10; found C 37.28, H 4.60, N 8.88.

$[Cu_{13}\{(2S,3S)\text{-MBSH}\}_3(OH)_2(CH_3COO)_6(C_5H_5N)_2(DMF)_8]\cdot 6H_2O$ (6): Prepared in a way similar to that of **5** by using (2*S*,3*S*)-MBSH instead of (2*R*,3*R*)-MBSH, yield 75%. IR (KBr pellet): $\tilde{\nu}$ = 3358 (br., s), 1604 (s), 1588 (s), 1546 (vs), 1467 (m), 1434 (m), 1388 (m), 1309 (w), 1246 (m), 1216 (m), 1106 (m), 1083 (w), 964 (w), 855 (w), 747 (m), 626 (m), 596 (w) cm^{-1}. $C_{106}H_{146}Cu_{13}N_{22}O_{52}$ (3386.47): calcd. C 37.59, H 4.35, N 9.10; found C 37.78, H 4.28, N 9.02.

X-ray Crystallography: The X-ray diffraction data of **1**–**6** were collected with a Bruker Smart Apex-II CCD diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Absorption correction were applied by using the multiscan program SADABS.[21] The structures were solved by direct methods by using SHELXS-97[22] and were refined by using the SHELXL-97 program[23] or the corresponding programs in the SHELXTL package.[24] Full-matrix least-squares refinements on F^2 by using all data were performed with anisotropic displacement parameters applied to all non-hydrogen atoms. H atoms attached to C atoms were included in geometrically calculated positions for all structures by using a riding model and were refined isotropically. H atoms on N and O atoms were placed in calculated positions. Figures were created with the OLEX program.[25] In **1** and **2**, one ClO_4^- anion, two

Table 1. Crystallographic data for compounds **1**–**6**.

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_{193}H_{179}Cl_7Cu_{12}N_{40}O_{53}$	$C_{193}H_{179}Cl_7Cu_{12}N_{40}O_{53}$	$C_{123}H_{155}Cu_{13}N_{27}O_{44}$	$C_{123}H_{155}Cu_{13}N_{27}O_{44}$	$C_{106}H_{146}Cu_{13}N_{22}O_{52}$	$C_{106}H_{146}Cu_{13}N_{22}O_{52}$
M_r [g mol^{-1}]	4917.39	4917.39	3541.76	3541.76	3386.47	3386.47
T [K]	298(2)	298(2)	296(2)	296(2)	296(2)	296(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic	trigonal	trigonal	orthorhombic	orthorhombic
Space group	$P2_12_12$	$P2_12_12$	R_3	R_3	$C222_1$	$C222_1$
a [Å]	17.8627(18)	17.8876(19)	25.8714(18)	25.9123(14)	17.302(6)	17.281(7)
b [Å]	24.089(3)	24.194(3)	25.8714(18)	25.9123(14)	26.280(10)	26.362(11)
c [Å]	24.676(3)	24.719(3)	19.639(3)	19.427(2)	31.411(11)	31.331(13)
α [°]	90	90	90	90	90	90
β [°]	90	90	90	90	90	90
γ [°]	90	90	120	120	90	90
V [Å^3]	10618(2)	10698(2)	11383.6(19)	11296.5(15)	14283(9)	14274(10)
Z	2	2	3	3	4	4
$\rho_{calcd.}$ [g cm^{-3}]	1.538	1.527	1.550	1.562	1.575	1.576
μ [mm^{-1}]	1.351	1.341	1.866	1.881	1.982	1.983
F(000)	5016	5016	5433	5433	6916	6916
Crystal size [mm]	0.38 × 0.30 × 0.20	0.40 × 0.28 × 0.25	0.48 × 0.42 × 0.38	0.48 × 0.42 × 0.38	0.45 × 0.28 × 0.25	0.43 × 0.35 × 0.25
θ range [°]	1.18 to 25.02	1.18 to 25.02	2.62 to 25.02	2.62 to 25.01	2.40 to 25.01	2.36 to 25.02
Reflns. collected	49336	54796	26892	20640	43813	48714
Data/parameters	18696/1438	18859/1434	8657/598	8568/628	12123/638	12391/745
R_{int}	0.0748	0.0630	0.0528	0.0317	0.1519	0.0974
GOF on F^2	1.032	1.051	1.045	1.017	1.190	1.021
R_1 [$I > 2\sigma(I)$]	0.0555	0.0571	0.0482	0.0574	0.1550	0.0619
wR_2 [$I > 2\sigma(I)$]	0.1177	0.1256	0.1129	0.1377	0.3567	0.1457
R_1 (all data)	0.1080	0.0999	0.0737	0.0763	0.2165	0.0948
wR_2 (all data)	0.1253	0.1339	0.1315	0.1523	0.4078	0.1699
Flack parameter	–0.033(13)	–0.011(13)	–0.007(18)	0.02(2)	0.10(6)	–0.01(2)

$C_6H_5NH^+$ cations, and one methanol molecule were refined in a disordered manner. One water molecule in **3** and **4** was disordered over two positions. The two HO^- ions (O12 and O13) in **3** and **4** were located at the special sites with occupancies of 0.3333. Some geometric restraints (DFIX, FLAT, SADI, or SIMU) were used in modeling the poor geometries of one coordinated pyridine molecule and one coordinated CH_3COO^- ion in **3** and **4**. Some geometric restraints were also used in modeling the poor geometries of some coordinated DMF molecules and CH_3COO^- ions in **5**. Of 12123 intensity reflections used in the refinement of **5**, only 6796 reflections were considered "observed"; consequently, about 44% of the data represent weak reflections, which led to R and wR values that were higher for **5** than for the other compounds. However, the model for the structure of **5** was determined without any doubt. Crystallographic data of **1**–**6** are given in Table 1. Selected bond lengths and angles for **1**–**6** are listed in Tables S1–S6.

CCDC-866564 (for **1**), -866565 (for **2**), -866566 (for **3**), -866567 (for **4**), -866568 (for **5**), and -866569 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Synthesis details and characterization of (2*R*,3*R*)-BSH/(2*S*,3*S*)-BSH and (2*R*,3*R*)-MBSH/(2*S*,3*S*)-MBSH, bond lengths and bond angles of **1**–**6**, and additional figures.

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Chiral Magnetic Cu Clusters

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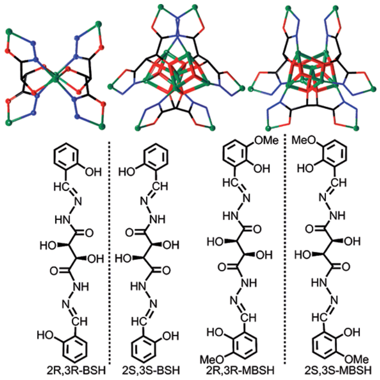
Copper(II) Clusters of Two Pairs of 2,3-Dihydroxybutanedioyl Dihydrazones: Synthesis, Structure, and Magnetic Properties

Keywords: Cluster compounds / Copper / Magnetic properties / Chirality / Structure elucidation



Six chiral clusters of two pairs of 2,3-dihydroxybutanedioyl dihydrazones, four of which represent the first examples of chiral clusters bearing dicubane cores, are presented. All six compounds are enantiomers of each other. Magnetic studies reveal the presence of overall antiferromagnetic interactions in these compounds.