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# Structural Diversity and Modulation of Coordination Architectures with Flexible Dithioether or Disulfoxide Ligands

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Metal complexes of flexible dithioether and disulfoxide ligands are briefly reviewed, focusing on the structural investigations based on X-ray crystallographic analyses. Recent investigations from our laboratory have produced compelling experimental evidence that flexible dithioether and disulfoxide ligands exhibit rich coordination chemistry towards metal ions and have great potential in constructing metal complexes with diverse structures. The design and synthesis of the ligands and their complexes are described. A wide variety of crystal structures of mononuclear, discrete multinuclear complexes and coordination polymers are classified by their assembling fashions, and the coordination modes of the two types of ligands are summarized. Series of structurally related ligands with varied spacer lengths or terminal groups were systematically used to coordinate the same metal ion in similar reaction conditions to afford complexes with different structures, indicating that the spacer lengths and terminal groups of ligands have important effects on the structures of the complexes. Using the same ligand to coordinate with different metal ions gave distinct complexes, showing the influences of the affinity and geometry of metal ions on the structures of the complexes. In addition, varying the anions, the solvent used, and the ratio of reactants in synthesis also led to the formation of complexes with different structures. These results present a feasible way to control the structures of complexes with these or other ditopic flexible ligands by modifying the ligands, selecting metal ions, as well as adjusting reaction conditions, which has been regarded as a long-time challenge in engineering metal–organic coordination architectures.

## Introduction

A large number of metal complexes have been prepared and structurally characterized in this half century, and many of them were of mono- or dinuclear structures. On the other hand, in the recent years, much effort has also been focused on the designs and constructions of oligo- and poly(nuclear) coordination architectures because of their novel structural topologies, intriguing architectures, intertwining phenomena, and potential technological applications, such as optoelectronic devices, microporous materials for shape and size separations, ion exchange, and cataly-

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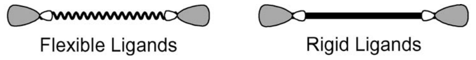
sis.[1] The judicious combination of organic ligand "spacers" and metal ion "nodes" has been considered as one of the most common synthetic approaches to produce coordination polymers with predictable networks.[2] The advantage of constructing these metal–organic framework architectures is to allow a wide choice in various parameters, including diverse electronic properties and coordination geometry of the metal ions, as well as versatile functions and structures of organic ligands. That is also the aspiration for achieving the ultimate aim of crystal engineering: gaining control of the topology and geometry of the networks formed through judicious choice of ligand, metal precursor geometry, and synthesis conditions.[3]

In a sense, supramolecular chemistry has advanced to a stage up to now, at which it is possible to select molecular building blocks that will assemble into structures with specific and desired network topologies, so that a rational design of molecular solids with potentially interesting properties is possible.[1f,4] However, there is presently still very little understanding concerning the factors that determine the syntheses and resulting structures, and the attainment of rational control over desired topologies and specific properties still remains a great challenge. Namely, no general method gave consistently reliable predictions for the engineering, as stated by Dunitz,[5] because molecular assembly is usually affected by several factors such as characteristics of the ligands,[6] solvents,[7] templates (or guests),[8] and counteranions,[9] and so on. Therefore, the investigation and understanding of the relationships between the structure of the complexes and the nature of the ligands, as well as other factors is still important.

Bridging ligands, especially rigid ligands such as cyanide and 4,4-bipyridyl, as building blocks have been extensively utilized to construct supramolecular coordination species and/or frameworks. Rigid building blocks are anticipated to retain their geometry in coordination, and numerous target coordination supramolecular architectures based on this fixed geometry have been designed and synthesized up to date.[10] In contrast, a flexible building block (flexible ligand) with conformational freedom has uncertain fashions of coordination in linking metal nodes and thus a higher possibility of producing unpredictable and unique structures.[11] However, the investigation in this area is still not extensive. Furthermore, to some extent, complexes with flexible ligands are more sensitive to structural influence than those with rigid ones, because of the configurational varieties of the ligands. In the recent years, we and others have made some efforts in the design and synthesis of novel coordination architectures by using flexible multifunctional ligands. Herein, the complexes obtained with flexible dithioether[12] and disulfoxide[13] ligands are summed up, as two representatives, with the intention of exploring the effects of ligand modification, the geometries of metal ions, the solvents used, and the ratios of metal and ligand used in the syntheses on the structures of the complexes obtained.



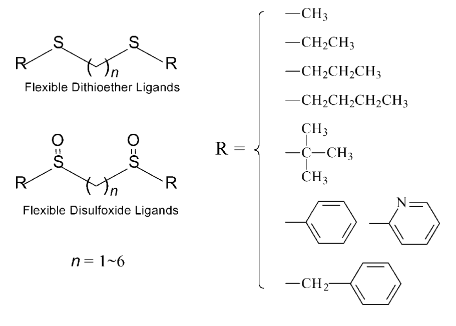
Although they are structurally related, flexible dithioether and disulfoxide ligands are two different types of bridging ligands. For the former, the S atoms take part in the coordination with metal ions in the mono or $\mu_2$ bridging modes, and the ligands can adopt chelating or bridging fashions of coordination. The latter has several intriguing features, such as bidentate ditopic nature as the former, the inherent chiral property of the sulfur atom, and the diastereomeric *meso* and *rac* forms. They can coordinate to metal ions through either O or S donors, according to the electronic and steric factors. In addition, configuration inversion of sulfur atoms may take place in the disulfoxide molecules when treated with metal ions, which probably leads to the formation of some complexes with unpredictable structures.

This article begins with a description of the design and synthesis of such dithioether and disulfoxide ligands. In the following paragraphs, we survey their coordination modes and structural coordination chemistry, focusing on supramolecular assemblies, and then, we discuss controlling the structure through ligand modification and variation of other conditions, in relation not only to basic chemistry but also to crystal engineering. The related properties of some complexes are also mentioned.

## 1. Design and Synthesis of Ligands and Complexes

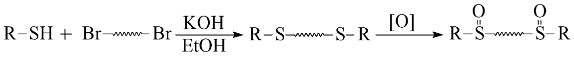
### Ligands

The ligands used (Scheme 1) are simple enough and also easy to synthesize, and more importantly, they can be modified systematically by changing the spacer lengths and terminal groups. Changing the size of the terminal groups and the spacer lengths can lead to variations in steric hindering upon formation of the metal complexes. Furthermore, the electronic effect of the terminal groups is also a considerable factor; for example an aryl and alkyl group directly linked to the coordination donors (S or S=O) may have a great influence on the coordination ability of such ligands.



Scheme 1. Schematic representation of the flexible dithioether and disulfoxide ligands discussed in this review.

As shown in Scheme 2, the dithioether ligands can easily be synthesized by using a general substitution reaction, and the products can be separated from the reaction system by only washing with water. Most of the disulfoxide compounds can be synthesized by oxidizing the corresponding dithioether compounds directly. Different oxidants have been used in different systems, such as hydrogen peroxide and its derivatives, halogen derivatives, etc.[14] The oxidation power of the oxidant is very important in the synthesis. As we know, a stronger oxidant can transfer the sulfoxide further to sulfone or other substances, but a weaker one is not able to achieve such a synthesis. In our studies, $HNO_3$ was used as oxidant.[13] Although the concentration of the $HNO_3$ was adjusted in the synthesis in order to fit the situation, indeed, in most cases, it does not affect the products. Using this method, the resulting products do not contain sulfone, the yield is high, and the purification is simple (washing with water). The disulfoxide ligands synthesized by this approach are a mixture containing *rac* and *meso* isomers, which can be separated by fractional crystallization.



Scheme 2. Schematic representation of the syntheses of dithioether and disulfoxide ligands.

## Complexes

Series of the aforementioned ligands have been used in the construction of metal complexes. In order to compare the structures of the resulting complexes, we always fix one or two variable factor(s) and synthesize a series of complexes under similar conditions. For the dithioether ligands, the S donor has a higher affinity for soft metal ions, such as $Ag^I$, $Pd^{II}$, and $Pt^{II}$. In our research, the $Ag^I$ ion was used mainly because it is a well-known, favorable, and fashionable connecting node for the construction of coordination architectures because of its coordination diversity and flexibility.[15] For the disulfoxide ligands, both S and O donors can take part in the coordination, so both transition and lanthanide metals were used. By systematically changing the geometries of the ligands, metal ions, and other environmental factors such as counteranions, solvents, etc., several series of metal complexes have been obtained and structurally characterized by X-ray crystallography.

These complexes were synthesized as crystal products by two general methods: slow solvent evaporation and diffusion at room temperature. However, all our attempts to obtain crystals of the complexes by using the solvothermal (hydrothermal) method were unsuccessful.

In the syntheses of dithioether metal complexes, a typical diffusing method was used: to a solution of silver salt in acetone (or methanol) was slowly added a chloroform solution of the ligand. The mixture was stirred for about 10 min and filtered. Single crystals were obtained by slow diffusion of diethyl ether into the above filtrate in the dark. In some cases, the crystals can also be obtained when the filtrate was allowed to stand for several days in the dark, without using a diffusing solvent.

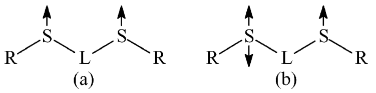
In synthesizing disulfoxide metal complexes, a layer diffusing method was always used. Typically, single crystals of the complexes were obtained by diffusion between an acetone (or methanol) solution containing the metal salts and an anhydrous chloroform solution of the ligand by using diethoxyethane (or triethylorthoformate) as an interlayer and a dehydrating reagent in a straight-type glass tube at room temperature. Crystals appeared in the interlayer after several days. Another method was also used: diethoxyethane (or triethylorthoformate) was added to an anhydrous acetone (or methanol) solution of the metal salts, and the mixture was stirred for ca. 30 min. The ligand in chloroform was added dropwise to the above mixture, which was further stirred at room temperature or 70–80 °C for several hours and then cooled to room temperature. After filtration, the filtrate was left to stand at room temperature, and single crystals were obtained after several days with slow evaporation of the solvent. It is noteworthy that, in the syntheses of disulfoxide complexes, a dehydrating agent must be used.

As a whole, such complexes are stable in air at ambient temperature and have good thermal stability. For (dithioether)$Ag^I$ complexes, all of them are stable up to 100 °C and decompose on further heating, and some are stable up to 200 °C. The complexes with disulfoxide ligands have higher thermal stability than those with dithioether ligands. Most of them begin to decompose at above 150 °C, and some stay intact even up to 300 °C. Furthermore, it should be pointed out that some $Ag^I$ complexes are moderately sensitive to light, thus the synthetic manipulation should be performed in the dark.

## 2. Coordination Modes of the Ligands

### Dithioether Ligands

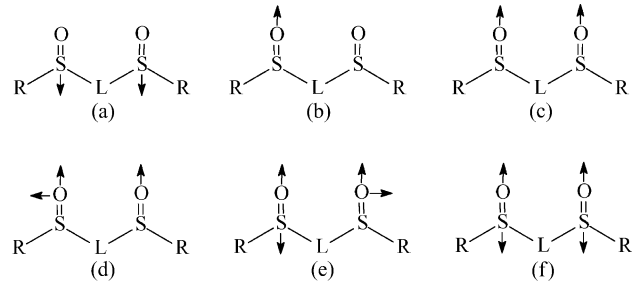
These dithioether compounds are typical ditopic ligands, which can adopt bridging or chelating coordination modes to coordinate to metal ions. For the single S donor coordination, two modes, monocoordination and $\mu_2$-S bridging coordination, were observed in our investigations, as shown in Scheme 3. The (a) mode is a normal mode for this type of ligands, but only two examples of (b) were observed up to now. In such systems, the steric hindrance and ring tension probably determine the coordination modes of the ligands adopted in the complexes.



Scheme 3. Observed coordination modes of dithioether ligands.

### Disulfoxide Ligands

On the basis of the coordination of the S=O donors to metal ions, five types of coordination modes of such flexible disulfoxide ligands were observed in their metal complexes (a–e in Scheme 4). For the soft metal ions, such as $Ag^I$, $Pd^{II}$, and $Pt^{II}$, in most cases, mode (a) was adopted. For $Cu^{II}$ and lanthanide metals, the (c) mode is the normal fashion. In addition, for almost all of the O-coordinated complexes, the ligands prefer the bridging coordination mode, excepting only one example, in which the ligands adopt both chelating (c) and chelating-bridging modes (e). The mode (f) has not been observed up to now. In such complexes, the affinity of metal ions and steric hindrance are considered to be responsible for the adopted coordination modes.



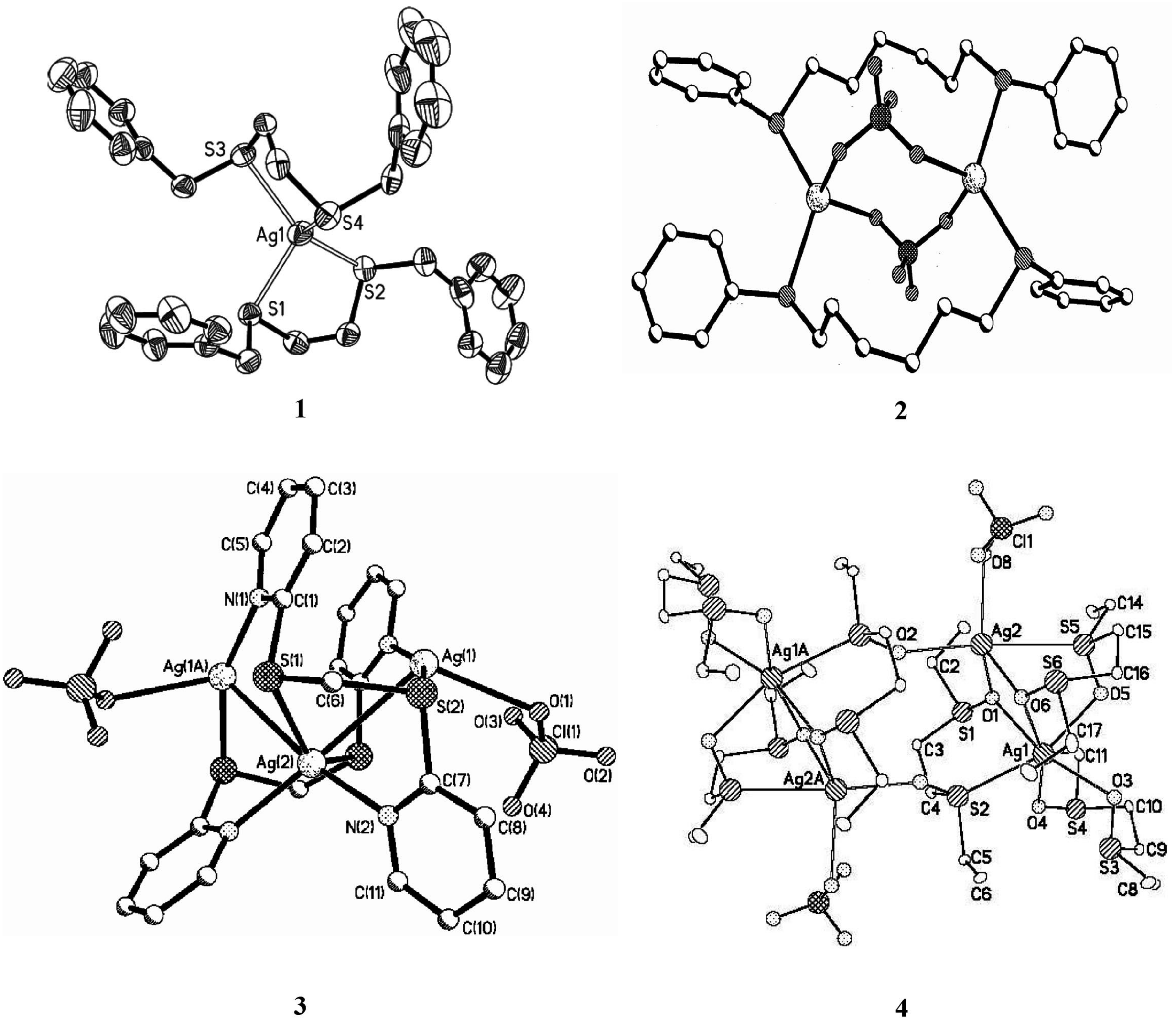
Scheme 4. Coordination modes of disulfoxide ligands.

## 3. Structural Diversity

The metal complexes of such dithioether or disulfoxide ligands have a variety of structural features ranging from mononuclear complexes to three-dimensional (3D) network polymers, giving a wealth of information on structural chemistry and coordination chemistry.

### Zero-Dimensional (0D) Structures

Although such bridging ligands have a higher tendency to form extended structural complexes, some mono- and multinuclear discrete structural complexes have been obtained. As shown in Figure 1, complex $[Ag(\mathbf{L})_2]ClO_4$ [**1**, **L** = 1,2-bis(benzylthio)ethane][12l] has a discrete mononuclear structure, in which two ligands bond one $Ag^I$ center in a



**1** **2**

**3** **4**

Figure 1. Molecular/cationic structures of some representative 0D complexes (H atoms omitted for clarity).

bidentate chelating coordination mode to form two five-membered rings. It is interesting that the two ligands show different conformations, *cis* and *trans*, based on the two phenyl rings of each ligand. In addition, the S atoms of the two ligands have different configuration: *R*,*S* for one ligand (*cis*), and *S*,*S* for the other (*trans*). Complex $[Ag\mathbf{L}ClO_4]_2$ [**2**, **L** = 1,6-bis(phenylthio)hexane][12g] has a dinuclear structure in which two $Ag^I$ ions are linked by two distinct **L** ligands through their S donors to form an 18-membered macrocycle. The $ClO_4^-$ anions also coordinate to two $Ag^I$ ions in the rare $\mu_2$ double-bridging mode through two O atoms to form an eight-membered ring. Both macrometallacycles make up a centrosymmetric dinuclear cage structure. $[Ag_3(\mathbf{L})_2(ClO_4)_2]ClO_4$ [**3**, **L** = bis(2-pyridylthio)methane][12j] is a trinuclear complex. In **3**, each **L** ligand behaves in tetradentate coordinating fashion. Ag(2) is chelated by a pyridine N atom and a S atom at the other end of the same ligand to form two six-membered rings, and the remaining pyridine N and S atoms of the ligand bridge Ag(1) and Ag(1A) in *cis* form. $Ag^I$ atoms have two different coordination geometries: Ag(1) is coordinated to a pyridine N atom, a S atom from another ligand and an O atom from a $ClO_4$, but Ag(2) lies on a twofold axis and is coordinated to two pyridine N atoms and two S atoms from two **L** ligands. The structural formation of the complex depends on the N donor of the terminal group pyridine ring, which takes part in the coordination. There exist a lot of complexes with N-donor thioether ligands, which are outside the scope of this review. Complex $[\{Ag_2(O,O\text{-}\mathbf{L})(\mu\text{-}O\text{-}\mu\text{-}\{SO\}\text{-}\mathbf{L})_2ClO_4\}ClO_4]_2$ [**4**, **L** = 1,2-bis(ethylsulfinyl)ethane][13n] has a novel tetranuclear structure, in which the $Ag^I$ atoms exhibit two kinds of coordination modes: trigonal-bipyramidal and octahedral, and the ligands adopt bidentate (*O*,*O*) chelating and tridentate μ-O-μ-(SO) bridging-chelating coordination modes. Such a ligand coordination mode is unprecedented in the metal complexes of disulfoxide ligands, and it is the only example in disulfoxide–metal systems. This example also indicates the rich coordination chemistry of disulfoxide ligands.

### One-Dimensional (1D) Structures

Figure 2 shows some representative 1D structural complexes. On the basis of the numbers of bridging ligands linked two metal ions, these 1D structures can be classified as single, double, and single-double-bridging chains. In addition, a helical chain complex was also obtained. Complex $[Ag\mathbf{L}NO_3]_n$ [**5**, **L** = bis(phenylthio)methane][12f] has a 1D single-bridging chain structure, in which the $Ag^I$ ion coordinates to two distinct S donors of **L** and one O atom of the nitrate group. Each **L** connects two $Ag^I$ ions in a pseudo-4-helical fashion to form the 1D chain. Complex $[Ag\mathbf{L}ClO_4]_n$ [**6**, **L** = 1,3-bis(ethylthio)propane][12l] is a chiral helical chain polymer. The S donors of the ligands **L** adopt both $\mu_2$-bridging and monodentate terminal coordination modes. The whole chain can be described as two opposite single helical chains bound together by $\mu_2$-S donors. In each single chain, the ligands bridge $Ag^I$ centers in a bis(monodentate) coordination mode to form a left- or right-handed single helix $(Ag\text{–}\mathbf{L_a}^3\text{–})_n$. Two such helical single chains are linked together by $\mu_2$-bridging S donors of **L** to form a double chain. Interestingly, on the basis of the $\mu_2$-S bridging $Ag^I$ ions, a left-handed chiral helical chain entity $(Ag\text{–}S\text{–})_n$ related by a $2_1$ screw axis is also formed simultaneously. Complex $[Cd_2(\mathbf{L})_2(NO_3)_4]_n$ [**7**, **L** = 1,4-bis(ethylsulfinyl)butane][13h] has a double-bridging chain structure, in which two $Cd^{II}$ centers are bridged by $\mu_2$-O atoms of sulfoxide

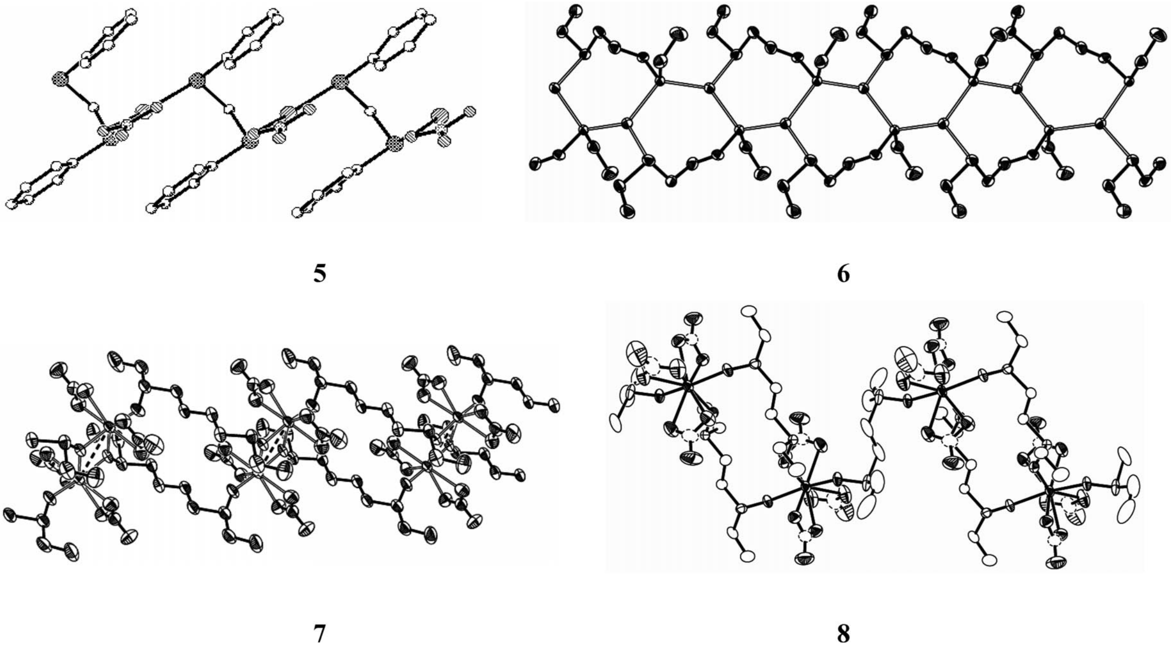
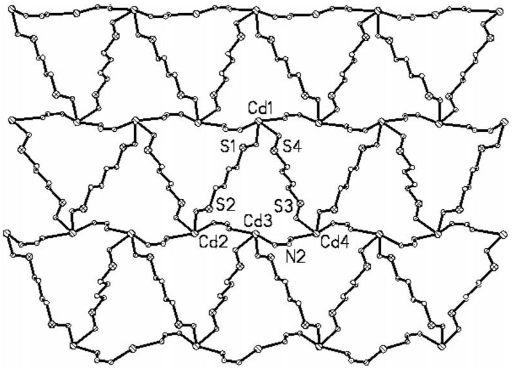


Figure 2. Molecular/cationic structures of some representative 1D complexes (H atoms omitted for clarity).

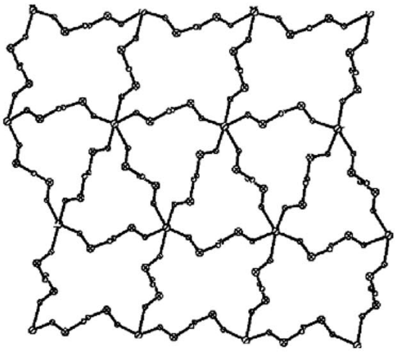
groups to form a dinuclear unit, and **L** ligands link such dinuclear units to form a 1D double-bridging chain containing macrometallacyclic units. In each macrometallacycle, the two bridging **L** ligands have different configurations: one is *R*,*R* and the other is *S*,*S*, and the result is that the whole molecule is in the *meso* form. Complex $[Yb(\mathbf{L})_{1.5}(NO_3)_3]_n$ [**8**, **L** = 1,2-bis(ethylsulfinyl)ethane][13k] exhibits a single-double-bridging chain structure, in which the dinuclear macrometallacycles formed through bridging two $Yb^{III}$ by two **L** ligands are further linked by another **L** ligand. All the **L** ligands act as bridges to link $Yb^{III}$ centers in a bis(monodentate) coordination mode and present *R*,*S* configuration and *trans*-*trans* arrangement.

## Two-Dimensional (2D) Structures

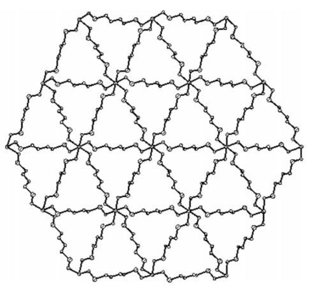
Figure 3 shows some 2D structural complexes. Complex $[Cd(\mathbf{L})(NO_3)_2H_2O]_n$ [**9**, **L** = 1,4-bis(phenylsulfinyl)butane][13h] has a unique 2D (4,4) network structure, in which the adjacent $Cd^{II}$ centers are linked by bidentate coordinated nitrates to form infinite zigzag $[Cd(NO_3)]_n$ chains, which are further linked by bis(monodentate) bridging **L** to form a 2D layer with quasi-trigonal 26-membered macrometallacyclic grids. It is interesting that these triangles are not equilateral; the separations between the $Cd^{II}$ centers across **L** are 10.701(4) and 10.480(2) Å, and the $NO_2$–Cd–$NO_2$ segment has a length of 10.163(1) Å. Complex $[La(\mathbf{L})_{2.5}(NCS)_3]_n$ [**10**, **L** = 1,2-bis(ethylsulfinyl)ethane][13k] has a 2D structure with a (3/4,5) topological net. Each $La^{III}$ center is linked to five other $La^{III}$ centers by the **L** bridges to form the 5-connected 2D network containing two types of macrometallacyclic arrays. One type is a 28-membered ring with a quadrilateral grid formed by four metal centers and four **L** ligands, and the other one is a 21-membered triangle ring made up of three metal centers and three **L** ligands. In **10**, all the ligands present a bis(monodentate) coordination mode and *trans*-*trans* arrangement and adopt the same *R*,*S*-configuration. It is interesting that $\{[Cd(\mathbf{L})_3](ClO_4)_2\}_n$ [**11**, **L** = 1,4-bis(ethylsulfinyl)butane][13h] has an unusual 2D (3,6) network structure containing triangular grids. Each $Cd^{II}$ center is linked to adjacent six $Cd^{II}$ centers through six ligands to form a non-interpenetrated (3,6) net, which comprises regular 27-membered trigonal macrometallacycles. The $ClO_4^-$ anions are partially infixed into the triangular cavities in an up-and-down way in each layer. Complex $\{[Ag(\mathbf{L})_2]ClO_4\}_n$ [**12**, **L** = 1,4-bis(phenylsulfinyl)butane][13b] is also a 2D molecular square array with 36-membered macrometallacycles. The adjacent $Ag^I$ ions are linked through **L** ligands in the orthogonal directions, which results in a molecular domain constituted by a highly symmetrical 36-membered $Ag_4L_4$ macrocycle. Two $Ag^I$ corners in the diagonal position fold upwards or downwards to form a "valley-like" molecular unit, which has $S_4$ symmetry. Two of the four S atoms bound to the O atoms have *R*-configuration, whereas the other two have *S*-configuration. The perchlorate anions filling in the cavities of the "valley"



**9**



**10**



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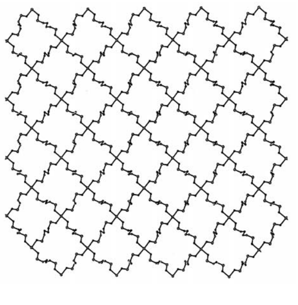

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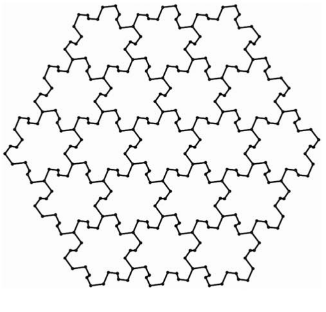


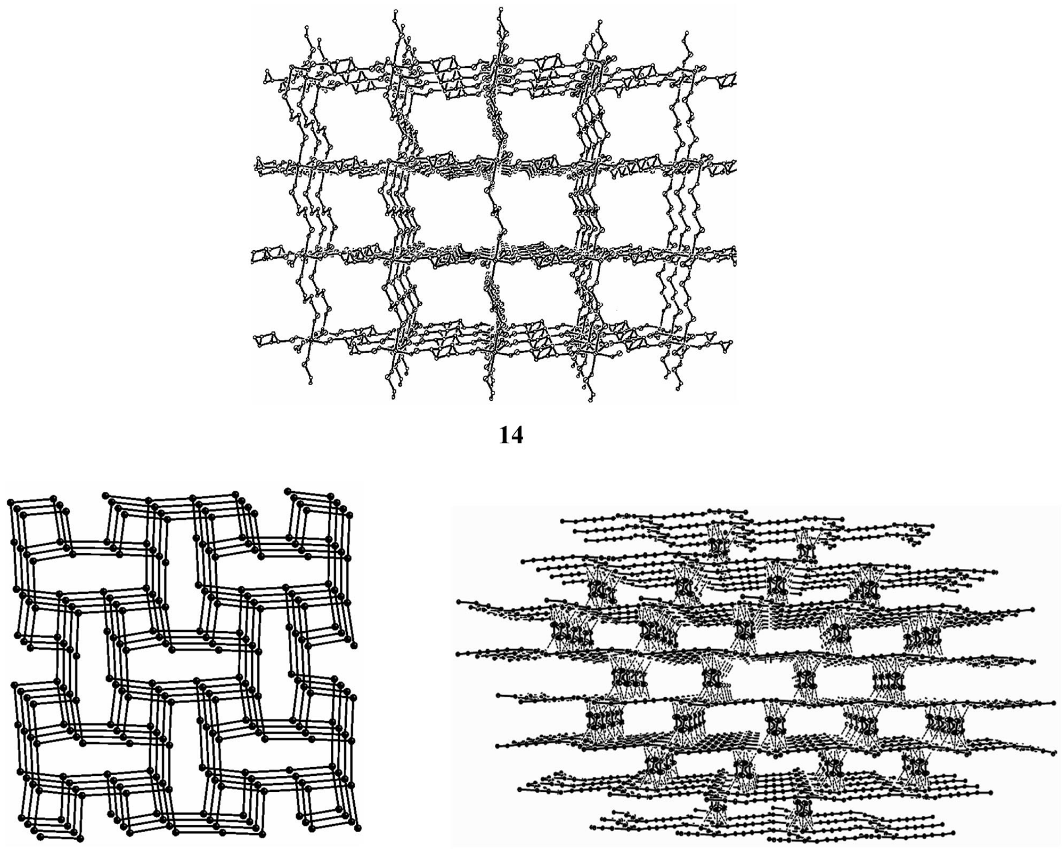
**13**

Figure 3. Views of some representative 2D layer complexes (the terminal groups of ligands, counterions, coordinated water molecules in **9** and H atoms omitted for clarity).

may act as templates for the formation of the network and consequently keep the structure stable. It is interesting that the disulfoxide ligands coordinate to $Ag^I$ ions by O but not S atoms. Complex $\{[Ag(\mathbf{L})_{1.5}]ClO_4\}_n$ [**13**, **L** = 1,2-bis(*tert*-butylthio)ethane][12h] also has a 2D (6,3) topologic network structure. Each ligand links two $Ag^I$ centers through the S atoms, and each $Ag^I$ center is coordinated by three **L** ligands to form a centrosymmetric, hexagonal, 30-membered macrometallacyclic unit, in which six $Ag^I$ centers are located at two different planes: alternately up and down.

### Three-dimensional (3D) Structures

Relative to the 2D structures, 3D structures are rare in the complexes obtained: only three examples were structurally determined. As shown in Figure 4, complex $\{[Cu(\mathbf{L})_3](ClO_4)_2\}_n$ [**14**, **L** = 1,4-bis(phenylsulfinyl)butane][13c] is a 3D structural polymer, in which the adjacent $Cu^{II}$ anions are linked by **L** ligands in three orthogonal directions to form a 3D framework with three types of channels running in the three directions and three kinds of 36-membered $Cu_4\mathbf{L}_4$ macrocycles. The $Cu^{II}$ center has a distorted octahedral coordination geometry formed by six O atoms from six ligands. There are three types of ligand conformations (*S*,*S*, *R*,*R*, and *S*,*R*) in a 1:1:1 ratio in the unit cell. Furthermore, the perchlorate anions fill in the channels, thus very small free volumes remain. In complex $\{[Ag(\mathbf{L})_{1.5}]ClO_4\}_n$ [**15**, **L** = bis(phenylthio)methane],[12f] each $Ag^I$ atom is connected to three S-donors of three distinct **L** ligands, and each ligand bridges two $Ag^I$ atoms. The 3D network formed here can be classified as a (10,3)-a network when the ligands are considered as spacers and $Ag^I$ ions as nodes. Two types of channels can be seen in the network when it is viewed along either the fourfold or threefold axis. These channels are perfectly filled by the phenyl groups and anions. The shortest closed circuits contain ten $Ag^I$ ions and ten moieties of **L** ligands and have nonplanar geometry. Complex $\{[Ag_2(\mathbf{L})_3ClO_4]ClO_4\}_n$ [**16**, **L** = 1,3-bis(benzylthio)propane][12l] is also a 3D framework structure constructed from cationic 2D (6,3) $[Ag(\mathbf{L})_{3/2}]^{n+}$ layers, similar to those in **13**, bridged by $ClO_4^-$. In the cationic layer, each ligand links two $Ag^I$ centers through two S donors in a bis(monodentate) bridging mode to form centrosymmetric 36-membered macrometallacyclic units. The $ClO_4^-$ anions are highly disordered and are located at the symmetry point; half reside in the hexagonal macrometallacyclic cavity of each layer, which may act as a template, and the other half link these layers to form the 3D structure.



**14**

**15**

**16**

Figure 4. Views [or schematic representation (**15**)] of three 3D framework complexes (the terminal groups of ligands, counterions, and H atoms omitted for clarity).

## 4. Structural Modulation – The Influencing Factors

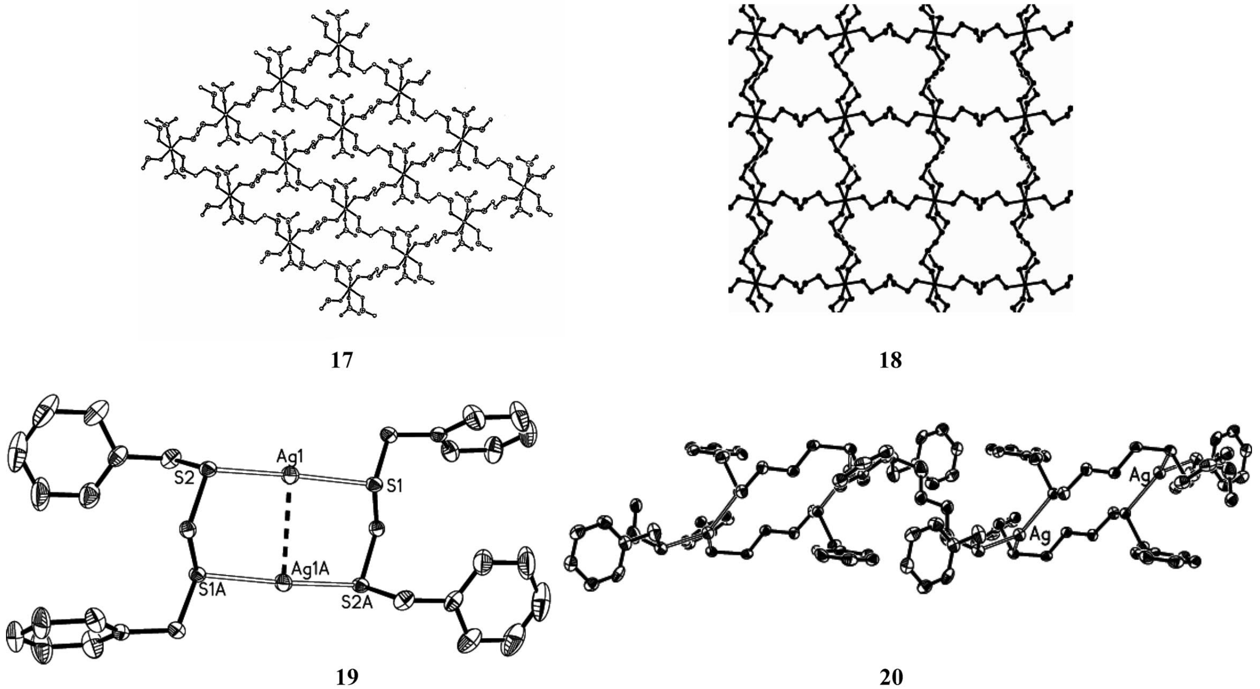
### Spacer Lengths of the Ligands

The spacers of the ligands have an important effect on the complex structures in these systems. Herein, we give two groups of examples. By using three structurally related disulfoxide ligands that differ only in spacer length (each time adding one more $CH_2$ group between the two coordinated S=O donors) to react with $Cu(ClO_4)_2$ under the same conditions, three complexes, $\{[Cu(\mathbf{L})_2](ClO_4)_2\}_n$ [**17**, **L** = 1,2-bis(phenylsulfinyl)ethane], $\{[Cu(\mathbf{L})_3](ClO_4)_2\}_n$ [**18**, **L** = 1,3-bis(phenylsulfinyl)propane],[13c] (Figure 5) and **14** (Figure 4), with different structures were obtained. As described above, **14** has a 3D framework structure. However, **17** has a 2D lamellar network structure, in which the adjacent $Cu^{II}$ ions are linked by **L** ligands in two directions to form a 28-membered rhombic macrometallacyclic unit, and the repeating units are fused to form a 2D rhombohedral array. The $Cu^{II}$ atom coordinates to four sulfoxide O atoms in the equatorial plane and two perchlorate O atoms at the axial positions in an elongated octahedral environment. Complex **18** is also a 2D complex but has a different structure from that of **17**. In **18**, the adjacent $Cu^{II}$ ions are linked by **L** in the two essentially orthogonal directions, and there are two distinct ligand conformations (A and B) in a 2:1 ratio. Two ligands with the A conformation coordinate to $Cu^{II}$ centers in equatorial positions to form a smaller 16-membered ring. The ligands with B conformation link adjacent $Cu^{II}$ ions in the axial positions to form a larger 32-membered macrometallacyclic square domain containing $Cu^{II}$ centers at the corners. Adjacent rings are fused into the unique 2D network. The center $Cu^{II}$ ion coordinates to six sulfoxide O atoms in a slightly distorted octahedral environment.

In the dithioether–$Ag^I$ system, such an influence has also been observed. Four bis(benzylthio) ligands were treated with $AgClO_4$ under a similar reaction procedure to result in four complexes **1**, **16**, $[Ag\mathbf{L}ClO_4]_2$ [**19**, **L** = bis(benzylthio)methane], and $[Ag(\mathbf{L})_{1.5}ClO_4]_n$ [**20**, **L** = 1,4-bis(benzylthio)butane],[12l] with different structures. As shown in Figures 1, 4, and 5, **1** is a mononuclear complex, but **16** adopts a 3D framework structure as described above. However, **19** is a discrete dinuclear complex in which each $Ag^I$ center is two-coordinate to two S donors from two ligands in an approximate linear geometry, and two $Ag^I$ atoms are bridged equivalently by two ligands which adopt a bis(monodentate) coordination mode to form a unique box-like dimeric entity. Complex **20** consists of 1D single, double-bridging chain cations and $ClO_4^-$ anions. A pair of $Ag^I$ ions are linked by two bridging **L** ligands to form dinuclear 14-membered macrometallacyclic units, $[Ag\mathbf{L}]_2$. Adjacent $[Ag\mathbf{L}]_2$ units are further linked by other ligands in single-bridging fashion. Thus, the differences among these structures in each case can be attributed to the different spacer lengths of the related ligands.

### Terminal Groups of the Ligands

As that of spacers, the influence of the terminal groups of the ligands on the structures of the complexes is also great. As shown in Figure 6, $[Ag\mathbf{L}ClO_4]_n$ [**21**, **L** = bis(*tert*-butylthio)methane][12h] has a 1D chain structure, in which the $Ag^I$ centers are linked by **L** ligands in a single-bridging mode, and each center is two-coordinate to two S donors

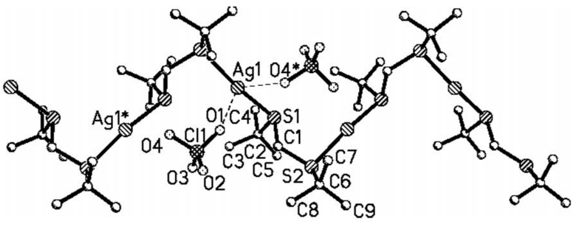


**17** **18**

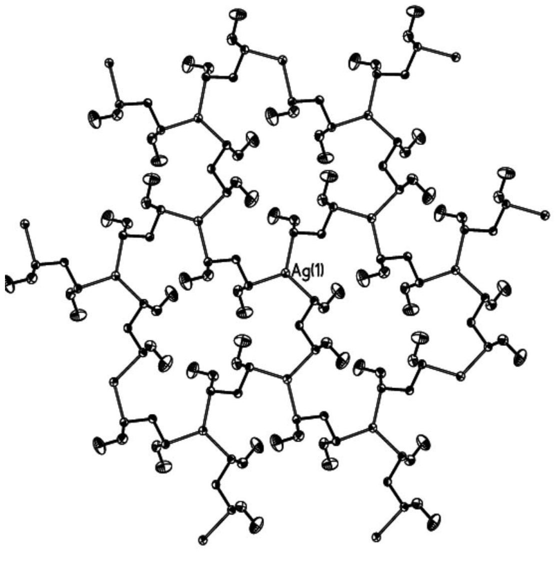
**19** **20**

Figure 5. Molecular/cationic structures of complexes **17**–**20** (the terminal groups of ligands in **17** and **18** and H atoms omitted for clarity).

of two distinct ligands. Whereas complex [Ag(**L**)$_{1.5}$ClO$_4$]$_n$ [**22**, **L** = bis(ethylthio)methane][12l] has a 2D layer structure of (6,3) topology similar to that of **16**, in which each ligand links two Ag$^I$ centers through S atoms, and each three-coordinate Ag$^I$ ion is bridged to three neighboring Ag$^I$ ions by **L** ligands to form centrosymmetric hexagonal 24-membered macrometallacyclic units. Six Ag$^I$ ions in the cycle are located at two different planes, alternately up and down. In the two complexes, the ligands used have the same spacers and different terminal groups. Their structural differences can be attributed to the difference in their terminal groups. The same case was also observed for complexes **7** and **9**.



**21**



**22**

Figure 6. Molecular/cationic structures of complexes **21** and **22** (H atoms omitted for clarity).

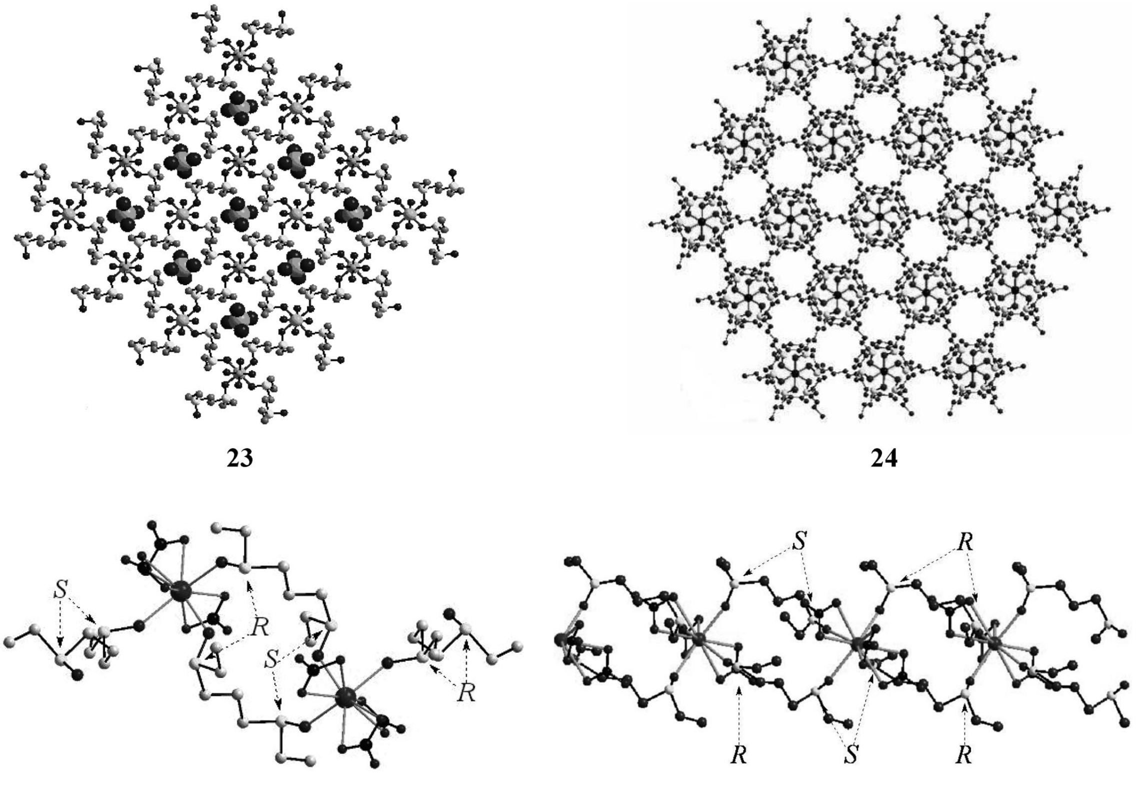
## Metal Ions

Generally, the influence of the metal ions on the complex structures can be attributed to the differences in their affinity, geometry, and ionic radius. Complex {[Cu(**L**)$_2$(ClO$_4$)](ClO$_4$)}$_n$ [**23**, **L** = 1,2-bis(ethylsulfinyl)ethane][13l] has a polymeric 2D layer structure of (4,4) topology (Figure 7), in which the coordination geometry of Cu$^{II}$ is square-pyramidal with four sulfoxide O donors in the equatorial plane and one O atom of ClO$_4^-$ in the apical position. Each ligand links two Cu$^{II}$ ions through the O atoms of the sulfoxide groups to form a 2D framework. The uncoordinated ClO$_4^-$ anions are fixed in the square cavities. In contrast, the AgClO$_4$ complex **4**[13n] with the same ligand has a tetranuclear structure, as described above, in which the Ag$^I$ ions exhibit trigonal-bipyramidal and octahedral coordination geometries, and the ligands adopt bidentate (*O*,*O*) chelating and tridentate μ-O-μ-(SO) bridging-chelating coordination modes. Another comparison can be made between complexes **14**[13c] and {[Cd(**L**)$_3$](ClO$_4$)$_2$(CHCl$_3$)}$_n$ (**24**),[13h] both of which have the same ligand [**L** = 1,4-bis(phenylsulfinyl)butane] and only different metal ions, Cu$^{II}$ and Cd$^{II}$, respectively. Complex **14** has a 3D framework structure, in which the Cu$^{II}$ center is octahedrally coordinated to six sulfoxide O atoms, and the ligands link Cu$^{II}$ ions in a single-bridging mode. However, **24** has a 2D (3,6) topology network structure, similar to that of **11**, containing 27-membered cyclic trigonal grids. Nevertheless, each Cd$^{II}$ center also coordinates to six O donors of six independent ligands in an octahedral coordination geometry, and the ligands adopt a bridging coordination mode similar to that in **14**. Moreover, in both complexes the perchlorate anions are infixed into the cavities.

The lanthanide contraction effect has also been confirmed for the disulfoxide complexes [La(**L**)$_2$(NO$_3$)$_3$]$_n$ (**25**) and [Dy(**L**)$_2$(NO$_3$)$_3$]$_2$ (**26**) [**L** = 1,3-bis(ethylsulfinyl)propane].[13m] As shown in Figure 7, complex **25** has a 1D double-bridging chain structure, in which the La$^{III}$ center binds to ten O atoms, four from S=O moieties of four **L** ligands and six from three chelating coordinated nitrate anions. The overall geometry is a distorted bicapped square antiprism. The **L** ligands act as bis(monodentate) bridges to link the adjacent metal centers, and two such ligands link two La$^{III}$ centers to form a 16-membered ring. The rings expand to form a 1D intercross double-bridging chain. The distance between two metal centers in the ring unit is 8.898 Å. The ligands adopt three kinds of configurations: *R*,*S*, *R*,*R*, and *S*,*S* forms, in which the same side chain has one kind of configuration, *meso* or *rac*. In contrast, compound **26** is a dinuclear structural complex. The Dy$^{III}$ ion is nine-coordinate to three O atoms of distinct **L** ligands and six O atoms of bidentate chelating nitrate groups to give a highly disordered tricapped trigonal prism configuration. In the dinuclear entity, the two metal centers are linked by two ligands to form a twisting 16-membered ring with a Dy···Dy separation of 8.265 Å. The **L** ligands in **26** exhibit two kinds of coordination modes: bis(monodentate) bridging and monodentate. Similar to those in **25**, the ligands also have three kinds of configurations.

## Counteranions and Solvents

In addition to the nature of the ligands and metal ions, the counteranions and solvents used in synthesis are also important factors to affect the structures of the metal com-

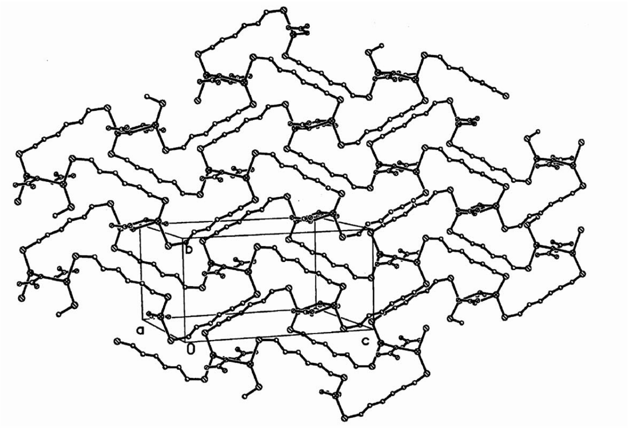


23 24 25 26

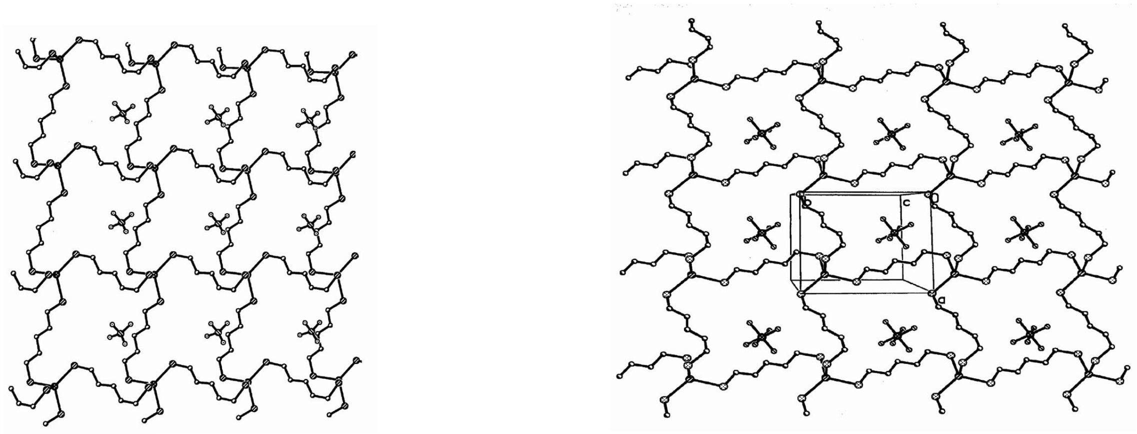
Figure 7. Molecular/cationic structures of complexes **23**–**26** (solvent $CHCl_3$ molecules in **24** and H atoms omitted for clarity).

plexes; the influence of counterions and solvents is due to the differences in their size, coordination ability, and coordination mode. The dithioether ligand 1,6-bis(phenylthio)-hexane reacted with $AgClO_4$ and $AgNO_3$, respectively to afford complexes **2** and $[Ag\mathbf{L}NO_3]_n$ (**27**).[12g] As described above, **2** is a dinuclear cage complex, but **27** (Figure 8) has a 2D structure, in which each nitrate anion links two neighboring $Ag^I$ ions in the $\mu_2$-O bridging mode to form a $Ag_2O_2$ ring, which is linked by 1,6-bis(phenylthio)hexane ligands to form a 2D layer containing two types of rings. The difference in the structures of the two complexes can be attributed to the difference in the coordination modes of the $NO_3^-$ and $ClO_4^-$ anions. Another example is the comparison between complexes $\{[Ag(\mathbf{L})_2]ClO_4\}_n$ (**28**)[12e] and $\{[Ag(\mathbf{L})_2]PF_6\}_n$ (**29**)[12b] [**L** = 1,5-bis(phenylthio)pentane]. As shown in Figure 8, both **28** and **29** have a 2D structure in which the $Ag^I$ centers coordinate to four S atoms and display a distorted tetrahedral geometry, and ligands link adjacent $Ag^I$ ions to form an extended framework. However, the two structures have different geometries with different ring sizes. This may be due to the difference of the sizes of the $ClO_4^-$ and $PF_6^-$ anions.

The solvents used in the synthesis can also affect the structures of the resulting complexes. For example, complexes $\{[Ag(\mathbf{L})_{1.5}CH_3OH]ClO_4\}_n$ (**30**) and $[Ag(\mathbf{L})_{1.5}ClO_4]_n$ (**31**) [**L** = 1,4-bis(phenylthio)butane][12e] were obtained by the reaction of the ligand **L** and $AgClO_4$ in methanol and acetone, respectively, by using a similar procedure. As shown in Figure 9, the two complexes have different structures. Complex **30** has a 2D honeycomb-like structure. The $Ag^I$ centers have two different environments, which brings about two different repeating units, A and B. The A and B macrometallacycles arrange alternately along the *c* direction, and each propagates along the *ab* plane to form a 2D structure. Each hexagonal unit is composed of a $Ag_6\mathbf{L}_6$ macrometallacycle, whose cavity is filled by six phenyl rings of **L** ligands and two perchlorate anions. The structure of **31** also has a 2D arrangement of honeycombs constructed from $Ag^I$ ions linked by the **L** ligands. In contrast to **30**, there is only one type of ring unit. Each **L** ligand bridges two $Ag^I$ centers to form a centrosymmetric hexagonal 42-membered macrometallacyclic ring made up of six $Ag^I$ ions and six ligands. In **30**, the $CH_3OH$ molecules take part in the coordination, but in **31**, the $ClO_4^-$ anions coordinate to the metal ion. A similar situation has also been observed in complexes $\{[Ag_2\mathbf{L}_2](ClO_4)_2CHCl_3\}_n$ (**32**) and $\{[Ag\mathbf{L}](ClO_4)C_3H_6O\}_n$ (**33**) [**L** = 1,4-bis(2-pyridylthio)butane].[12j] As shown in Figure 9, complex **32** has a 2D network structure. The basic structural block of the network is the dinuclear unit formed by two **L** ligands coordinating to two $Ag^I$ ions. In the dinuclear unit, the two pyridylsulfanyl groups from two **L** ligands bridge two $Ag^I$ ions to form an eight-membered ring, which adopts a chair configuration with two pyridine rings parallel to each other. Each dinuclear unit adopts a bidentate bridging mode, using two terminal pyridine N atoms in *trans* form to coordinate to $Ag^I$ of

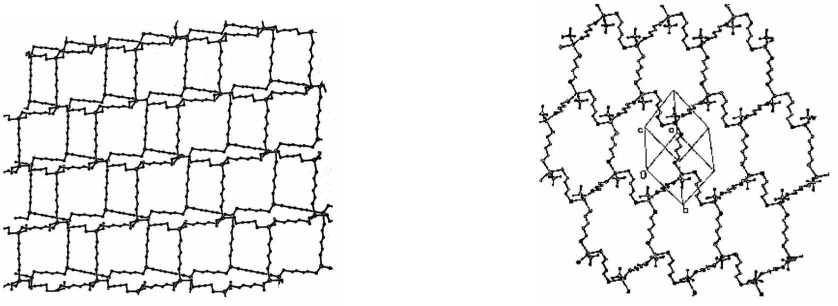


**27**

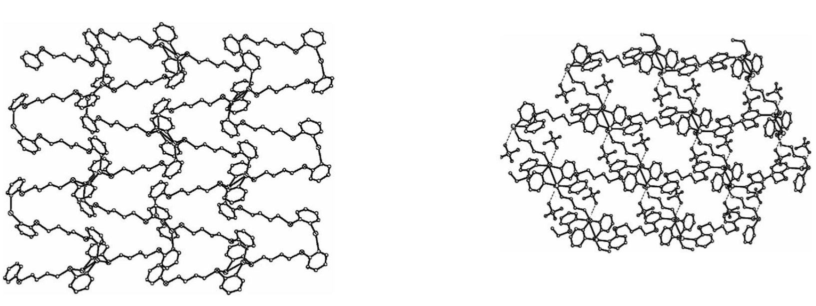


**28** **29**

Figure 8. Molecular structures of **27**–**29** (the terminal groups of ligands and H atoms omitted for clarity).



**30** **31**



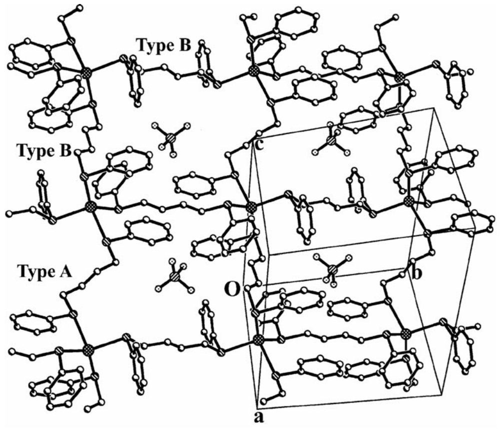
**32** **33**

Figure 9. Molecular/cationic structures of **30**–**33** (the terminal groups of ligands in **30** and **31**, solvent molecules in **30**, **32** and **33** and H atoms omitted for clarity).

other dinuclear units. Four dinuclear units further form a twisted macrometallacycle, and adjacent rings are fused into the 2D lamellar structure. Similarly, **33** also has a 2D grid structure, but the ligands adopt two different coordination modes: one adopts a tetradentate bridging mode bonding to $Ag^I$ ions forming 1D chains along the *a* direction, and the other one bridges, in a bidentate mode, those 1D chains into a 2D network. The solvents used in **32** and **33** are all noncoordinating; they only act as templates. Thus, the structural difference between the two complexes may arise from the different sizes and shapes of the acetone and chloroform molecules.

### Ratio of Metal Salts and Ligands

In these systems, the influence of the ratio of the metal salt and the ligand used in synthesis on the structures of the complexes formed was also observed. Complexes **31**[12e] and $\{[Ag(\mathbf{L})_2]ClO_4\}_n$ [**34**, **L** = 1,4-bis(phenylthio)butane][12e] (Figure 10) were synthesized by a similar procedure; the only difference was in the molar ratios of the $Ag^I$ salt and the ligand. Although both complexes have a 2D arrangement, the frameworks have different conformations. In comparing the structural units of the two complexes, we can find that the weakly coordinating perchlorate group in **31** as described above was substituted by an **L** ligand in **34**. In the structure of **34** each ligand bridges two adjacent $Ag^I$ centers to form a slightly twisted rectangular 28-membered ring, $Ag_4\mathbf{L}_4$. The ligand adopts two configurations: A and B. In A, each ligand bridges two $Ag^I$ centers, and the two S donors are at the apex of the trigonal pyramid. In the repeating unit, the ligands at the other three edges adopt the B conformation, and the two S donors reside at the base of the trigonal pyramid. Adjacent rectangular rings are fused to form the 2D sheet.



**34**

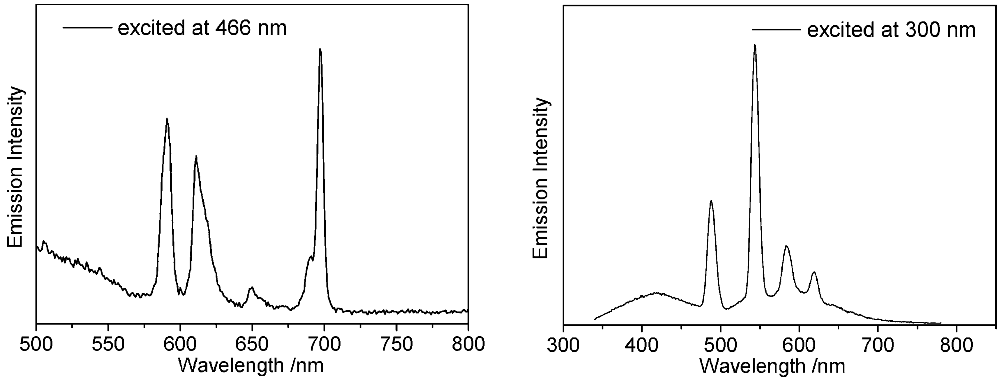
Figure 10. Molecular structure of **34** (H atoms were omitted for clarity).

## 5. Luminescent and Magnetic Properties of Some Complexes

### Luminescent Properties

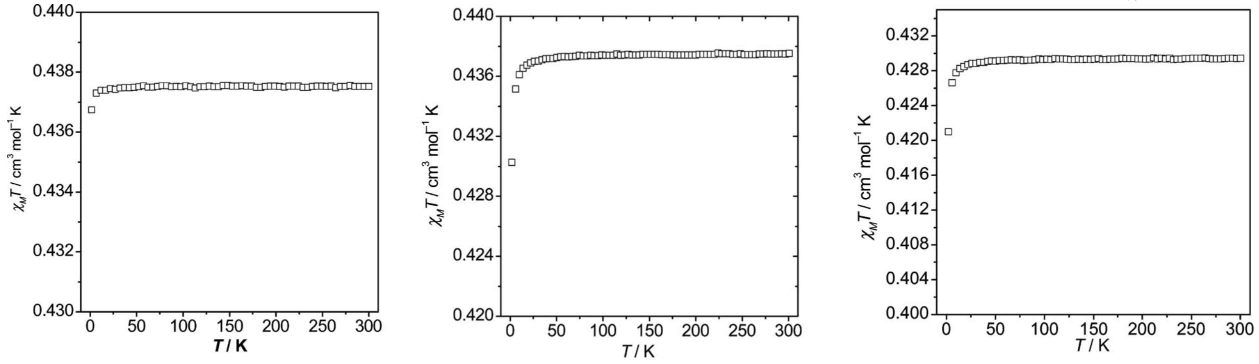
Photoluminescence of six lanthanide–disulfoxide complexes, $[Eu(\mathbf{L})_4](ClO_4)_3$ (**35**), $[Tb(\mathbf{L})_4](ClO_4)_3$ (**36**), $\{[Eu(\mathbf{L})_2(dmf)_4](ClO_4)_3\cdot 4H_2O\}_n$ (**37**), $\{[Tb(\mathbf{L})_2(dmf)_4](ClO_4)_3\cdot 3H_2O\}_n$ (**38**), $\{[Eu(\mathbf{L})_3(CH_3OH)_2](ClO_4)_3\}_n$ (**39**), and $\{[Tb(\mathbf{L})_3(CH_3OH)_2](ClO_4)_3\}_n$ (**40**) [**L** = 1,4-bis(phenylsulfinyl)butane for **35**–**38** and 1,2-bis(ethylsulfinyl)ethane for **39** and **40**] have been investigated in the solid state or in solution.[13i,13k]

The absorption spectra of **35**–**38** in MeCN show absorption bands at ca. 238–274 nm, similar to that observed in the free ligand, but the bands have a very slight shift in the absorption energy, which is consistent with their origins, as they arise from ligand-centered transitions. The excitation spectra of **35**–**38** show a broad band in approximately the 250–350 nm range, which is characteristic of the $\pi$–$\pi^*$ transitions of the ligand. The emission spectra of **35**–**38** show the typical narrow emission bands of $Eu^{III}$ and $Tb^{III}$, respectively. For example, for the solid-state emission spectrum of **35** (Figure 11), four bands corresponding to the $^5D_0 \rightarrow {}^7F_J$ ($J$ = 1–4) transitions of $Eu^{III}$ are resolved. While the solid-state emission spectra of **35** at room temperature



(a) (b)

Figure 11. Emission spectra of **35** in the solid state (a) and **36** in MeCN solution (b).



(a)

(b)

(c)

Figure 12. The temperature dependence of $\chi_m T$ for **14** (a), **17** (b), and **18** (c).

and 77 K resemble each other well, those in MeCN solution are different. This indicates that the solvent may play an important role in affecting the coordination environments of Eu$^{III}$. In solution emission spectra of **36**, four emission bands corresponding to the $^5D_4 \rightarrow ^7F_J$ ($J$ = 3–6) transition were observed (Figure 11). In addition, very little temperature effect on the lifetime is observed in such systems. Comparisons of the emission spectra and lifetimes of **35**, **36**, **37**, and **38** show that **35** and **36** have relatively stronger emission intensity and a longer emission lifetime than those of the corresponding **37** and **38**. This may be attributed to the presence of a larger number of aromaticity-containing ligands around the metal center and the absence of solvent molecules directly coordinated to the lanthanide center.[13i]

The excitation spectra of **39** and **40** also show the absorption of the ligand and Ln$^{III}$ ions.[13k] The emission spectrum of **39** in the solid state shows four emission bands corresponding to the transitions from $^5D_0$ to $^7F_J$. The split of the so-call hypersensitive $^5D_0 \rightarrow ^7F_2$ is not obvious, but the transition is the strongest in the four transitions, being three times as strong as the transition from $^5D_0$ to $^7F_1$. The emission spectrum of **40** contains also four bands corresponding to the $^5D_4 \rightarrow ^7F_J$ transitions of Tb$^{III}$, and each one is obviously split into two components. The intensity of the hypersensitive $^5D_4 \rightarrow ^7F_5$ transition is close to six times that of the other bands. These results show that this complex has excellent single color property.

### Magnetic Properties

Owing to the presence of long bridging ligands in all the complexes with paramagnetic ions, one could expect the lack of any noticeable magnetic coupling between the metal ions. The magnetic behavior of three selected Cu$^{II}$–disulfoxide complexes, **14**, **17**, and **18**, was studied.[13l] Figure 12 shows the temperature dependence of $\chi_m T$ for those complexes. With decreasing temperature, the observed $\chi_m T$ values of **14** are almost constant (0.4375 cm$^3$ mol$^{-1}$ K) down to 50 K. From 50 K to 2 K $\chi_m T$ slightly decreases, reaching a value of 0.4367 cm$^3$ mol$^{-1}$ K at 2 K. Calculating the theoretical Weiss constant with these $\chi_m T$ values yields a $\theta$ value of $-3.6 \times 10^{-3}$ K (almost zero). The calculated $g$ value is 2.16. Complexes **17** and **18** also exhibit a similar behavior. For **17**, $\chi_m T$ values start at 0.4375 cm$^3$ mol$^{-1}$ K at 300 K and reach 0.4302 cm$^3$ mol$^{-1}$ K at 2 K, with a Weiss constant of $\theta$ = –0.033 K and $g$ = 2.16. For **18**, $\chi_m T$ values start at 0.4294 cm$^3$ mol$^{-1}$ K at 300 K and reach 0.42101 cm$^3$ mol$^{-1}$ K at 2 K, with a Weiss constant of $\theta$ = –0.041 K and a $g$ value of 2.14. Thus, in fact, the susceptibility data indicate that the Cu$^{II}$ ions are not coupled in the three complexes.

## Conclusions

In conclusion, several series of dithioether or disulfoxide metal complexes have been summarized. Such complexes adopt various structural features ranging from mononuclear to 3D frameworks, in which the ligands and metal ions show a variety of coordination/bridging modes. These results demonstrate that the spacers and terminal groups of the flexible dithioether and disulfoxide ligands, the metal ions, counteranions, solvents, and the ratio of reagents have a great influence on the structures of the metal complexes formed. The structural differences of such complexes imply that the flexible $-(CH_2)_n-$ backbone can allow the ligands to rearrange so as to minimize steric hindrance when coordinating to metal ions, causing the conformational variation in such ligands to result in the structural variations of complexes. Furthermore, the coordination diversity of the metal ions, especially Ag$^I$, also plays important roles in affecting the formation of the frameworks of such complexes. It should also be noted that the coordination behaviors/modes of the ligands with metal ions are flexible and diverse. The S atom in thioether ligands has two lone electron pairs, which can take part in coordination to metal ions. In these complexes the S donors adopt monodentate or $\mu_2$-S bridging modes, and the former has priority over the latter, probably to reduce the steric hindrance. The S=O group in disulfoxide ligands can adopt different coordination modes to form different structures based on the steric and electronic cooperating effects. Such results present a feasible way for controlling the structures of complexes with these or other related ligands, by fine-tuning the ligand spacers and terminal groups, selecting metal ions, as well as changing other reaction conditions.

## Acknowledgments

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