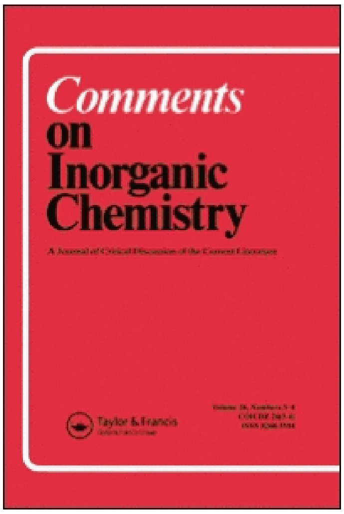

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Supramolecular Architectures Based on trans -Oxamidato-Bridged Copper(II) Synthons and Intramolecular Synergism

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Supramolecular Architectures Based on trans-Oxamidato-Bridged Copper(II) Synthons and Intramolecular Synergism

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The trans-*oxamidato dicopper(II) "synthons", $[Cu_2(\text{trans-}L)]^{2+}$ (L = oxen, oxpn, oxap, and oxpy) have been used as construction units when further connected by a second bridging ligand L′ (spacer) to fabricate supramolecular architectures via covalent and hydrogen bonding interactions. The structural topologies of the polymeric networks contained by these compounds depend mainly on the coordination modes of the spacers. When the spacers are 2-connectors bridging two synthons, the resulting compounds usually contain 1-D infinite chains, while 3- or 4-connector provides compounds containing 2-D extended coordination networks. The hydrogen bonds, in which the oxamidate, the spacer, and the water molecules are involved, are prevalent and the predominant intermolecular interactions. Compared with the polymeric networks constructed via covalent bonding interactions between synthons and spacers, the structural topologies of the 3-D supramolecular architectures fabricated via hydrogen bonding interactions are more complicated and difficult to predict. The structural parameters of the chelate rings in the*

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compounds have been discussed and found to change in rather small ranges and the skeleton of each synthon is rigid, which embodies the intramolecular synergistic effect in the supramolecular architectures.

Keywords: oxamidato complexes; synthons; supramolecular architectures; polymeric networks; synergism

INTRODUCTION

Crystal engineering, the planning and construction of crystalline supramolecular architectures from modular building blocks (synthons), continues to be a popular field of research[1–4] and offers the promise of purposefully designing new materials with particular structures possessing properties such as conductivity, superconductivity, microporosity, molecular magnetism, or non-linear optical behavior. Besides the new physical phenomena and novel applications resulting from the presence of building blocks with distinct properties in the assemblies, many new and exciting structural types unprecedented in inorganic compounds and minerals can be observed, which contribute ever more to our knowledge of the self-assembly processes and of the self-organization of supramolecular architectures. Among the building blocks employed in the design of supramolecular networks, most are obtained directly from metal salts and spacers with participation of organic ligand.[5] However, some mono-, di-, or oligo-nuclear metal complexes have recently been found to be efficient construction units for the fabrication of such frameworks.[6] A novel class of assemblies containing coordination polymeric networks with *trans*-oxamidato-bridged dicopper(II) complexes as the construction units (synthons) is described here. The robustness of the synthons depicted as synergistic effect makes it possible sometimes to predict the structural topologies of the polymeric frameworks according to the coordination modes of the spacers.

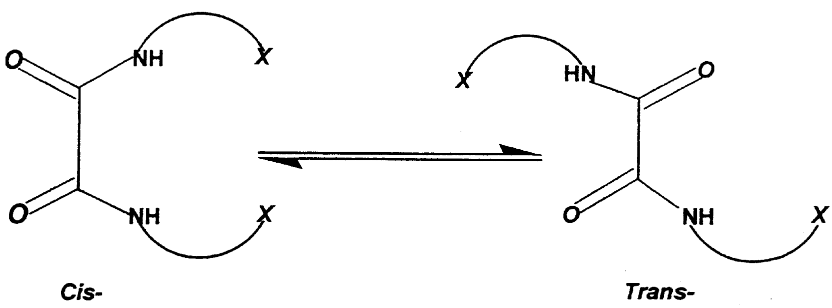
The N,N′-disubstituted oxamides, derivatives of $HNCOCONH^{2-}$, can adopt *cis*- or *trans*-conformation (Scheme 1) in the formation of metal complexes depending on the metal ions and the spacers. They overcome the difficulties that the oxamide $H_2NCOCONH_2$ itself is insoluble in common organic solvents and hydrolyzes easily with deprotonation to yield oxalate, thus providing a better chance to explore their coordination chemistry. Substituted oxamides are more reluctant toward the hydrolytic reaction and their solubility can be improved by providing the appropriate substituents X. In the presence of metal ions and when another coordinating functional group is present at a position that can form five- or six-membered chelate rings, the N,N′-disubstituted oxamide can acidically dissociate when promoted by the metal ion, while the amido group deprotonates and coordinates simultaneously.[7] When the amido nitrogen coordinates to a metal ion, it is

sp^2 hybridized to conjugate with the $p\pi$ electrons of the carbonyl group, which can coordinate to another metal ion via the oxygen atom(s) to form a binuclear system. In this case, the presence of an effective π-path between the two metal ions could transmit strong magnetic interactions despite the fact that the two metal ions are far from each other, separated by three atoms. Two review papers about the coordination chemistry of N,N′-disubstituted oxamide ligands have been published. Ojima and coworkers[7] introduced the syntheses of a series of N,N′-disubstituted oxamide ligands and their copper(II) complexes, while Julve and collaborators[8] illustrated the coordination properties of N,N′-bis(coordination group substituted)oxamides both in aqueous solution and in the solid state and described the design of some homo- and hetero-metallic species. Kahn[9,13] and others[10] were interested in the magnetic properties transmitted by the oxamidate ligand.

As a type of ligand with great versatility, some stable dinuclear copper(II) complexes can be used as building blocks toward other metal ions or preformed complexes. Concerned about the properties of the oxamidate ligand and the stability of the complexes, we proceeded with the following four ligands, namely H_2oxen, H_2oxpn, H_2oxap, and H_2oxpy (see Table I for abbreviations), and reacted them with copper(II) salts to form the binuclear units that were used as synthons for a series of supramolecular assemblies. This is a field not covered by the previous reviews.

SYNTHESES

As shown in Scheme 2, ethyl oxalate reacted with appropriate amines under proper conditions to yield the N,N′-dialkyl oxamide H_2L, L = oxen,



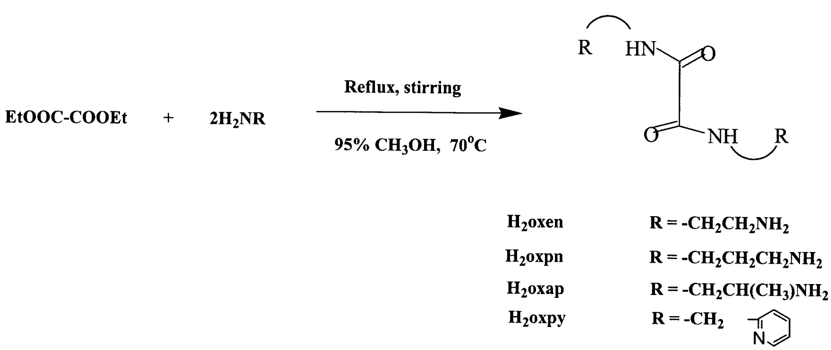
X = NR_2, Py, OH, COO^-, SO_3^-

SCHEME 1 *Cis*- and *trans*-equilibrium of N,N′-disubstituted oxamides.

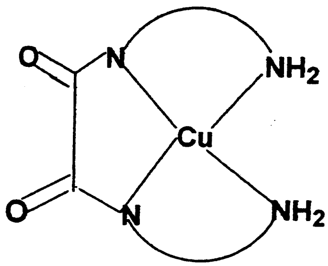
TABLE 1 Abbreviations of Ligands

H_2oxen	N,N′-bis(2-aminoethyl)oxamide
H_2oxpn	N,N′-bis(3-aminopropyl)oxamide
H_2oxap	N,N′-bis(2-aminopropyl)-oxamide
H_2oxpy	N,N′-bis(2-pyridylmethyl)oxamide
2,2′-bpy	2,2′-bipyridine
bpm	bipyrimidine
phth	phthalate
tp	terephthalate
isophth	isophthalate
dapm	diaminodiphenylmethane
suc	succinate
nic	nicotinate
4,4′-bpy	4,4′-bipyridine
bpe	1,2-bipyridylethelene
hyben	4-hydroxybenzoate
4-apy	4-aminopyridine
pyca	pyridine-4-carboxylate

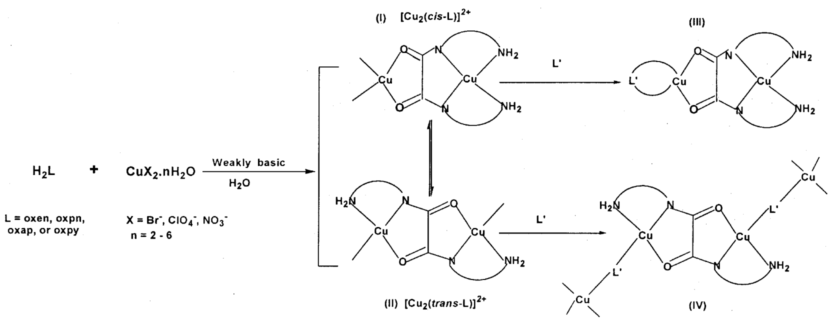
oxpn, oxap, or oxpy. While five- or six-membered chelate rings can be formed when the amido- and the amino- (or pyridyl) nitrogen atoms coordinate simultaneously to a metal ion, these ligands could react first with copper(II) salts under weakly basic conditions to yield mononuclear complexes with *cis*-form of the oxamide as depicted in Scheme 3, which then isomerizes to the *trans*-form on reaction with more of the copper salt to give the dinuclear unit. Or, as illustrated in Scheme 4, the reaction of H_2L with Cu(II) in the ratio 1:2 gave directly the binuclear units $[Cu_2L]^{2+}$ in aqueous solution. There is a dynamic equilibrium in solution between the two



SCHEME 2 Synthesis of N,N′-distributed oxamides.



SCHEME 3 Mononuclear copper complex of N,N′-disubstituted oxamides.



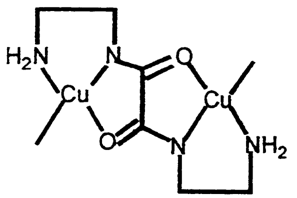
SCHEME 4 Formation of dicopper synthons and reactions with spacers.

species $[Cu_2(cis\text{-}L)]^{2+}$ (Scheme 4I) and $[Cu_2(trans\text{-}L)]^{2+}$ (Scheme 4II).[11,12] The key factor to control the conformation of L is the coordination mode of the second ligand L′. If L′ is 2,2′-bpy or bpm, which generally serves as chelate ligand, oligomeric complexes (Scheme 4III) such as [Cu(*cis*-oxpn)Cu(2,2′-bpy)]$(ClO_4)_2$[13] and [Cu(*cis*-oxpn)Cu(bpm)]$(ClO_4)_2$. CH_3OH[14] were obtained, in which the *cis*-conformation was maintained. Whereas if L′ acts as a bridging ligand that would maintain L in the *trans*-conformation, the *trans*-oxamidato-bridged units can then be further connected by L′ to yield compounds with extended structures (Scheme 4IV). In our work, such bridging ligands L′ were selected and compounds with a variety of novel extended structures were constructed.

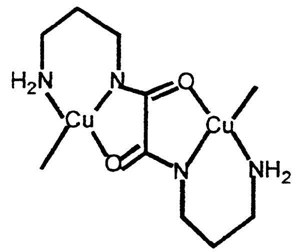
STRUCTURES

Synthons

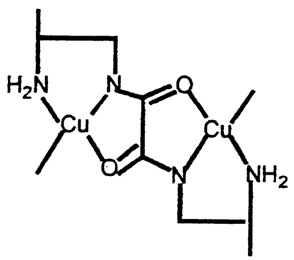
As shown in Scheme 5, the oxamidate L in the dinuclear units $[Cu_2(trans\text{-}L)]^{2+}$ adopts the *trans*-conformation and acts as the bis-tridentate ligand



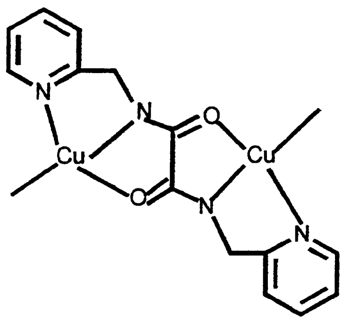
$[Cu_2(\textit{trans}\text{-oxen})]^{2+}$



$[Cu_2(\textit{trans}\text{-oxpn})]^{2+}$



$[Cu_2(\textit{trans}\text{-oxap})]^{2+}$



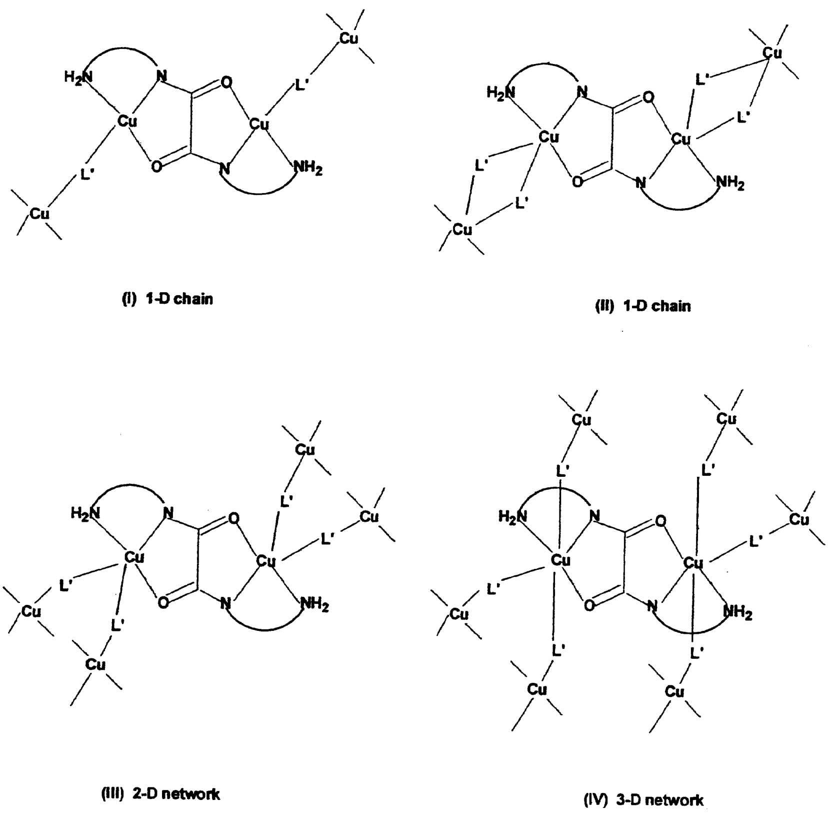
$[Cu_2(\textit{trans}\text{-oxpy})]^{2+}$

SCHEME 5 Four types of dicopper synthons $[Cu_2(\textit{trans}\text{-L})]^{2+}$ (L = oxen, oxpn, oxap, and oxpy) showing 5- and 6-membered chelate rings.

simultaneously chelating and bridging two copper(II) ions, which are the synthons for the fabrication of supramolecular architectures.

During the assembling process, the structural topology is generally influenced by a series of factors such as the organic spacer, the coordination geometry of the metal ion, the counter ion, the solvent, and even the reaction temperature. Since the coordination sphere of many metal ions is flexible, a large number of structural possibilities exist for the network for a given ligand topicity. However, if subtle constraints are applied to the coordination environment of the metal by capping its coordination sphere with a second ligand, then the predictability of the final network would increase. For copper(II), the coordination numbers are generally four to six. In the present synthons, three of the coordination sites of each Cu(II) have already been occupied by the oxamidate L, thus the residual coordination number, to be defined by the number of organic spacers (assuming each provides one donor atom) that could enter the coordination sphere, will be restricted to a maximum of three, which would reduce the possible topologies for the network. If weakly or noncoordinating counterion such as NO_3^-, ClO_4^-, or Br^- is used, an advantage will be provided by the fact that the remaining sites of the copper(II) ion can all be filled by the donors from the spacers. Connected by the 2-connecting spacer L′ as shown in Scheme 6, the copper with different coordination numbers led to structures with different topologies: when the copper(II) ion is four-coordinated, 1-D chains with single bridges (Scheme 6I) are formed; when five-coordinated, 1-D chains with double bridges (Scheme 6II) or 2-D extended networks (Scheme 6III) are obtained. As for six-coordinated Cu, 3-D networks (Scheme 6IV) can be constructed. When the spacer L′ is 3- or more-connecting linking three or more synthons, the structure obtained will be 2-D or 3-D coordination network.

In the compounds described below, the copper(II) ions are generally five-coordinated and the coordination geometry is square-based pyramidal with the basal plane simultaneously composed of N_2O from the oxamidate



SCHEME 6 Structural topologies of complexes with different dimensionality.

L and one other atom generally from L′, while the axial position is occupied by another atom from the spacer (or a water molecule or the counterion). Thus, the dimensionalities and structural motifs of the polymeric coordination networks depend mainly on the combinations of Cu(II) ions with a variety of bridging modes of spacers. The networks will be illustrated individually.

Polymeric Networks Constructed via Covalent Interactions

Net

The (6,3) net. When the synthon $[Cu_2(\textit{trans}\text{-oxen})]^{2+}$ is assembled by the hydroxyl group OH^-, compound $[Cu_6(\textit{trans}\text{-oxen})_3(OH)_2(H_2O)_2]_nBr_{4n}\cdot 3nH_2O$ **1**[15] was obtained in which the cation contains the 2-D extended network with hexagonal grids, (6,3) net (Figure 1). The group OH^- or the so-called 3-connected node, which acts as μ_3-bridges at the joints of the hexagons, coordinates to three copper(II) ions of three synthons $[Cu_2(\textit{trans}\text{-oxen})]^{2+}$ in different directions and completes the coordination environment of Cu(II) at the base plane.

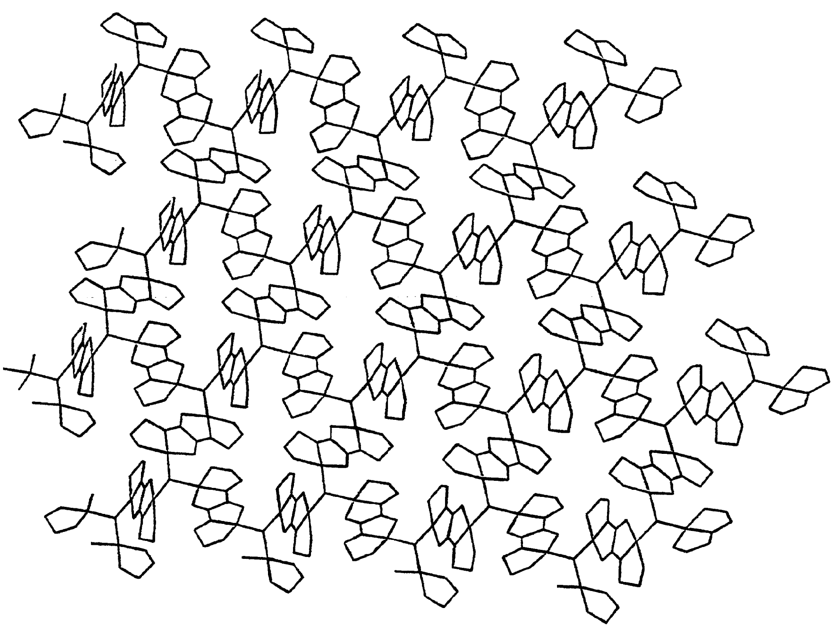
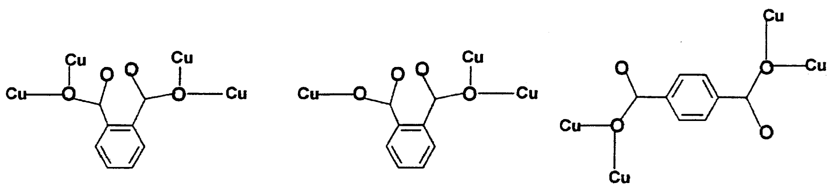


FIGURE 1 2-D network of $[Cu_6(\textit{trans}\text{-oxen})_3(OH)_2(H_2O)_2]_nBr_{4n}\cdot 3nH_2O$1 with hexagonal grids.

The (4,4) net. Three compounds $[Cu_2(\textit{trans}\text{-L})(L')]_n{\cdot}2nH_2O$ (L = oxen, L′ = phth, **2**; L = oxpn, L′ = phth, **3**; L = oxen, L′ = tp, **4**)[16,17] can be assigned to this category when the dicopper synthons were assembled by the spacers phth and tp. They adopt the coordination modes shown in Scheme 7 and act as 3- or 4-connector linking that many synthons to form the polymeric 2-D networks with rectangular grids, (4,4) net (Figure 2) which are geometrically different but topologically identical to each other. The 4-connected node is located at the center of the Cu_2O_2 plane between two synthons.

Mosaic Grid

Interestingly, complex $\{[Cu_2(\textit{trans}\text{-oxpn})(H_2O)_2][Cu_2(\textit{trans}\text{-oxpn})(isophth)_2]\}_n{\cdot}7nH_2O$ **5**[17] assembled from the synthon $[Cu_2(\textit{trans}\text{-oxpn})]^{2+}$



SCHEME 7 Coordination modes of phthalate (phth) and terephthalate (tp) in complexes **2** ~ **4**.

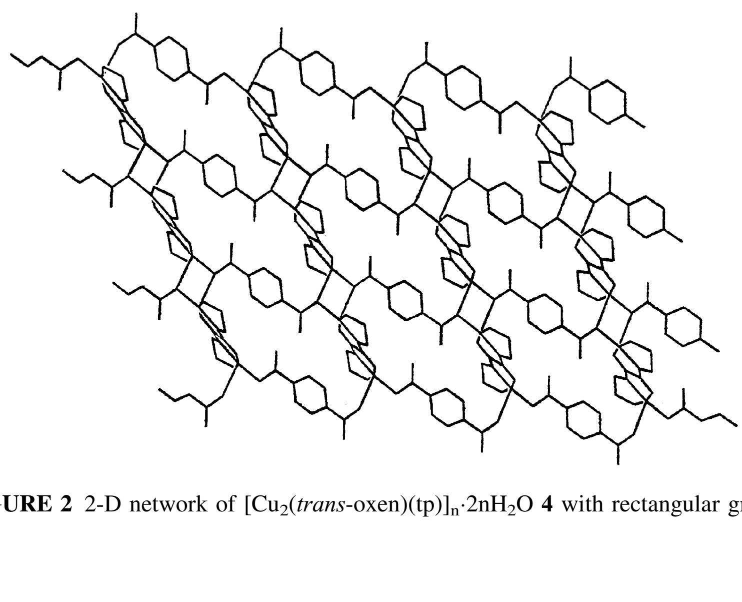


FIGURE 2 2-D network of $[Cu_2(\textit{trans}\text{-oxen})(tp)]_n{\cdot}2nH_2O$ **4** with rectangular grids.

and spacer isophth contains a 2-D network with the mosaic grid shown in Figure 3. The isophth adopts the coordination mode in Scheme 8 and acts as a 3-connector linking three synthons and the result is the formation of intercalated H-shaped grids consisting of four synthons and four isophth, different from the rectangular grids in **2–4**, which involve two synthons and two spacers. The square pyramidal basal plane of half of the copper(II) centers is completed by two carboxyl oxygen atoms from two different isophth, while that of the other half is completed by a water molecule.

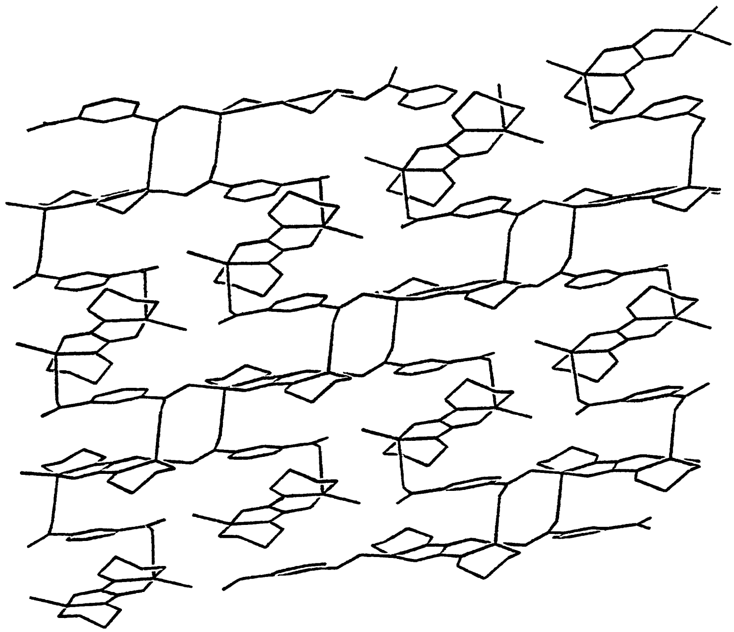
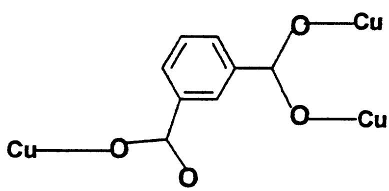


FIGURE 3 2-D network of $\{[Cu_2(\textit{trans}\text{-oxpn})(H_2O)_2][Cu_2(\textit{trans}\text{-oxpn})(\text{isophth})_2]\}_n \cdot 7nH_2O$ **5** with mosaic grids.

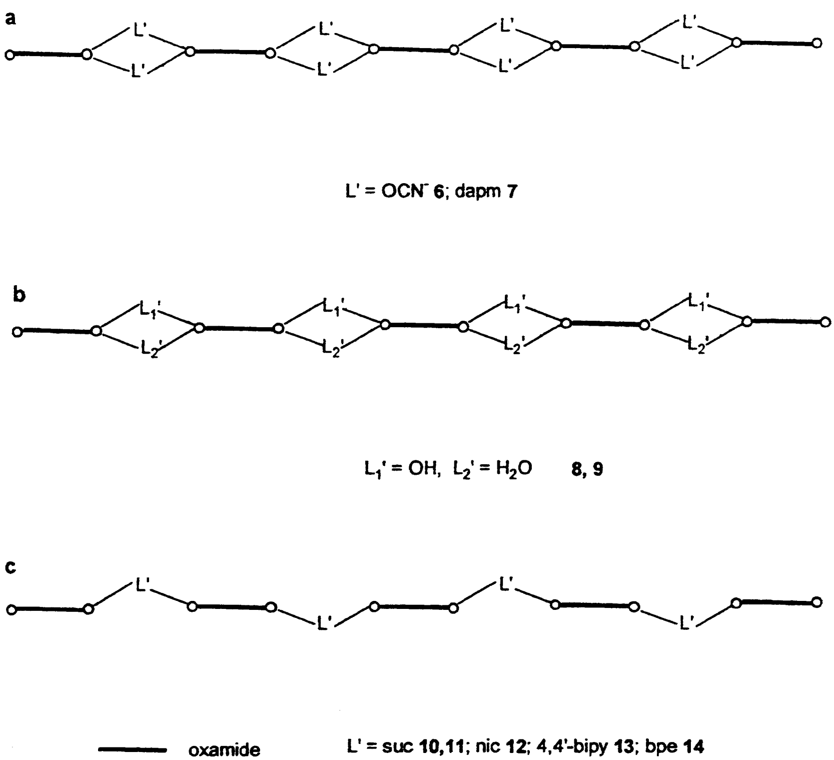


SCHEME 8 Coordination mode of isophthalate (isophth) in complex **5**.

Chain

In respect of spacers, three types of 1-D chains can be fabricated for these compounds: chains that contain synthons doubly bridged by the same spacers, those doubly bridged by two different spacers, and those singly bridged.

Chain containing double spacer bridges. Compounds $[Cu_2($*trans*-oxen$)(NCO)_2]_n \cdot nH_2O$ **6**[18] and $[Cu_2($*trans*-oxpy$)(dapm)_2]_n(NO_3)_{2n} \cdot 6nH_2O$ **7**[19] contain polymeric chains with double spacers OCN and dapm, respectively. The schematic view of the infinite chain in **6** or **7** is depicted in Scheme 9a. Figure 4 shows the garland ring-like chain in **7**. The square pyramidal environment of the copper(II) center in **6** is completed by the oxygen atoms from two OCN, while that in **7** is completed by two nitrogen atoms from two dapm.



SCHEME 9 1-D chains formed by bridging with spacers: a) homo-double bridge; b) hetero-double bridge; c) single bridge.

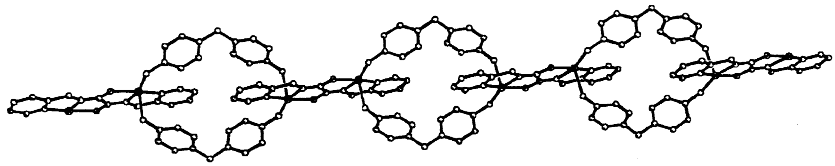


FIGURE 4 The garland ring-like chain in $[Cu_2(\textit{trans}\text{-oxpy})(dapm)_2]_n(NO_3)_{2n}\cdot 6nH_2O$ **7**.

The two compounds $[Cu_2(\textit{trans}\text{-oxen})(OH)(H_2O)]_nBr_n\cdot 2nH_2O$ **8**[18] and $[Cu_2(\textit{trans}\text{-oxpn})(OH)(H_2O)]_nBr_n\cdot 2nH_2O$ **9**[16] contain polymeric chains with synthons bridged by two different spacers. The groups OH^- and OH_2 act as 2-connectors linking the synthon $[Cu_2(\textit{trans}\text{-L})]^{2+}$ (L = oxen or oxpn) to form zigzag chains in the fashion depicted in Scheme 9b.

Chain containing single spacer bridge. Compounds $[Cu_2(\textit{trans}\text{-oxap})(suc)(H_2O)_2]_n\cdot 2nH_2O$ **10**,[20] $[Cu_2(\textit{trans}\text{-oxen})(suc)(H_2O)_2]_n\cdot 2nH_2O$ **11**,[20] $[Cu_2(\textit{trans}\text{-oxap})(nic)(H_2O)_2]_n(ClO_4)_n\cdot 0.5nH_2O$ **12**,[21] $[Cu_2(\textit{trans}\text{-oxpy})(4,4'\text{-bipy})(H_2O)_2]_n\cdot(NO_3)_{2n}\cdot 2nH_2O$ **13**,[19] and $[Cu_2(\textit{trans}\text{-oxpy})(bpe)(H_2O)_2]_n\cdot(NO_3)_{2n}\cdot 3nH_2O$ **14**[19] contain the polymeric chains with a single spacer bridge between the synthons. The spacer suc, nic, 4,4′-bpy, or bpe acts as 2-connector to form the zigzag chain in the fashion shown in Scheme 9c.

Binuclear Compound

In some cases, the spacers do not bridge the synthons but terminally attach to Cu(II) to give dinuclear compounds such as in $[Cu_2(\textit{trans}\text{-oxen})(nic)_2(H_2O)_2]\cdot 2H_2O$ **15**[21] Figure 5, $[Cu_2(\textit{trans}\text{-oxpn})(hyben)_2(H_2O)_2]\cdot 2H_2O$ **16**,[21] $[Cu_2(\textit{trans}\text{-oxen})(dapm)_2Br_2]$ **17**,[22] and $[Cu_2(\textit{trans}\text{-oxen})$-

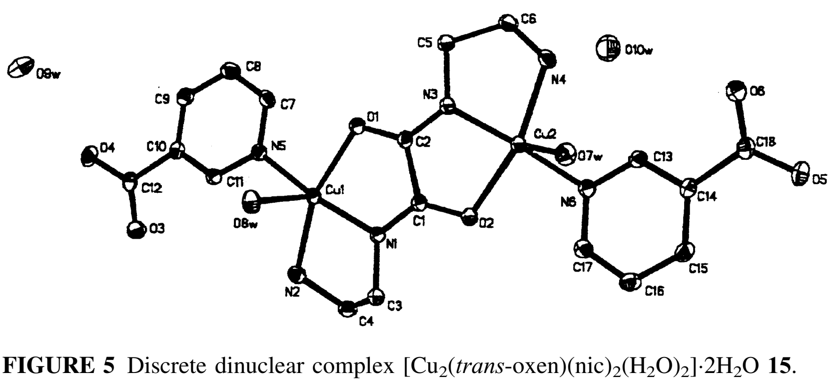


FIGURE 5 Discrete dinuclear complex $[Cu_2(\textit{trans}\text{-oxen})(nic)_2(H_2O)_2]\cdot 2H_2O$ **15**.

$(4\text{-apy})_2]\cdot(ClO_4)_2$ **18**[22]. However, due to the abundant hydrogen bond donors and acceptors, supramolecules can be constructed (see next sections).

Supramolecular Architectures Fabricated via Intermolecular Interactions

It is known that the strategies used for designing the architecture of functional systems depend on the nature of the interactions responsible for networking. One of the best strategies to fabricate 3D supramolecular systems is to utilize hydrogen bonding of the coordinated ligands to interlink the 1-D or 2-D coordination molecules. The strong hydrogen bonding character of the oxamidato bridges and the water molecules makes it possible to obtain architectures with higher dimensionality with a vast variety of supramolecular topologies.

3-D Network from 2-D Coordination Polymers Directed by Hydrogen Bonds

The hydrogen bonding linkages in $[Cu_2(\textit{trans}\text{-oxen})(\text{phth})]_n\cdot 2nH_2O$ **2**[17] occur among the solvated H_2O, the amido O and N and the uncoordinated carboxyl oxygen of the spacer phth. The two solvated water molecules act as two μ_3-bridges in the hydrogen bonding systems and the 3-D network is shown in Figure 6.

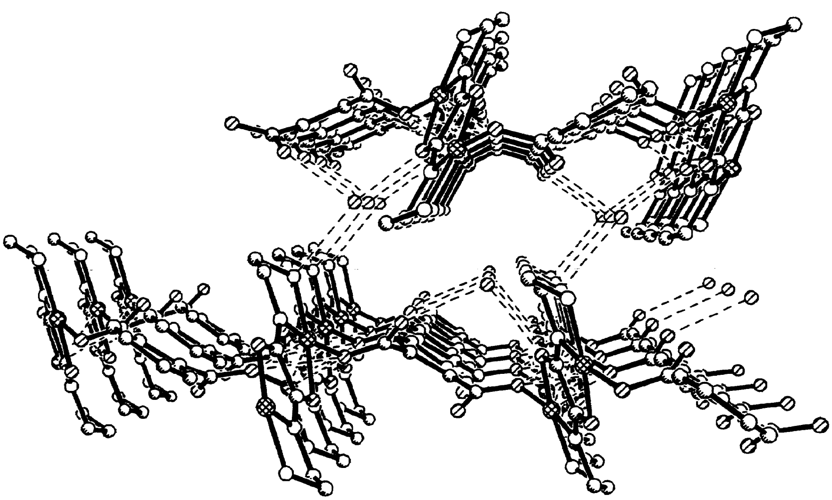


FIGURE 6 3-D network of $[Cu_2(\textit{trans}\text{-oxen})(\text{phth})]_n\cdot 2nH_2O$ **2** formed from 2-D polymer directed by hydrogen bonds.

3-D Network from 1-D Coordination Chains Directed by Hydrogen Bonds

Figure 7 illustrates the 3-D aggregation of $[Cu_2(\textit{trans}\text{-oxen})(OH)(H_2O)]_n Br_n \cdot 2nH_2O$ **8**[18] in which the polymeric chains $[Cu_2(\textit{trans}\text{-oxen})(OH)(H_2O)]_n^{n+}$ are symmetry-related by C_3-axis, which intersect with each other to produce an interwoven network through the inter-chain hydrogen bonds formed among OH^-, H_2O, and the solvated water molecules by means of linkages (oxen)Cu-OH—OH-Cu(oxen) and (oxen)Cu-H_2O—H_2O—H_2O-Cu(oxen).

The compound $[Cu_2(\textit{trans}\text{-oxap})(nic)(H_2O)_2]_n(ClO_4)_n \cdot nH_2O$ **12**[21] exhibits a 2-D network by joining 1-D coordination chains $[Cu_2(\textit{trans}\text{-oxap})(nic)(H_2O)_2]_n{}^{n+}$ by two types of hydrogen bonds as shown in Figure 8, viewed along *ac* plane. One of the connections is (H_2O)Cu(oxap)· · ·(H_2O)Cu (oxap) between amido O and the coordinated H_2O. The other is (oxap)Cu(-nic)· · ·(H_2O)Cu(oxap) between noncoordinated carboxyl oxygen atom, of nic and the coordinated H_2O. The perchlorates are located between the 2-D sheets

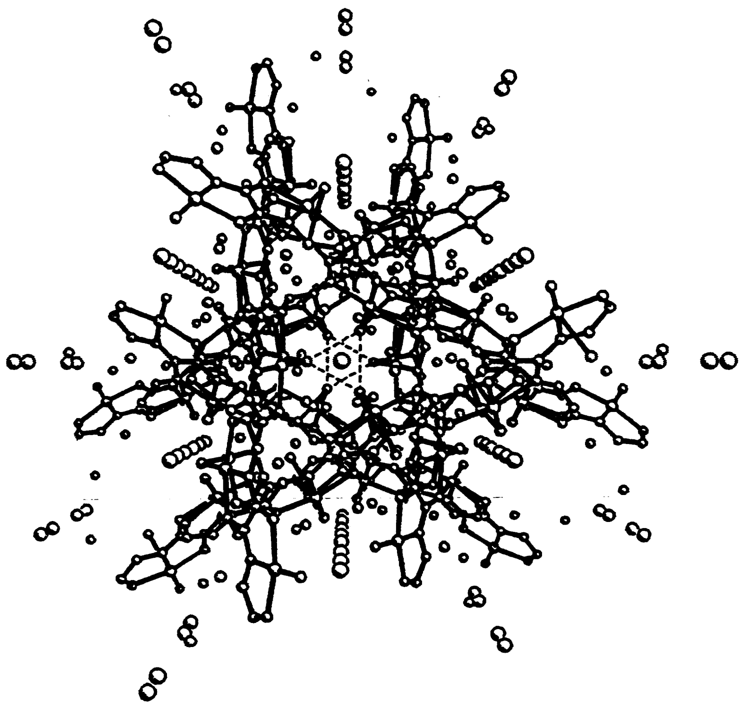


FIGURE 7 3-D aggregation of $[Cu_2(\textit{trans}\text{-oxen})(OH)(H_2O)]_n Br_n \cdot 2nH_2O$ **8** formed by inter-chain hydrogen bonding interactions.

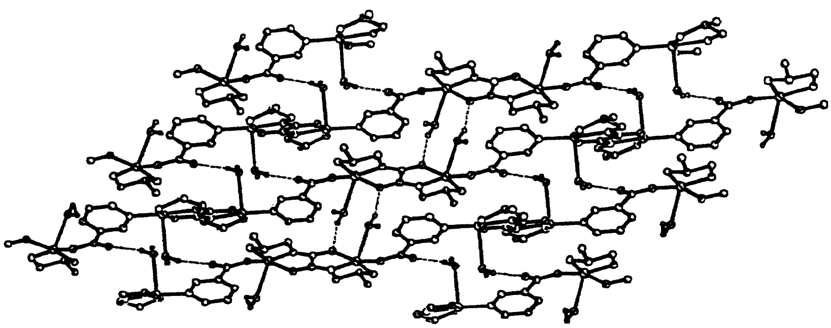


FIGURE 8 2-D network of $[Cu_2($*trans*-oxap)(nic)$(H_2O)_2]_n(ClO_4)_n \cdot nH_2O$ **12** formed by two types of hydrogen bonds.

and associated with the coordination frameworks through hydrogen bonds O1w-H—O13 and O3w′-H—O13. Such a location of the perchlorates is similar to that found in $[Cu_2($*trans*-oxen)(pyca)$(H_2O)]_n[ClO_4]_n \cdot 2nH_2O$[23] with pyca as the spacer. However, although both compounds show 2-D motifs, the latter is derived from coordination connection only while the former involves both coordination and hydrogen bonding linkages.

3-D Network from Binuclear Compounds Directed by Hydrogen Bonds

The supramolecular network (Figure 9) of **16**[21] is derived from intermolecular hydrogen bond connections of binuclear molecules $[Cu_2$ (*trans*-oxen)(hyben)$_2(H_2O)_2]$ via two types of linkages (oxen)Cu(H_2O)··· (oxen)Cu(H_2O) and (oxen)Cu(hyben)···(hyben)-Cu(oxen).

Intramolecular Synergism

Surveying all these coordination polymers or discrete complexes containing the synthon $[Cu_2($*trans*-L$)]^{2+}$, intramolecular synergism is embodied and can be interpreted by the structural parameters. As already shown in Scheme 5, the synthons $[Cu_2($*trans*-oxen$)]^{2+}$, $[Cu_2($*trans*-oxap$)]^{2+}$, and $[Cu_2($*trans*-oxpy$)]^{2+}$ contain four edge sharing 5-membered chelate rings, while $[Cu_2$ (*trans*-oxpn$)]^{2+}$ contains two 5- and two 6-membered rings. The structural parameters of these chelating rings are listed in Table II, which showed that the average atomic distances and bond angles in the 5-membered chelate rings of oxen, oxap, and oxpy are nearly constant, while those for oxpn are slightly changed, obviously affected by the neighboring 6-membered rings sharing an edge with it. The chelate angles Cu-N_{amide}-C_{amine} and Cu-$N_{amine(py)}$-C showed obvious

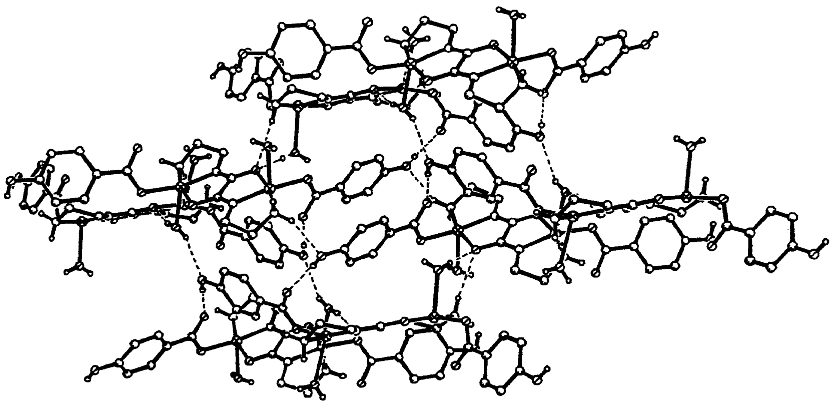


FIGURE 9 Hydrogen bondings between dinuclear molecules of [Cu_2(*trans*-oxen)(hyben)$_2$(H_2O)$_2$] **16**.

differences: those in 6-membered rings are all larger than in 5-membered, with the bite angle N_{amide}-Cu-$N_{amine(py)}$ the most significant. This is a result that could be reasoned by synergistic effect within the same sized rings: the atoms dissipate

TABLE 2 Average Atomic Distances (Å) and Bond Angles (°) of the Chelate Rings in the Synthons [Cu_2(*trans*-L)]$^{2+}$ (L = oxen, oxap, oxpy, or oxpn)

[Cu_2(*trans*-L)]$^{2+}$ / Structural parameters	5-membered chelate rings			6- & 5-membered chelate rings
	oxen	oxap	oxpy	oxpn
Cu-O_{amide} (Å)	2.028	2.013	2.030	1.987
Cu-N_{amide} (Å)	1.918	1.917	1.916	1.955
Cu-$N_{amine(py)}$ (Å)	2.020	2.023	2.035	1.988
Cu . . . Cu (Å)	5.264	5.237	5.268	5.266
O_{amide}-Cu-N_{amide}[a]	83.11	83.24	82.98	83.69
N_{amide}-Cu-$N_{amine(py)}$[b]	82.87	82.20	80.88	95.4
Cu-N_{amide}-C_{amide}[a]	116.38	116.2	116.8	113.5
Cu-N_{amide}-C_{amine}[b]	117.49	117.7	118.2	128.0
Cu-O_{amide}-C_{amide}[a]	109.64	109.6	109.4	110.4
Cu-$N_{amine(py)}$-C[b]	107.79	108.5	114.0	118.2

[a]Bond angle in 5-membered chelate ring.

[b]Bond angle in 5-membered chelate ring for oxen, oxap, and oxpy, but in 6-membered ring for oxpn.

the strain energy in chelate rings of the same size to the same extent, but different for varied sizes. Integrity of the skeleton of the synthon $[Cu_2(trans\text{-}L)]^{2+}$ is thus declared for all the compounds.

The rigidity of the synthons is also exemplified by the magnetic exchange interactions transmitted by the oxamidato bridges, which provide extended planar conjunction between the copper(II) ions with strong antiferromagnetic exchange in the range $-300 \sim -450\,cm^{-1}$, even though the metal···metal distances are larger than 5.2 Å and the spacers vary.

CONCLUSION

N,N′-disubstituted oxamides are a type of promising organic ligands for shaped molecular design and molecular self-organization. The *trans*-oxamidato-bridged binuclear units $[Cu_2(trans\text{-}L)]^{2+}$ (L = oxen, oxpn, oxap, and oxpy) are excellent synthons for the construction of materials with variously shaped grids or nets. The second bridging ligand (spacer) is the key to the construction of desired structural motifs. For example, the group OH^- shows two coordination fashions: either as 2-connector (in **8** and **9**) to give 1-D polymeric chain or as a triangular tridentate 3-connector (in **1**) to produce a 2-D network with hexagonal grids. Thus, from work described in above sections, it is possible to predict that if the spacer is a 2-connector, 1-D polymeric structure will be formed, while 3- or more-connecting spacer will induce 2-D networks with different grids. In a word, by careful selection of organic spacers, the topology of the obtained coordination polymers can be rationally designed.

In addition, the formation of a vast range of hydrogen bonds provides a variety of topologies of hydrogen bond directed self-assembly. The coordination polymeric structures were first constructed via covalent interactions between the synthons and spacers, and then fabricated into 3-D network via hydrogen bonding interactions. The structural topology of networks constructed via covalent interaction is predictable according to the coordination mode of the spacer while the 3-D network topology of the supramolecular architectures is difficult to foresee due to the infinite diversity of the hydrogen bonding interactions. However, the hydrogen bond systems often influence the crystal packing. How to control the crystal packing via weak interactions is still a challenging task. Nonetheless, as the compounds assembled from the *trans*-oxamidato-bridged synthons are non-interpenetrating, it might be a promising aspect of crystal engineering for new materials. To further understand the factors affecting the structure of an assembly and the relationship of structure and function, more work needs to be done.

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