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Two Novel Flexible Multidentate Ligands for Crystal Engineering: Syntheses, Structures, and Properties of Cu^{II}, Mn^{II} Complexes with *N*-[(3-Carboxyphenyl)-sulfonyl]glycine and *N*,*N′*-(1,3-Phenylenedisulfonyl)bis(glycine)

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One novel *N*-[(3-carboxyphenyl)sulfonyl]glycine (H_3L^1) ligand (**1**) was prepared in high yield, and its structure was determined by single-crystal X-ray diffraction. Reaction of H_3L^1 with $Mn(ClO_4)_2·6H_2O$ at different pH values gave two new dinuclear complexes: $[Mn_2(HL^1)_2(phen)_4]·16H_2O$ (**2**) and $[Mn_2L^1(phen)_4(H_2O)]ClO_4·3H_2O$ (**3**) (phen = 1,10-phenanthroline). Additionally, two copper(II) complexes, $[K_2Cu(L^2)_2(H_2O)_2]_n$ (**4**) and $[CuL^2(H_2O)]_2·2H_2O$ (**5**), involving another novel ligand, *N*,*N′*-(1,3-phenylenedisulfonyl)bis(glycine) (H_2L^2), were prepared by a one-pot reaction of 1,3-phenylenebis(sulfonyl chloride), glycine, and KOH or triethylamine in the presence of Cu^{II} ions. A self-assembled $(H_2O)_{30}$ cluster containing a puckered $(H_2O)_{12}$ ring core was found in **2**, which presents a new mode of association of water molecules not predicted theoretically or previously observed experimentally. Furthermore, **2** forms a 2-D supramolecular structure through hydrogen bonding and unique π–π stacking interactions. In **3**, there also exist discrete trimeric water clusters. The identity of the base determines the specific structural characteristics of **4** and **5**. When potassium hydroxide was used for the synthesis of **4**, it led to a 3-D copper(II)–potassium(I) coordination polymer; when triethylamine was used, paddle-wheel dinuclear units of copper(II) carboxylate were produced. Magnetic measurements show that there are weak antiferromagnetic interactions in **2**–**4**. In **5** the $\chi_M T$ vs. T curve shows a minimum at 110 K and a climb from 110 K to 5 K, then a long-range antiferromagnetic ordering occurs, as revealed by a decrease in $\chi_M T$ with T.

Introduction

Crystal engineering of coordination polymers and supramolecules have attracted a lot of attention because of their potential as functional materials, as well as their intriguing compositions and topologies.[1] A successful strategy in building such networks is to employ appropriate bridging ligands that can bind metal ions in different modes and provide a possible way to achieve more robust polymeric structures.[2] In this context, benzenedicarboxylic acid and its derivatives (such as 1,3-benzenedicarboxylic acid, 1,4-benzenedicarboxylic acid, 5-hydroxyisophthalic acid) are widely used as building blocks to link metal ions to produce metal–organic frameworks with interesting structures and properties.[3] In these reports, most of the bridging ligands used in the construction of the frameworks are rigid, because the carboxylate groups in these ligands are attached to the central aromatic ring directly. However, significantly fewer studies on the coordination chemistry of flexible carboxylate-containing ligands have been carried out, possibly because of the difficulties in predicting the structures of the resulting complexes.[4] Now, searching for this kind of versatile polycarboxylato ligands is very important and deserves attention in the investigation of new topologies and various functional materials.

Recently, we introduced a versatile ligand, *N*-(phenylsulfonyl)-L-glutamic acid, to construct various coordination polymers in which *N*-(phenylsulfonyl)-L-glutamic acid opens up the possibility to obtain structures with different kinds of carboxylato bridges.[5] The interesting results inspired us to investigate its analogues, *N*-[(3-carboxyphenyl)-sulfonyl]glycine and *N*,*N′*-(1,3-phenylenedisulfonyl)bis(glycine) (Scheme 1), for the following reasons: (1) both of the ligands contain two bridging carboxylato moieties, which can lead to a variety of connection modes with metal centers and provide abundant structural motifs; (2) they can act as not only hydrogen-bond acceptors but also hydrogen-bond donors, which make them excellent candidates for the

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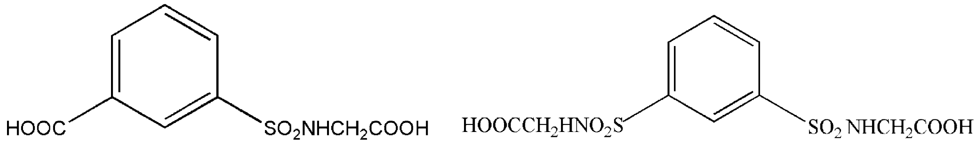


Scheme 1.

construction of supramolecular networks; (3) they possess two other potential groups in addition to benzenedicarboxylic acids, i.e., the nitrogen atoms and oxygen atoms of sulfonyl groups, which are good candidates to produce unique structural motifs with aesthetics and useful functional properties; (4) they are flexible: *N*,*N′*-(1,3-phenylenedisulfonyl)bis(glycine) can freely rotate with certain spacers to meet the requirement of coordination geometries of metal ions in the assembly process. In addition, the *N*-[(3-carboxyphenyl)sulfonyl]glycine ligand not only has one rigid carboxy group affixed to the aromatic ring but also extends one flexible carboxy group from its glycine moiety. This asymmetric geometry may lead to acentric crystal structures.

Recently, intense experimental and theoretical studies have focused on unraveling structural morphologies of water clusters to understand the nature of water–water interactions in bulk water or ice, probing its possible roles in the stabilization and functioning of biomolecules and in the design of new materials.[6] Structural studies on discrete water clusters within the lattice of a crystal host have significantly advanced our knowledge toward the first step of understanding the behavior of bulk water. Until now, a number of different discrete water clusters, namely tetrameric,[7] hexameric,[8] octameric,[9] decameric,[10] undecameric,[11] dodecameric,[12] tetradecameric,[6f] hexadecameric,[13] and heptadecameric[14] clusters have been structurally characterized and assigned different conformations. However, the units in these clusters are all small water clusters. The investigation of larger water aggregates is still a challenge in this field, although several examples of larger water clusters have been reported in crystal hosts very recently. Notable examples are a discrete large protonated water cluster, $H^+(H_2O)_{27}$, in a 3-D metal–organic framework, and the formation of an infinite 2-D layer of a $(H_2O)_{45}$ cluster in a cryptand–water supramolecular compound.[15] Chen and co-workers also reported an unprecedented $(H_2O)_{32}$ water cluster containing a central cyclic $(H_2O)_4$ in a Cd complex containing succinic acid (H_2adi) and *N*,*N′*-bis(picolinamide)azine (bpa) ligands: $\{[Cd_2(bpa)_2(adi)_2]\cdot 11H_2O\}_n$.[16] These studies provide novel structural aspects of and new insights into water with implications in the biological environment. Moreover, organic compounds with functional groups similar to those present in biological molecules can stabilize water clusters of different sizes and shapes in environments resembling those in living systems.[17] The glycine–water complex provides the simplest molecular model of biologically important amino acid–water interactions and represents the initial step of the hydration process.[18]

With the aim of understanding the coordination chemistry of *N*,*N′*-(1,3-phenylenedisulfonyl)bis(glycine) and *N*-[(3-carboxyphenyl)sulfonyl]glycine and preparing new materials with interesting structures and excellent physical properties, we have recently engaged in the research of metal complexes with these two ligands. The two ligands can be viewed either as sulfonamide derivatives or as *N*-substituted amino acids, and were expected to stabilize water clusters with their biologically relevant functional moieties. Herein, we report the syntheses, structures, and properties of $H_3L^1\cdot H_2O$ (**1**) and its two dinuclear Mn^{II} complexes, $[Mn_2(HL^1)_2(phen)_4]\cdot 16H_2O$ (**2**) and $[Mn_2L^1(phen)_4(H_2O)]ClO_4\cdot 3H_2O$ (**3**), and two new copper(II) complexes, $[K_2Cu(L^2)_2(H_2O)_2]_n$ (**4**) and $[CuL^2(H_2O)]_2\cdot 2H_2O$ (**5**). Interestingly, an unprecedented $(H_2O)_{30}$ cluster consisting of a basic puckered 12-membered ring fused with six dangling trimeric water clusters was stabilized by **2**.

Results and Discussion

Syntheses

(Phenylsulfonyl)amino acids were usually prepared in two steps: reaction of starting materials and then acidification.[19] The ligand *N*-[(3-carboxyphenyl)sulfonyl]glycine was synthesized in aqueous solution, and the reaction could be accomplished within 2 h. The product could be handled easily by using hydrochloric acid, and the yield was above 60%. A reaction of $Mn(ClO_4)_2\cdot 6H_2O$, H_3L^1, and phen at 70 °C at different pH values produced yellow crystals of **2** and **3**. In **2**, $(HL^1)^{2-}$ behaves just as a simple carboxylato group coordinated to the metal ions, and the sulfonamide nitrogen atom is free from coordination, whereas in **3**, as the pH value increases, it switches to an *N*,*O*-bidentate chelating ligand because of the environment of the deprotonated amide nitrogen atom as an additional donor site.

Unfortunately, when the reaction solution of 1,3-phenylenebis(sulfonyl chloride), glycine, and KOH was acidified to pH = 4 with 6 M hydrochloric acid, no precipitates were obtained. In attempts to seek an efficient synthesis, we found that a one-pot method with 1,3-phenylenebis(sulfonyl chloride), glycine, $Cu(OAc)_2\cdot 2H_2O$, and KOH or triethylamine in water could produce complexes **4** and **5** of this ligand. In addition, the same reaction was carried out with different salts of Ni, Mn, Co, Zn, and Cd. However, no complexes in crystalline form suitable for an X-ray study were obtained, which indicates that the copper(II) ion is an effective template for synthesizing this ligand.

Crystal Structures

Crystal Structure of 1

The structure of $H_3L^1 \cdot H_2O$ was determined by IR spectroscopy, elemental analysis, and single-crystal X-ray structure analysis. The IR spectra of $H_3L^1 \cdot H_2O$ exhibit several characteristic strong bands. The band observed at 3285 cm^{-1} is attributed to the N–H stretching vibration, while those at 1337 and 1171 cm^{-1} are due to $\nu_{as}(-SO_2-)$ and $\nu_s(-SO_2-)$ in $H_3L^1 \cdot H_2O$, respectively. The strong absorptions at 1709 and 1441 cm^{-1} are attributed to the asymmetric stretching vibration $\nu_{as}(COO^-)$ and the symmetric $\nu_s(COO^-)$ vibration, respectively. The structure of $H_3L^1 \cdot H_2O$, which was further confirmed by X-ray diffraction techniques, is shown in Figure 1. Both of the carboxylate groups are protonated. There are intermolecular hydrogen bonds between carboxylate oxygen atoms from the $C_6H_5COO^-$ motif (O···O distance: 2.630 Å) and hydrogen bonds between carboxylate oxygen atoms from the amino acid motif and the lattice water molecules (O···O distances: 2.837 and 2.823 Å, respectively), forming 1-D hydrogen-bonding chains in which six-membered-ring and eight-membered-ring units are alternately arranged along the *c* axis. These chains are assembled by hydrogen bonds between sulfonamide nitrogen atoms and sulfonamide oxygen atoms from adjacent chains to give rise to a 2-D layered supramolecular structure (N···O distance: 2.881 Å), as shown in Figure 2. Furthermore, the adjacent layers are connected by hydrogen bonds between the water molecules and oxygen atoms from the *N*-protected amino acid motif to afford a 3-D supramolecular structure (O···O distance: 2.573 Å).

Crystal Structure of 2

The structure analysis shows that the two Mn^{II} ions in **2** are both six-coordinate with a distorted octahedral geometry, as shown in Figure 3. The six atoms coordinated to each Mn^{II} ion come from four nitrogen atoms of two chelating phenyl groups and one oxygen atom of the COO^- group of benzoic acid, as well as one oxygen atom of the *N*-sulfonylglycine group. The Mn–O bond lengths are both 2.124(3) Å, and the Mn–N bond lengths are in the range 2.266(4)–2.342(3) Å, which are in the normal range of lengths observed in manganese(II) carboxylate complexes containing 2,2′-bipy or 1,10-phen. The Mn1 and Mn1A ions are linked together to form a dinuclear unit where $(HL^1)^{2-}$ acts as the bridging ligand. The two phen molecules are almost perpendicular with an intersecting angle of 99.7°.

Eight crystallographically unique free water molecules are observed in the unit of **2**, in which five water molecules form a $(H_2O)_{30}$ cluster associated by O–H···O hydrogen bonds as shown in Figure 4a. The $(H_2O)_{30}$ cluster consists of one $(H_2O)_{12}$ subunit and six $(H_2O)_3$ subunits. The lattice water molecules (O8 and O12) are associated by hydrogen bonds to form a puckered 12-membered ring (Figure 4b). Six dangling trimeric water clusters (O10, O4, and O7) at the periphery are attached to the 12-membered-ring core to

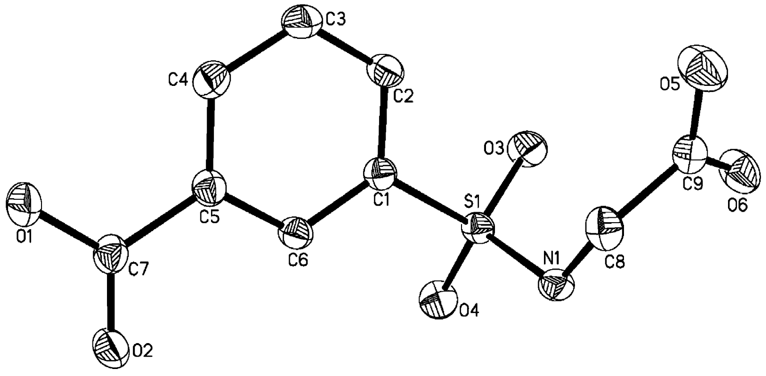


Figure 1. ORTEP representation (30% thermal probability ellipsoids) of the crystal structure of compound **1**. Hydrogen atoms and lattice water have been omitted for clarity.

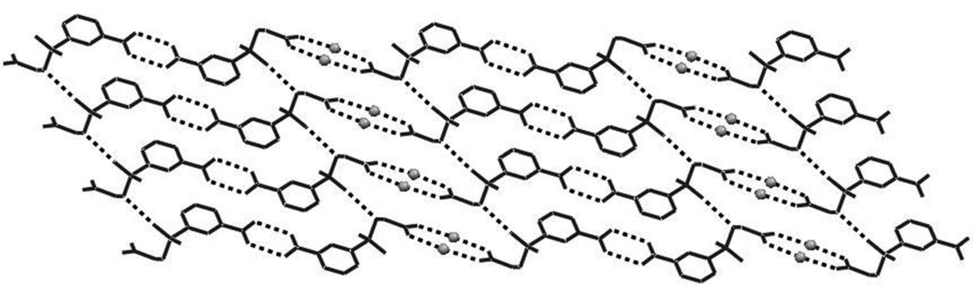


Figure 2. Perspective view of the 2-D structure through hydrogen bonds in compound **1**. Hydrogen atoms have been omitted for clarity.

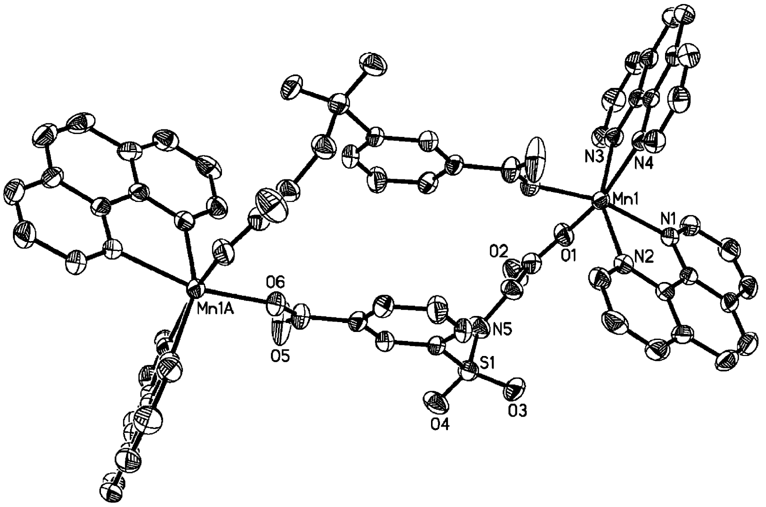
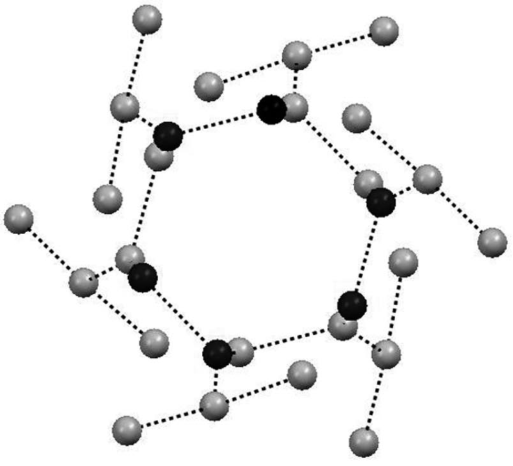
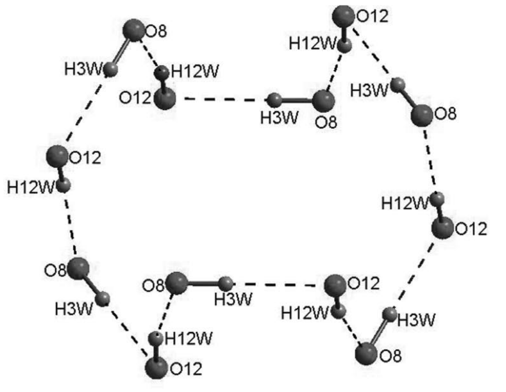


Figure 3. Molecular structure of **2** (30% thermal probability ellipsoids). Symmetry operations: i: *x*, *y*, *z* – 1; ii: –*x* + 1, –*y*, –*z*.

form an overall $(H_2O)_{30}$ cluster. The trimeric water clusters at the periphery are situated alternately above and below the puckered 12-membered ring so as to accommodate the six large dinuclear molecules. Apart from the interactions with the surrounding water molecules, O7 and O8 also act as hydrogen-bond donors to the uncoordinated oxygen atom (O2) of the *N*-protected amino acid with O···O distances of 2.779(9) and 2.728(9) Å, respectively. In the $(H_2O)_{30}$ cluster, the O···O distances range from 2.697(2) to 3.04(2) Å with an average distance of 2.80 Å, which is shorter than those observed in liquid water (2.85 Å)[20] and comparable to the corresponding value in the ice II phase (2.77–2.84 Å).[21] Furthermore, the inter-$(H_2O)_{12}$ ring water–water connections have an average O···O distance of 2.743 Å, which is close to the corresponding value of 2.759 Å in hexagonal ice (I_h)[22] but 0.033 Å shorter than 2.776 Å in the 2-D supramolecular ice-like layer containing $(H_2O)_{12}$ rings in the organic compound bpedo·$5H_2O$ [bpedo = (*E*)-1,2-bis(4-pyridyl)ethene dioxide].[23] This may be attributed to its different modes of connectivity with the surrounding water molecules and the interaction with the host molecule. The O···O distance between the water molecule at the core and the one connected to it at the periphery is 2.697(2) Å, which is the strongest hydrogen bonding in the $(H_2O)_{30}$ cluster. The O···O···O angles vary widely (ca. 95.12–132.83°) with an average of 109.54°, which is close to the corresponding value of 109.3° in hexagonal ice. Each O atom of the 12-membered ring shows tricoordination, just like water molecules at the surface of ice or liquid water where hydrogen-bond-deficient water molecules are present.[24] It is interesting to note that the other two types of water molecules, O9 and O13, form the water dimer as acceptor and donor, respectively. The dimers attach to the dinuclear unit by hydrogen bonds between O13 and O5 as well as hydrogen bonds between O9 and N5. The O···O and O···N distances are 2.688(2) and 2.959(9) Å, respectively.



(a)



(b)

Figure 4. Perspective view of the discrete $(H_2O)_{30}$ cluster (a) with the puckered 12-membered-water-ring core (b) in **2** (H14W of O8 and H11W of O12 are omitted for clarity).

Moreover, there exist orderly aromatic-ring-stacking interactions between phen ligands. The hexaatomic ring of the phen ligand forms strong π–π stacking with the same part of a phen ligand in another molecule with the distance of 3.468 Å. Interestingly, these hydrogen-bonding and π–π stacking interactions lead to a giant supramolecular unit consisting of six dinuclear molecules surrounding the $(H_2O)_{30}$ cluster (Figure 5). Each of these units acts as a secondary building unit and further form the 2-D supramolecular structure through π–π stacking and hydrogen-bonding interactions (Figure 6). It can be seen that more hydrophilic cavities are likely to be formed by choosing appropriate ligands containing hydrophilic groups, which prefer to interact with water molecules filled in the cavities through hydrogen bonding in the aqueous system.

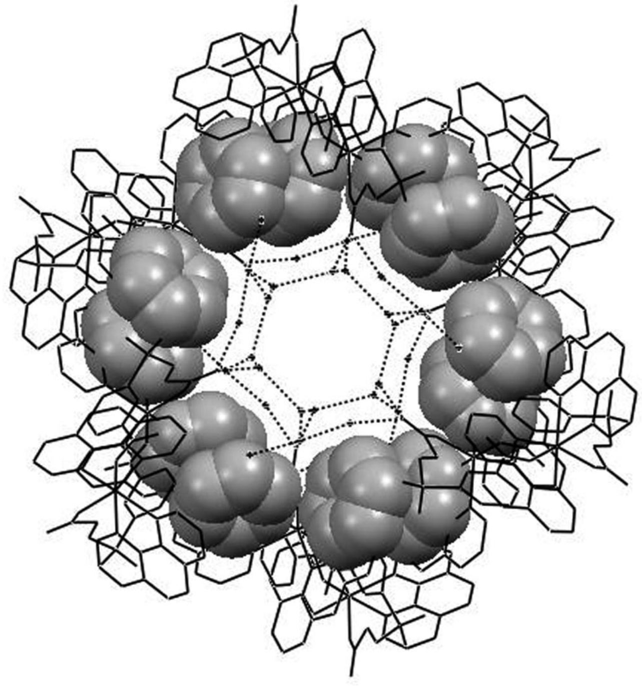


Figure 5. View showing the hydrogen bonding and π–π stacking interactions in the supramolecular unit in **2**.

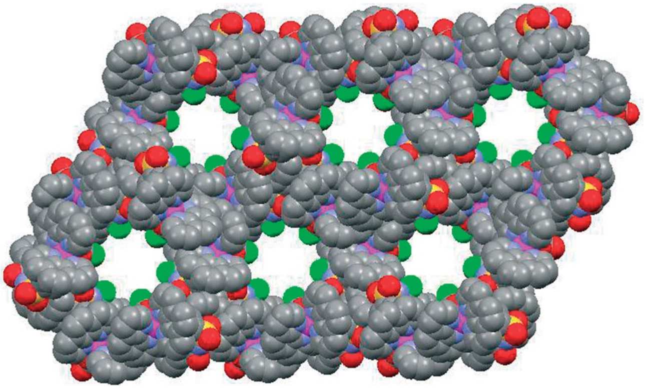


Figure 6. View of the 2-D supramolecular system of **2** showing hydrophilic cavities [green balls represent the hydrophilic oxygen atoms, $(H_2O)_{30}$ clusters are omitted for clarity].

A search of the latest version of the Cambridge Structural Database (CSD)[25] reveals rare examples of water $(H_2O)_{12}$ rings. Moreover, the reported water $(H_2O)_{12}$ rings are often planar or form 2-D water layers by inter-hydrogen-bonding interactions.[22,26] Here, the present mode of the discrete $(H_2O)_{12}$ ring core and the additional six dangling trimeric water clusters in compound **2** is rather unusual.

Crystal Structure of 3

The perchlorate ions display disorder in the crystal. Figure 7 only shows the structure of the coordinated cation. The structural unit of **3** contains two independent Mn^{II} ions: the Mn1 ion has a slightly distorted octahedral arrangement ($MnON_5$) with four nitrogen atoms from the phen ligand as well as one nitrogen atom and one carboxylate oxygen atom from the coordinated *N*-(phenylsulfonyl)-glycine dianion motif. The Mn(2) ion also has a slightly distorted octahedral environment (MnO_2N_4): four nitrogen atoms from two different phen molecules and one oxygen atom from the $C_6H_5COO^-$ motif as well as one water molecule. The Mn–O bond lengths are in the range 2.126(4)–2.148(4) Å, and the Mn–N bond lengths are in the range 2.153(4)–2.288(4) Å. The H_3L^1 ligand displays different coordination modes in **2** and **3**. In **3**, the $(L^1)^{3-}$ group acts as a trianion in a mono(bidentate) mode (O and N,O) and bridges two Mn atoms resulting in a dinuclear structure, whereas in **2**, each $(HL^1)^{2-}$ group acts as a bis(monodentate) (O,O) ligand to bridge two Mn^{II} ions. Overall, the li-

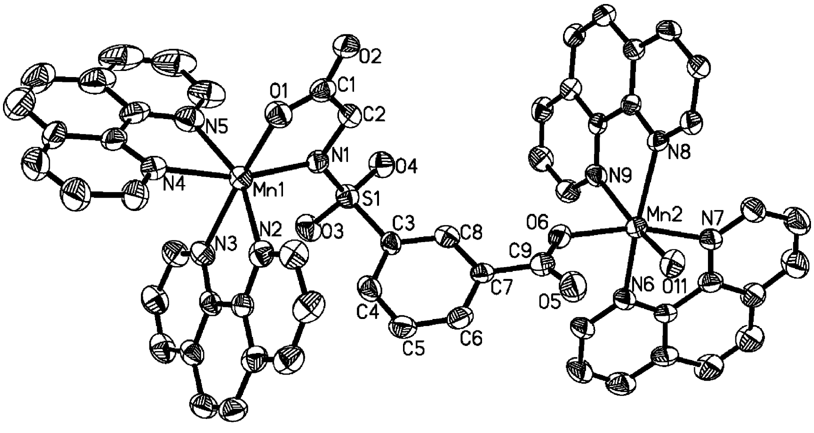
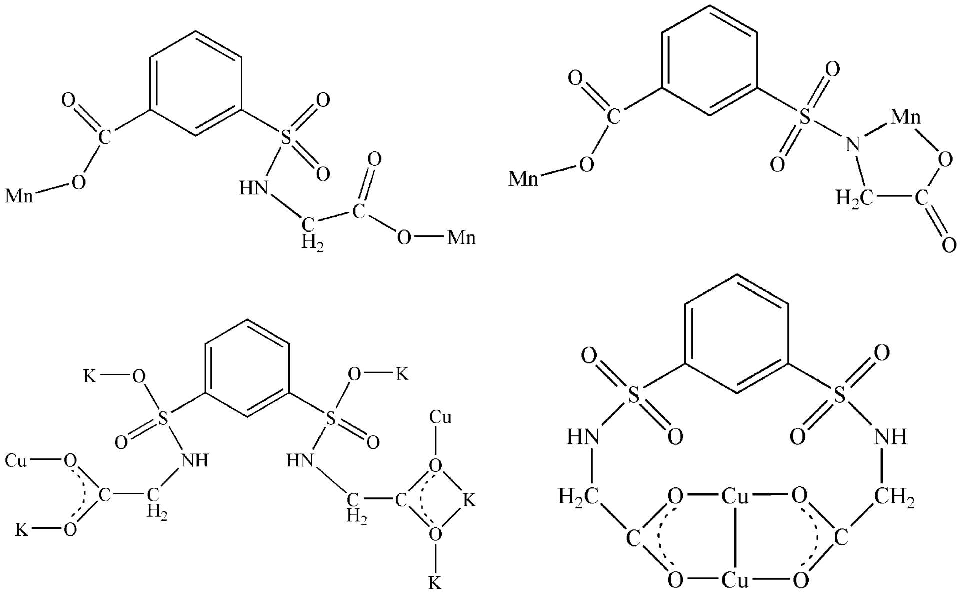


Figure 7. View of the coordination environment of Mn^{II} in compound **3**. Hydrogen atoms and perchlorate anions have been omitted for clarity.



Scheme 2. Coordination modes of $H_3L^1$and H_2L^2.

gand H_3L^1 can be used as a polydentate ligand to coordinate transition-metal ions into coordination polymers in different modes (Scheme 2). Further investigation of this structure suggests that discrete trimeric water clusters exist. Interestingly, the dinuclear structure is connected into a high-dimensional structure by the water trimer through hydrogen bonding between the water trimer and coordinated water molecules, sulfonamide oxygen atoms, carboxylate oxygen atoms, and perchlorate anions (Figure 8). It is obvious that the water trimer plays a crucial role in contributing to the stability of the host of **3**.

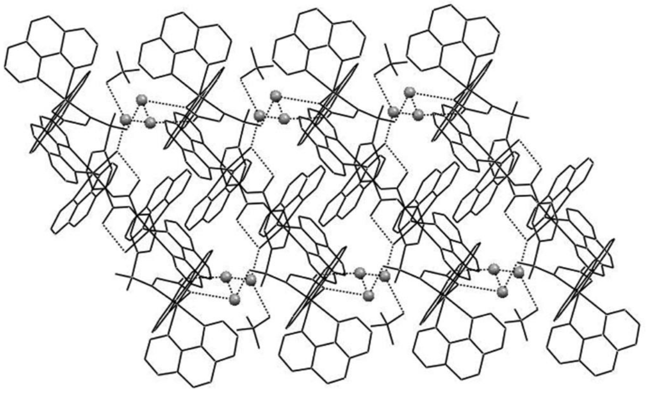


Figure 8. High-dimensional structure of **3** formed by the water trimer, perchlorate ions, and dinuclear units through hydrogen bonding.

Crystal Structure of 4

The crystal structure of $[K_2Cu(L^2)_2(H_2O)_2]_n$ consists of an asymmetric polynuclear $[K_2Cu(L^2)_2(H_2O)_2]$ structural unit. The copper atom is four-coordinate (CuO_4) (Figure 9). Four oxygen atoms from four different $(L^2)^{2-}$ ligands describe an approximately square coordination environment around the copper atom. The Cu–O bond lengths are 1.9260(13) and 1.9654(10) Å. Both of the potassium atoms are seven-coordinate by four carboxylate oxygen atoms (O7, O8, O3, O8A) from three $(L^2)^{2-}$ groups, two sulfonamide oxygen atoms (O2, O5) from the other two $(L^2)^{2-}$ groups, as well as one water molecule (O9) (Figure 9). The K–O bond lengths are in the range 2.6141(13)–3.1346(17) Å, which are in agreement with those reported for carboxylate and potassium heterometallic complexes.[27]

For every *N*,*N′*-(1,3-phenylenedisulfonyl)bis(glycine) ligand there are six oxygen atoms participating in coordination; the other two sulfonamide oxygen atoms (O1, O6) are free. One sulfonamide oxygen atom (O2 or O5) of every *N*-sulfonylglycine motif coordinates a potassium atom in a monodentate mode. The two flexible carboxylate groups of $(L^2)^{2-}$ exhibit different coordinating modes. One adopts a bis(monodentate) bridging mode, while the other displays an unusual μ_3-η^2:η^2 coordinating mode (each oxygen atom coordinates to two metal atoms, and the carboxylate group coordinates to three metal atoms). To the best of our knowledge, this type of coordinating mode of the amino acid ligand has not been observed in previously reported amino acid or *N*-protected amino acid complexes. Overall, the $(L^2)^{2-}$ group acts in a nonadentate coordination to link seven metal centers, as shown in Scheme 2.

It is worth noting that pairs of K atoms and a single Cu atom are arrayed alternately where the $(L^2)^{2-}$ group acts as a bridging ligand. The dimetallic K_2Cu units grow along the 101 direction to lead to the formation of the 1-D regular alternating chain (Figure 10). These chains are linked by K–O (sulfonamide oxygen atom) bonds to build 2-D planes, which constitute further a complicated 3-D structure owing to the K–O (carboxylate oxygen atom) bonds (Figure S1,

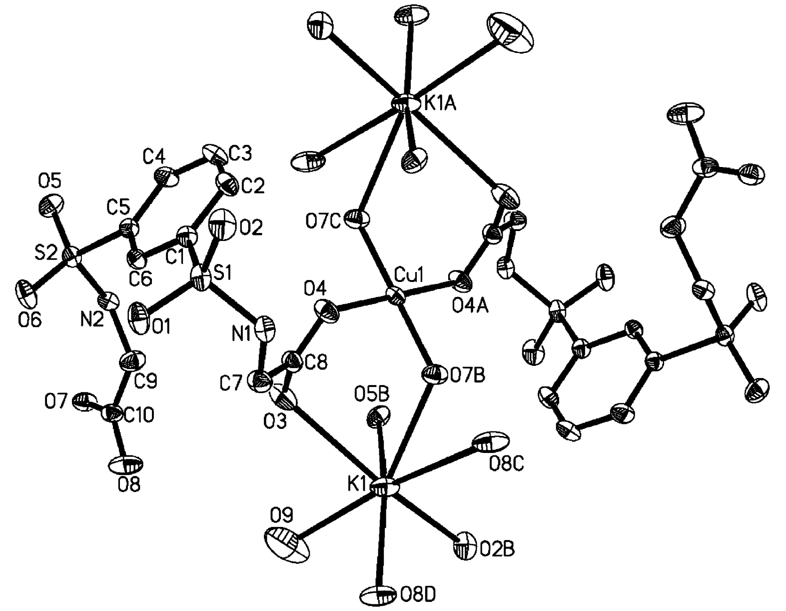


Figure 9. View of the Cu^{II} and K^{I} coordination environments in **4**. Symmetry operations: (a) $x + 1, y, z$; (b) $-x + 1, -y, -z + 1$; (c) $-x + 2, -y, -z + 1$; (d) $-x + 1, -y + 1, -z + 1$; (e) $x, y, z + 1$; (f) $-x + 2, -y + 1, -z + 1$; (g) $x, y, z - 1$; (h) $x - 1, y, z$.

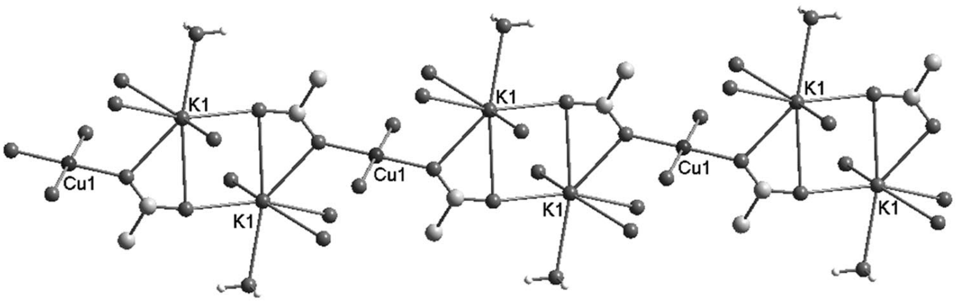


Figure 10. View of the K_2Cu dimetallic chain arrangement growing along the [101] direction in **4**. Unnecessary atoms are omitted for clarity.

Supporting Information). Obviously, the K–O bonds formed between the neighboring structural units play an important role in constructing the high-dimensional coordination polymer.

Crystal Structure of 5

The structure of **5** consists of a centrosymmetric dinuclear paddle-wheel unit in which four carboxylate groups bridge two copper atoms in a *syn*-*syn* disposition (Figure 11). Each copper atom has a square-pyramidal coordination environment in which four oxygen atoms of two $(L^2)^{2-}$ groups form an equatorial plane and one water molecule occupies an axial position. The axial $Cu–O_{water}$ distance is longer than the $Cu–O_{carboxylate}$ bond. Thus, the coordination geometry around the copper(II) atom can be regarded as a distorted square-pyramidal one, and the Jahn–Teller effect in the polymer manifests itself as an asymmetric elongation along the axial direction. The Cu–Cu distance is 2.643(2) Å. In general, copper(II) carboxylate complexes exhibit dinuclear paddle-wheel cage structures. Some 500 X-ray crystal structures containing the $Cu_2(OOCR)_4$ core can be found in the Cambridge Structural Database. In most structures, four different ligands are involved in coordination. Our results are different from those reported coordination polymers, because the second carboxylate group of $(L^2)^{2-}$ is also included in a paddle-wheel unit. Only one crystal structure of this type involving two ligands has been reported in the literature.[28] The ligand 2,9-bis(methoxymethyl)-2,9-dimethyl-4,7-dioxadecanedioic acid in the literature and our reported ligand are both flexible, and the distances between the two carboxylate groups are so long that they can rotate to embrace two copper ions in the opposite direction.

Several kinds of hydrogen bonding are observed in the structure: (a) hydrogen bonding between lattice water and coordinated water [the O···O distance is 3.001(8) Å.]; (b) hydrogen bonding between lattice water and sulfonamide nitrogen atom [the N···O distance is 2.929(6) Å]; (c) hydrogen bonding between lattice water and coordinated carboxylate oxygen atom [the O···O distances are 2.965(6) and 3.001(8) Å, respectively]; (d) hydrogen bonding between sul-

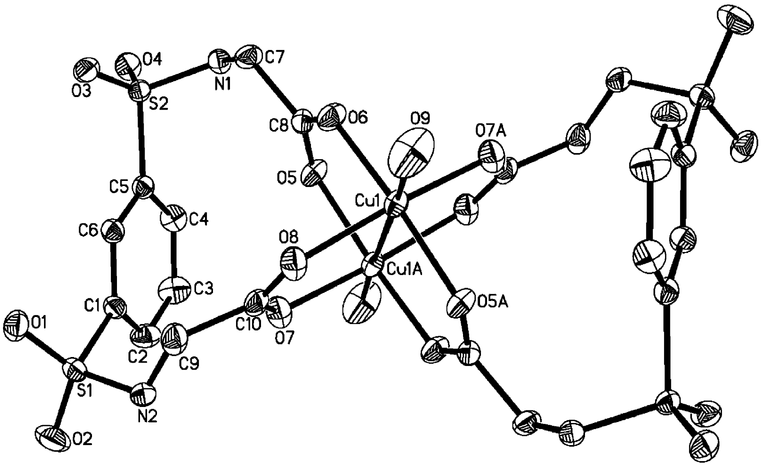


Figure 11. Representation of the dinuclear unit in **5**. Symmetry operation: $-x + 2$, $-y + 1$, $-z + 2$.

fonamide nitrogen atom and sulfonamide oxygen atom [the N···O distance is 2.962(5)]. Interestingly, the paddle-wheel units are associated by the above hydrogen bonds to form a one-dimensional chain (Figure 12). These chains are assembled by hydrogen bonds between sulfonamide oxygen atoms and water molecules from adjacent chains (the O···O distance is 2.797 Å) to give rise to a 2-D layer supramolecular structure.

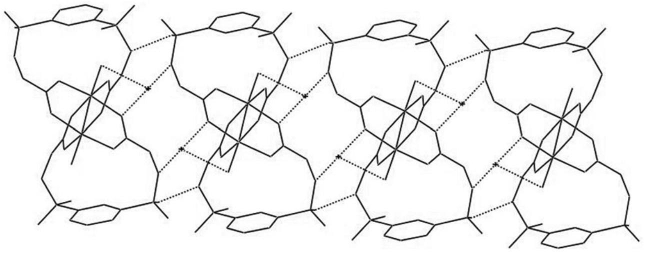


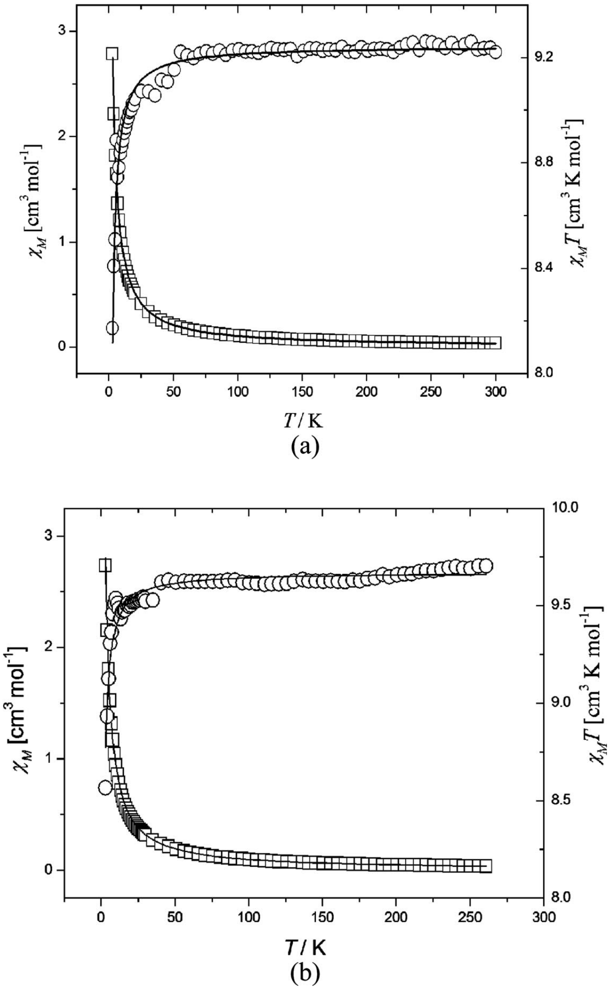
Figure 12. H-bond system providing a one-dimensional array in **5**.

Thermogravimetric Analysis

The TG analysis of **2** shows the onset of water loss at 30 °C. Water removal takes place without showing any distinct plateau in the curve, giving a total loss of 17.87% at about 165 °C, which corresponds to loss of all water molecules (calcd. 17.63%). Complete decomposition of the compound is achieved above 700 °C. The TG analysis of **3** shows that the first weight loss of 5.36% (calcd. 5.73%) observed from 30 to 225 °C corresponds to the loss of three lattice water molecules and one coordinated water per formula unit. The second process might include two steps from 225 to 720 °C. This represents the decomposition of the material. The final residue of 11.41% is close to the 11.28% calculated on the basis of MnO (Figure S2, Supporting Information, shows the TG curves for **2** and **3**).

Magnetic Properties

The magnetic susceptibilities of **2–5** were measured in the 2–300 K temperature range and shown as $\chi_M T$ and χ_M vs. T plots in Figures 13 and 14. The experimental $\chi_M T$ values of **2** and **3** at room temperature are 9.22 and 9.66 cm^3 K mol^{-1}, respectively, both of which are larger than

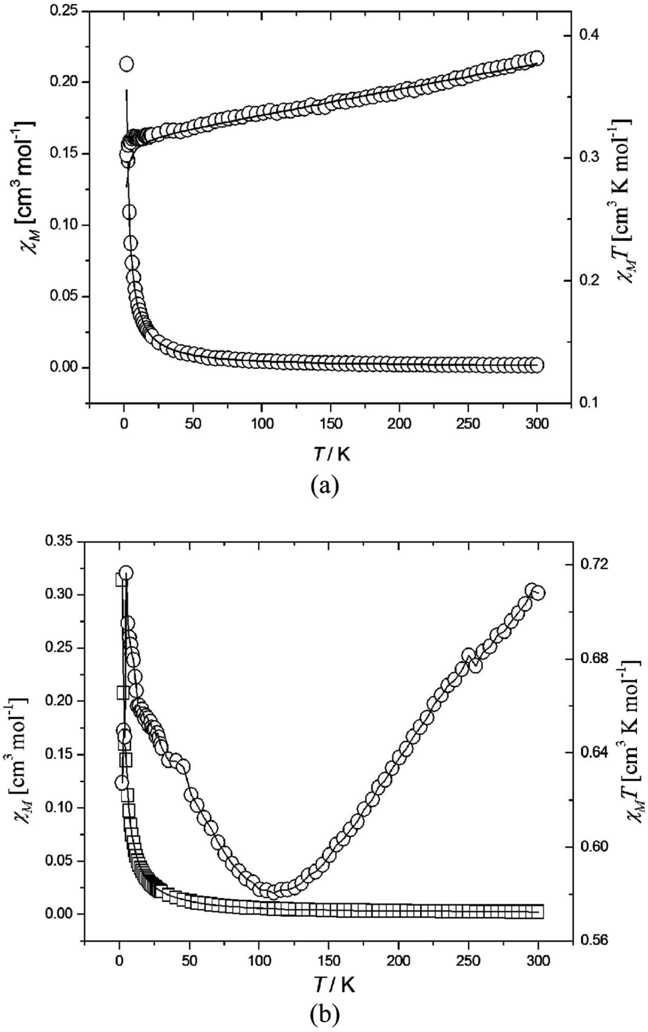


(a)

(b)

Figure 13. Temperature dependence of $\chi_M T$ and χ_M for **2** (a) and **3** (b). The solid line represents the theoretical values based on Equation (1) described in the text.

that expected for five independent coupled spins ($8.75\ \mathrm{cm^3\,K\,mol^{-1}}$, $S = 5/2$) of $\mathrm{Mn^{II}}$. As the temperature is lowered to 2 K, the $\chi_M T$ products decrease first slowly and then rapidly. This behavior suggests that antiferromagnetic interactions are operative in **2** and **3**.



(a)

(b)

Figure 14. Experimental temperature dependence of $\chi_M T$ and χ_M for **4** (a) and **5** (b).

In order to quantitatively evaluate these magnetic interactions in the system, for similar dinuclear $\mathrm{Mn^{II}}$ complexes, Equation (1) is induced from the Hamiltonian $\hat{H} = -JS_1S_2$.[29]

$$\chi_M = 2\,\frac{Ng^2\beta^2}{kT}\,\frac{A}{B} \qquad (1)$$

$A = \exp[2J/KT] + 5\exp[6J/KT] + 14\exp[12J/KT] + 30\exp[20J/KT] + 55\exp[30J/KT]$

$B = 1 + 3\exp[2J/KT] + 5\exp[6J/KT] + 7\exp[12J/KT] + 9\exp[20J/KT] + 11\exp[30J/KT]$

The least-squares analysis of the magnetic susceptibility data leads to $J = -0.09\ \mathrm{cm^{-1}}$, $g = 2.21$, and $R = 2.88 \times 10^{-4}$ for **2** and $J = -0.07\ \mathrm{cm^{-1}}$, $g = 2.10$, and $R = 2.06 \times 10^{-4}$ for **3**. The J values indicate a weakly antiferromagnetic interaction between the two $\mathrm{Mn^{II}}$ ions bridged by *N*-[(3-carboxyphenyl)sulfonyl]glycine. Their low magnitude can be associated with the excessive span of the $\mathrm{H_3L^1}$ bridge.

The experimental $\chi_M T$ value of **4** at room temperature is $0.38\ \mathrm{cm^3\,K\,mol^{-1}}$ per $\mathrm{Cu^{II}}$ ion, close to the spin value expected for an uncoupled $\mathrm{Cu^{II}}$ ion ($0.375\ \mathrm{cm^3\,K\,mol^{-1}}$). As the temperature is lowered to 2 K, the $\chi_M T$ value decreases. This behavior suggests that an antiferromagnetic interaction is operative in **4**. The temperature dependence of the reciprocal susceptibilities ($1/\chi_M$) obeys the Curie–Weiss law above 5 K with $\theta = -6.113$ K. The negative θ value further supports the presence of overall antiferromagnetic interactions in **4**.

Although **4** leads to a three-dimensional network, magnetic interactions are operative between the shortest Cu–Cu distances, and no magnetic coupling could be taking place through the K atoms. The magnetic susceptibility data were fitted by assuming that the $(\mathrm{L^2})^{2-}$ bridges between the $\mathrm{Cu^{II}}$ ions form a uniform chain with a Cu–Cu separation of 8.662 Å (Figure S3, Supporting Information). To simulate the experimental magnetic behavior, we used the analytical expression for a one-dimensional Heisenberg chain of classical spins ($S = 1/2$), which is similar to **4**.[30]

$$\chi_M = (Ng^2\beta^2/KT)[(A + BX + CX^2)/(1 + DX + EX^2 + FX^3)]$$

where χ_M denotes the susceptibility per $\mathrm{Cu^{II}}$ complex, $X = |J|/KT$, $A = 0.25$, $B = 0.14995$, $C = 0.30094$, $D = 1.9862$, $E = 0.68854$, and $F = 6.0626$.

The least-squares analysis of the magnetic susceptibility data led to $J = -0.15\ \mathrm{cm^{-1}}$, $g = 2.17$, and $R = 3.92 \times 10^{-4}$. The J value indicates a weakly antiferromagnetic interaction between the two $\mathrm{Cu^{II}}$ ions bridged by $(\mathrm{L^2})^{2-}$.

The $\chi_M T$ value of **5** at room temperature is $0.71\ \mathrm{cm^3\,K\,mol^{-1}}$, which falls in the normal range of two non-coupled $\mathrm{Cu^{II}}$ ions. Upon cooling, $\chi_M T$ decreases continuously down to a minimum of $\chi_M T = 0.58055\ \mathrm{cm^3\,K\,mol^{-1}}$ about 110 K before rapidly reaching a sharp maximum of $\chi_M T = 0.71654\ \mathrm{cm^3\,K\,mol^{-1}}$ at 5 K. This behavior is characteristic of a ferrimagnet. Below 5 K, $\chi_M T$ quickly decreases. This is a classical behavior with antiferromagnetic order.[31] Further studies probing this phenomenon are currently in progress.

Conclusions

Two novel versatile glycine derivatives were synthesized successfully by the reaction of 3-carboxybenzenesulfonyl chloride or 1,3-phenylenebis(sulfonyl chloride) with glycine. They will enrich the coordination chemistry of organic aromatic polycarboxylates and amino acids. The versatile ligands have been introduced to construct four $\mathrm{Cu^{II}}$ and $\mathrm{Mn^{II}}$ complexes simply by changing the pH value or the base. We have observed a hitherto unknown discrete $(\mathrm{H_2O})_{30}$ cluster in **2**. The present mode of association of a puckered 12-membered ring fused with six dangling trimeric water clusters has not been predicted theoretically nor previously reported experimentally. Magnetic properties of the four complexes were also measured. Future studies will focus on the construction of new metal–organic coordination polymers from these two ligands and their isomers.

Experimental Section

Materials and Instruments: All reagents used in the syntheses were of analytical grade. Elemental analyses for carbon, hydrogen, and nitrogen atoms were performed with a Vario EL III elemental analyzer. Infrared spectra (4000–600 cm^{-1}) were recorded by using KBr pellets with an Avatar™ 360 ESP IR spectrometer. Crystal determination was performed with a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å). Variable-temperature magnetic susceptibilities were measured with an MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms. Thermogravimetric (TG) analyses were carried out with an STA449C integration thermal analyzer.

Synthesis of $H_3L^1{\cdot}H_2O$ (1): To a solution of glycine (2.25 g, 0.03 mol) in NaOH (2 M, 30 mL), 3-carboxybenzenesulfonyl chloride (6.78 g, 0.03 mol) was added. The mixture was stirred at room temperature for 2 h. Then the aqueous solution was acidified to pH = 4 with hydrochloric acid (6 M), and a white solid derivative began to crystallize at once. The crystals were collected on a filter and recrystallized from alcohol (50%), with a yield of about 65%. $C_9H_{11}NO_7S$ (277.25): calcd. C 38.99, H 4.0, N 5.05; found C 38.90, H 3.92, N 4.95. IR (KBr): $\tilde{\nu}$ = 3285 (s), 1709 (s), 1441 (s), 1171 (m), 753 (m), 1337 (s), 894 (m) cm^{-1}.

Synthesis of $[Mn_2(HL^1)_2(phen)_4]{\cdot}16H_2O$ (2): A mixture of $Mn(ClO_4)_2{\cdot}6H_2O$ (0.18 g, 0.5 mmol) and H_3L^1 (0.23 g, 1 mmol) in water (15 mL) was stirred. Then the pH was adjusted to around 5 with NaOH (1 M), and an ethanol solution of phen (0.2 g, 1 mmol, 3 mL) was added. The reaction mixture was heated with a water bath at 70 °C for 10 h and then filtered. Yellow crystals separated from the mother liquor by slow concentration at room temperature after 2 weeks. $C_{66}H_{78}Mn_2N_{10}O_{28}S_2$ (1633.39): calcd. C 48.53, H 4.81, N 8.57; found C 48.64, H 4.69, N 8.50. IR (KBr): $\tilde{\nu}$ = 3415 (s), 1599 (s), 1425 (s), 1169 (m), 729 (m), 1383 (s), 847 (m) cm^{-1}. The IR spectrum shows a broad band centered around 3415 cm^{-1}, which is comparable to the O–H stretching vibrations of water clusters in other complexes.[6d,6f]

Synthesis of $[Mn_2L^1(phen)_4(H_2O)]ClO_4{\cdot}3H_2O$ (3): Complex **3** was synthesized in a procedure analogous to that of **2**, except that the pH value was adjusted to around 7 with NaOH (1 M). $C_{57}H_{46}ClMn_2N_9O_{14}S$ (1258.42): calcd. C 54.40, H 3.68, N 10.01; found C 54.31, H 3.57, N 9.91. IR (KBr): $\tilde{\nu}$ = 3452 (s), 1592 (s), 1423 (s), 1102 (s), 1172 (m), 725 (m), 1385 (s), 849 (m) cm^{-1}.

Synthesis of $[K_2Cu(L^2)_2(H_2O)_2]_n$ (4): To a solution of 1,3-phenylenebis(sulfonyl chloride) (0.289 g, 1 mmol), glycine (0.150 g, 2 mmol), and KOH (0.175 g, 3 mmol) was added a hot water (30 mL) solution of $Cu(OAc)_2{\cdot}2H_2O$ (0.193 g, 1 mmol). The reaction mixture was then heated with a water bath at 70 °C for 8 h and then filtered. Blue crystals separated from the mother liquor by slow concentration at room temperature after 2 weeks. $C_{20}H_{24}CuK_2N_4O_{18}S_4$ (878.41): calcd. C 27.35, H 2.75, N 6.38; found C 27.46, H 2.92, N 6.29. IR (KBr): $\tilde{\nu}$ = 3257 (s), 1585 (s), 1423 (s), 1161 (m), 709 (m), 1393 (s), 884 (m) cm^{-1}.

Synthesis of $[Cu(L^2)(H_2O)]_2{\cdot}2H_2O$ (5): Complex **5** was prepared in a similar manner to that of **4** by using triethylamine instead of KOH. $C_{20}H_{28}Cu_2N_4O_{20}S_4$ (899.78): calcd. C 26.70, H 3.14, N 6.23; found C 26.79, H 3.25, N 6.15. IR (KBr): $\tilde{\nu}$ = 3297 (s), 1651 (s), 1431 (s), 1156 (m), 715 (m), 1383 (s), 872 (m) cm^{-1}.

Crystallographic Data Collection and Structural Determination: Single-crystal X-ray diffraction analyses of the five compounds were carried out. The single crystals of **1**–**5** were placed in a Bruker SMART APEX II CCD diffractometer, and diffraction data were obtained by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) with an ω-2θ scan technique at room temperature. The structures were solved by direct methods with SHELXS-97.[32] A full-matrix least-squares refinement on F^2 was carried out by using SHELXL-97.[33] The final agreement factors are R_1 = 0.0400, wR_2 = 0.1119 for **1**, R_1 = 0.0775, wR_2 = 0.2255 for **2**, R_1 = 0.0711, wR_2 = 0.1612 for **3**, R = 0.0330, wR_2 = 0.0918 for **4**, and R = 0.0448, wR_2 = 0.1049 for **5**. Crystallographic data and selected bond lengths and angles for **1**–**5** are listed in Table 1 and Tables S1–S2 in the Supporting Information. CCDC-632830, -632586, -632588, -632589, and -632590 contain the supplementary crystal-

Table 1. Crystallographic data for **1**–**5**.

Compound	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_9H_{11}NO_7S$	$C_{66}H_{78}Mn_2N_{10}O_{28}S_2$	$C_{57}H_{46}ClMn_2N_9O_{14}S$	$C_{20}H_{24}CuK_2N_4O_{18}S_4$	$C_{20}H_{28}Cu_2N_4O_{20}S_4$
Formula weight	277.25	1633.39	1258.42	878.41	899.78
Crystal system	monoclinic	rhombohedral	triclinic	triclinic	triclinic
Space group	$C2/c$	$R\bar{3}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	a = 40.620(6) Å b = 5.1473(7) Å c = 11.326(2) Å β = 99.170(2)°	a = 33.9311(7) Å b = 33.9311(7) Å c = 19.7253(8) Å γ = 120°	a = 8.6762(14) Å b = 17.202(3) Å c = 20.879(3) Å α = 104.806(2)° β = 91.646(2)° γ = 104.082(2)°	a = 8.6624(10) Å b = 9.8659(11) Å c = 10.6864(12) Å α = 62.9880(10)° β = 84.0450(10)° γ = 78.2360(10)°	a = 8.398(8) Å b = 9.360(9) Å c = 10.788(10) Å α = 88.813(11)° β = 75.571(11)° γ = 78.950(11)°
Volume [Å^3], Z	2337.8(6), 8	19667.5(10), 9	2908.4(8), 2	796.50(16), 1	805.7(13), 1
Calculated density [Mg m^{-3}]	1.575	1.241	1.437	1.831	1.854
F(000)	1152	7650	1292	447	458
Crystal size [mm]	0.34 × 0.23 × 0.07	0.39 × 0.28 × 0.22	0.25 × 0.14 × 0.10	0.37 × 0.30 × 0.25	0.22 × 0.16 × 0.11
Goodness of fit	1.082	1.016	1.013	1.060	1.054
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0400, wR_2 = 0.1119	R_1 = 0.0775, wR_2 = 0.2255	R_1 = 0.0711, wR_2 = 0.1612	R_1 = 0.0330, $wR2$ = 0.0918	R_1 = 0.0448, $wR2$ = 0.1049
R indices (all data)	R_1 = 0.0470, $wR2$ = 0.1171	R_1 = 0.1322, $wR2$ = 0.2839	R_1 = 0.1754, $wR2$ = 0.2119	R_1 = 0.0357, $wR2$ = 0.0940	R_1 = 0.0644, $wR2$ = 0.1165
Largest diff. peak/hole [e Å^{-3}]	0.449/–0.551	0.790/–0.516	0.955/–0.426	0.586/–0.893	0.689/–0.706

lographic data for this paper. These data can be obtained free of charge at 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 (see footnote on the first page of this article): Thermogravimetric curves, selected bond lengths and angles, additional crystallographic figures.

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[1] a) L. F. Anne-Marie, A. L. David, J. L. Paul, M. Z. Alexandra, D. B. Walker, *J. Am. Chem. Soc.* **2005**, *127*, 12612–12619; b) D. M. Shin, I. S. Lee, Y. K. Chung, *Inorg. Chem.* **2003**, *42*, 8838–8846; c) M. Dinca, A. F. Yu, J. R. Long, *J. Am. Chem. Soc.* **2006**, *128*, 8904–8913; d) Y. Kubota, M. Takata, R. Matsuda, R. Kitaura, S. Kitagawa, K. Kato, M. Sakata, T. C. Kobayashi, *Angew. Chem. Int. Ed.* **2005**, *44*, 920–923.

[2] a) I. M. Müller, R. Robson, *Angew. Chem. Int. Ed.* **2000**, *39*, 4357–4359; b) B. F. Abrahams, J. Coleiro, B. F. Hoskins, R. Robson, *Chem. Commun.* **1996**, 603–604; c) Y. L. Wei, H. W. Hou, L. K. Li, Y. T. Fan, Y. Zhu, *Cryst. Growth Des.* **2005**, *5*, 1405–1413.

[3] a) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330; b) H. Abourahma, A. W. Coleman, B. Moulton, B. Rather, P. Shahgaldian, M. J. Zaworotko, *Chem. Commun.* **2001**, 2380–2381; c) Q. Y. Liu, L. Xu, *Eur. J. Inorg. Chem.* **2006**, 1620–1628; d) X. J. Li, R. Cao, D. F. Sun, W. H. Bi, Y. Q. Wang, X. Li, M. C. Hong, *Cryst. Growth Des.* **2004**, *4*, 775–780; e) L. Y. Zhang, J. P. Zhang, Y. Y. Lin, X. M. Chen, *Cryst. Growth Des.* **2006**, *6*, 1684–1689.

[4] a) A. D. Burrows, A. S. Donovan, R. W. Harrington, M. F. Mahon, *Eur. J. Inorg. Chem.* **2004**, 4686–4695; b) J. E. V. Babb, A. D. Burrows, R. W. Harrington, M. F. Mahon, *Polyhedron* **2003**, *22*, 673–686; c) H. F. Zhu, J. Fan, T. Okamura, Z. H. Zhang, G. X. Liu, K. B. Yu, W. Y. Sun, N. Ueyama, *Inorg. Chem.* **2006**, *45*, 3941–3948.

[5] a) L. F. Ma, L. Y. Wang, J. G. Wang, Y. F. Wang, X. Feng, *Inorg. Chim. Acta* **2006**, *359*, 2241–2245; b) L. F. Ma, Y. F. Wang, L. Y. Wang, J. G. Wang, X. Feng, *Z. Anorg. Allg. Chem.* **2006**, *632*, 675–678; c) L. F. Ma, L. Y. Wang, J. G. Wang, Y. F. Wang, X. Feng, *Z. Anorg. Allg. Chem.* **2006**, *632*, 487–490.

[6] a) B. Sreenivasulu, J. J. Vittal, *Angew. Chem. Int. Ed.* **2004**, *43*, 5769–5772; b) S. Pal, N. B. Sankaran, A. Samanta, *Angew. Chem. Int. Ed.* **2003**, *42*, 1741–1743; c) K. Raghuraman, K. K. Katti, L. J. Barbour, N. Pillarsetty, C. L. Barnes, K. V. Katti, *J. Am. Chem. Soc.* **2003**, *125*, 6955–6961; d) J. N. Moorthy, R. Natarajan, P. Venugopalan, *Angew. Chem. Int. Ed.* **2002**, *41*, 3417–3420; e) J. Lu, J. H. Yu, X. Y. Chen, P. Cheng, X. Zhang, J. Q. Xu, *Inorg. Chem.* **2005**, *44*, 5978–5979; f) M. S. Deshpande, A. S. Kumbhar, V. G. Puranik, K. Selvaraj, *Cryst. Growth Des.* **2006**, *6*, 743–748.

[7] S. Supriya, S. Manikumari, P. Raghavaiah, S. K. Das, *New J. Chem.* **2003**, *27*, 218–220.

[8] a) U. Mukhopadhyay, I. Bernal, *Cryst. Growth Des.* **2005**, *5*, 1687–1689; b) R. J. Doedens, E. Yphannes, M. I. Khan, *Chem. Commun.* **2002**, 62–63.

[9] a) J. L. Atwood, L. J. Barbour, T. J. Ness, C. L. Raston, P. L. Raston, *J. Am. Chem. Soc.* **2001**, *123*, 7192–7193; b) S. K. Ghosh, P. K. Bharadwaj, *Eur. J. Inorg. Chem.* **2005**, 4886–4889.

[10] a) L. J. Barbour, G. W. Orr, J. L. Atwood, *Nature* **1998**, *393*, 671–673; b) L. J. Barbour, G. W. Orr, J. L. Atwood, *Chem. Commun.* **2000**, 859–860; c) U. Mukhopadhyay, I. Bernal, *Cryst. Growth Des.* **2006**, *6*, 363–365.

[11] P. S. Lakshminarayanan, E. Suresh, P. Ghosh, *Angew. Chem. Int. Ed.* **2006**, *45*, 3807–3811.

[12] a) S. K. Ghosh, P. K. Bharadwaj, *Angew. Chem. Int. Ed.* **2004**, *43*, 3577–3580; b) S. Neogi, G. Savitha, P. K. Bharadwaj, *Inorg. Chem.* **2004**, *43*, 3771–3773.

[13] S. K. Ghosh, P. K. Bharadwaj, *Inorg. Chem.* **2004**, *43*, 6887–6889.

[14] a) L. Beitone, C. Huguenard, A. Gansmüller, M. Henry, F. Taulelle, T. Loiseau, G. Fèrey, *J. Am. Chem. Soc.* **2003**, *125*, 9102–9110; b) M. Henry, F. Taulelle, T. Loiseau, L. Beitone, G. Fèrey, *Chem. Eur. J.* **2004**, *10*, 1366–1372.

[15] a) M. L. Wei, C. He, W. J. Hua, C. Y. Duan, S. H. Li, Q. J. Meng, *J. Am. Chem. Soc.* **2006**, *128*, 13318–13319; b) P. S. Lakshminarayanan, E. Suresh, P. Ghosh, *J. Am. Chem. Soc.* **2005**, *127*, 13132–13133.

[16] L. Cheng, J. B. Lin, J. Z. Gong, A. P. Sun, B. H. Ye, X. M. Chen, *Cryst. Growth Des.* **2006**, *6*, 2739–2746.

[17] E. Westhoff (Ed.), *Water and Biological Macromolecules*, CRC Press, Boca Raton, FL, **1993**.

[18] J. L. Alonso, E. J. Cocinero, A. Lesarri, M. E. Sanz, J. C. López, *Angew. Chem. Int. Ed.* **2006**, *45*, 3471–3474.

[19] a) C. A. Bonamartini, E. Gozzoli, L. Menabue, M. Saladini, L. P. Battaglia, P. Sgrabtto, *J. Chem. Soc. Dalton Trans.* **1994**, *3*, 273–278; b) G. Battistuzzi, M. Borsari, L. Menabue, M. Saladini, *Inorg. Chem.* **1996**, *35*, 4239–4247.

[20] a) R. J. Speedy, J. D. Madura, W. L. Jorgensen, *J. Phys. Chem.* **1987**, *91*, 909–913; b) A. H. Narten, W. E. Thiessen, L. Blum, *Science* **1982**, *217*, 1033–1034.

[21] G. A. Jeffrey, *An Introduction to Hydrogen Bonding 1*, Oxford University Press, Oxford, **1997**.

[22] The value is taken from the data at 200 K. D. Eisenberg, W. Kauzmann, *The Structure and Properties of Water*, Oxford University Press, Oxford, **1969**.

[23] B. Q. Ma, H. L. Sun, S. Gao, *Angew. Chem. Int. Ed.* **2004**, *43*, 1374–1376.

[24] C. J. Gruenloh, J. R. Carney, C. A. Arrington, T. S. Zwier, S. Y. Fredericks, K. D. Jordan, *Science* **1997**, *276*, 1678–1681.

[25] There are some related examples of the $(H_2O)_{12}$ rings in the Cambridge Structural Database (CSD) (ref. codes: WECDAJ, ZAWNIU, ZAWNEQ, ZUDBUV, ZAWMUF, YOMVIF, MPYRHG).

[26] C. Janiak, T. G. Scharman, *J. Am. Chem. Soc.* **2002**, *124*, 14010–14011.

[27] X. Q. Shen, H. B. Qiao, Z. J. Li, H. Y. Zhang, H. L. Liu, R. Yang, P. K. Chen, H. W. Hou, *Inorg. Chim. Acta* **2006**, *359*, 642–648.

[28] G. Ferguson, A. J. McAlees, R. McCrindle, R. J. Restivo, P. J. Roberts, *J. Am. Chem. Soc.* **1977**, *99*, 3170–3171.

[29] R. L. Carlin, *Magnetochemistry*, Springer, Berlin, **1986**.

[30] a) H. Ojima, K. Nomoyama, *Coord. Chem. Rev.* **1988**, *92*, 85–111; b) X. H. Bu, M. Du, Z. L. Shang, R. H. Zhang, D. Z. Liao, *Inorg. Chem.* **2000**, *39*, 4190–4199.

[31] a) M. B. Salah, S. Vilminor, G. André, M. Richard-Plouet, F. Bourée-Vigneron, T. M. Hiri, M. Kurmoo, *Chem. Eur. J.* **2004**, *10*, 2048–2057; b) J. H. Yu, L. Ye, H. Ding, Y. Chen, Q. Hou, X. Zhang, J. Q. Xu, *Inorg. Chem. Commun.* **2007**, *10*, 159–162.

[32] G. M. Sheldrick, *SHELXS97, Program for the Solution of Crystal Structures*, University of Göttingen, Germany, **1997**.

[33] G. M. Sheldrick, *SHELXL97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

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