Flexible *meso*-Bis(sulfinyl) Ligands as Building Blocks for Copper(II) Coordination Polymers: Cavity Control by Varying the Chain Length of Ligands[**]

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Crystal engineering of coordination polymers with fascinating structural topologies has attracted a great deal of attention in recent years because of their potential as functional materials.[1] Concurrent with this has been the development of multidimensional networks based primarily on the linking of metal centers by rigid bridging components.[2] Far less common has been the use of flexible bridging units in the construction of extended networks,[3] this approach is attractive because the flexibility and conformational freedom of such ligands offer the possibility of generating unique frameworks with useful properties.

Herein we report the synthesis of three novel Cu^{II} complexes with unique macrometallacyclic networks formed by using flexible *meso*-bis(sulfinyl) ligands (**1**–**3**; Figure 1)[4] as building blocks. The underlying principles of our design are as follows: a) the ditopic coordination sites of bis(sulfinyl) may allow coordination polymers with higher dimensions; b) the pyramidal S atom is an asymmetric center to introduce acentric sites into the resulting crystals; c) the dimensions and cavity sizes of the frameworks with such ligands may be easily controlled by ligand modifications; d) bis(sulfinyl) ligands, the chemistry of which is still undeveloped, are likely to be applicable to a vast variety of metal moieties.

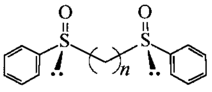

Figure 1. Ligands **1** ($n=2$), **2** ($n=3$), and **3** ($n=4$).

The two-dimensional (2D) polymers $[\mathrm{Cu}\mathbf{1}_2(\mathrm{ClO}_4)_2]^2_\infty$ (**4**), $\{[\mathrm{Cu}\mathbf{2}_3](\mathrm{ClO}_4)_2\}^2_\infty$; (**5**), and the three-dimensional (3D) polymer $\{[\mathrm{Cu}\mathbf{3}_3](\mathrm{ClO}_4)_2\}^3_\infty$ (**6**), were prepared from $\mathrm{Cu(ClO_4)_2}$ and the corresponding purified *meso* form ligand. These polymers are insoluble in most standard solvents but slightly soluble in DMF. The IR peaks for $\nu_{\mathrm{S=O}}$ in **4**–**6** are shifted to lower frequencies compared to those in the free ligands.[5] Thermogravimetric analysis (TGA) studies of **4**–**6** revealed that they decompose at 216, 207, and 227 °C, respectively. Attempts to exchange $\mathrm{ClO_4^-}$ for $\mathrm{NO_3^-}$, $\mathrm{BF_4^-}$, or $\mathrm{PF_6^-}$ gave only noncrystalline complexes, the structural motifs of which were not clear.

In **4**, each Cu^{II} center is six-coordinated by four O atoms of the S=O groups of four different **1** ligands in equatorial positions (Cu–O bonds: 1.918(3), 1.942(3) Å), and two other O atoms from $\mathrm{ClO_4^-}$ ions in axial positions (Cu–O bond: 2.518 Å); while in **5** and **6**, each Cu^{II} is six-coordinated by the O atoms of the S=O groups of six distinct bis(sulfinyl) ligands (Cu–O bonds: 1.980(3), 1.987(3), 2.311(3) Å in **5**; 1.965(4), 1.970(4), 2.362(5) Å in **6**). It is clear that every Cu^{II} center in **4**–**6**[7, 8] is in an axially elongated pseudo-octahedral coordination geometry with normal Cu–O bonds in the equatorial plane and longer Cu–O bonds in the axial positions because of the Jahn–Teller effect.

Figure 2 shows the lamellar network of **4**, in which the adjacent Cu^{II} ions are linked by **1** in two directions to form a 28-membered rhombic macrometallacyclic unit with dimensions of 8.05 × 9.16 Å and the repeating units fused to form a 2D rhombohedral array. The $\mathrm{ClO_4^-}$ ions coordinate to the Cu^{II} centers rather than occupying the rhombus cavity, probably because the $-\mathrm{CH_2CH_2}-$ chain in **1** is too short to form a cavity with a large enough void to accommodate a $\mathrm{ClO_4^-}$ ion.

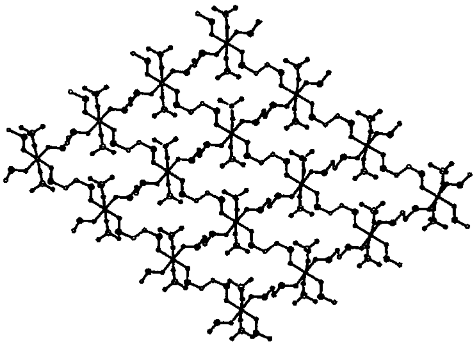

Figure 2. The lamellar structure of **4**. Phenyl groups and H atoms are omitted for clarity.

As shown in Figure 3, **5** forms an unprecedented lamellar molecular-square array. The adjacent Cu^{II} ions are linked by **2** in 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 $\mathrm{Cu_2}\mathbf{2}_2$ ring. The ligands with **B** conformation link adjacent Cu^{II} ions in the axial positions to form a 32-membered macrometallacyclic square domain containing Cu^{II} centers at the corners. Adjacent rings are fused to a unique 2D network, with the smaller rings disposed along the *a* direction. Unlike **4**, the square cavity with dimensions of 9.44 × 10.96 Å can accommodate a $\mathrm{ClO_4^-}$ ion. Other $\mathrm{ClO_4^-}$ ions are sandwiched between layers to maintain the electric balance.

In **6**, the adjacent Cu^{II} ions are linked by **3** in two orthogonal directions and the third direction, to form a 3D structure with three types of channels running in three directions

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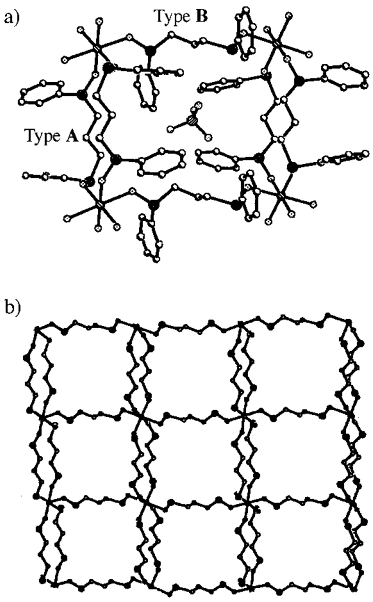

Figure 3. a) View of the repeating unit of **5** showing the 16- and 32-membered macrometallacycles and the **A** and **B** ligand conformations. b) The molecular-square network of **5**.

(Figure 4), which is a key difference to **4** and **5**. Compound **6** is composed of three kinds of 36-membered $\mathrm{Cu}_4\mathbf{3}_4$ macrocycles. There are three types of ligand conformations in a 1:1:1 ratio in the unit cell. Two carbon atoms of **3** on the *c* axis are disordered. A feature of **6** is the nature of the polymeric array resulting from the linking of adjacent Cu^{II} ions with M-O $\cdots$ O-M bridges in three directions. The basic repeating unit with dimensions of $11.2 \times 11.8 \times 11.0$ Å encapsulates two ClO_4^- ions.

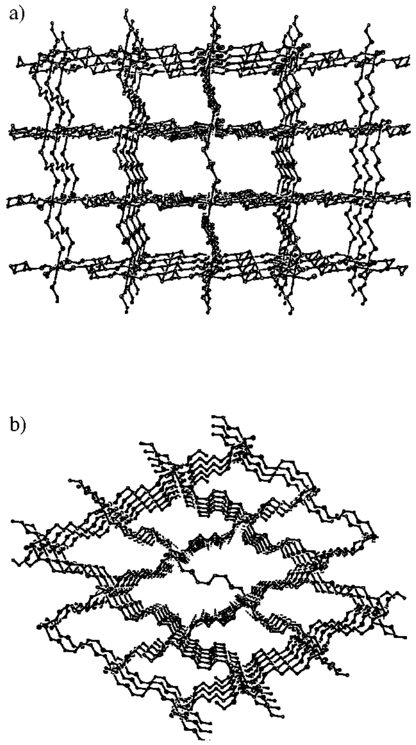

Figure 4. Projection of **6** a) along *a* axis showing the square channels and b) along *c* axis showing the rhombic channels.

The space-filling diagrams of the repeating units of **4**–**6** (Figure 5) clearly show that the cavity in **4** is too small to accommodate a ClO_4^- ion, and is big enough to fully encapsulate a ClO_4^- ion in **5**, and because of the longer spacer units in **6** the octahedral cavity can encapsulate two ClO_4^- ions. Therefore, varying the chain length of ligands controls the cavity sizes of such networks.

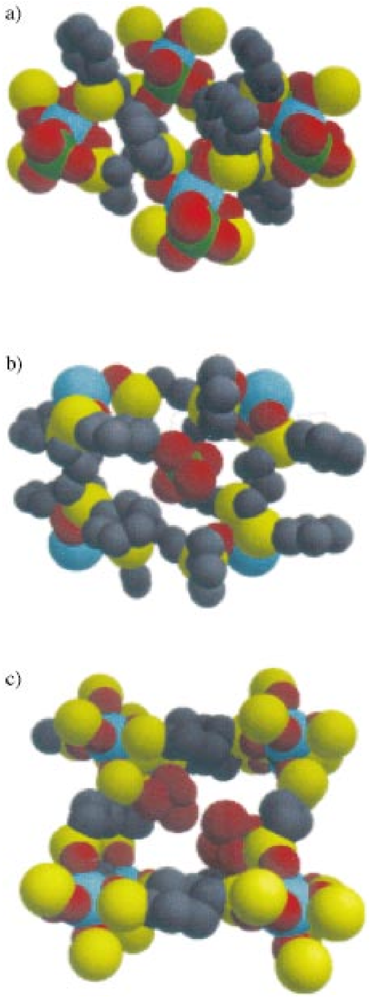

Figure 5. The space-filling diagrams of the cavities for the repeating units of a) **4**, b) **5**, and c) **6**. H atoms are omitted for clarity, and the phenyl groups in **6** are omitted to reveal the ClO_4^- ions; O: red, Cl: green, Cu: turquoise, S: yellow.

The magnetic behavior of **4**–**6** was studied, and Figure 6 shows the temperature dependence of $\chi_M T$ for **4** and (insert) the field dependence for the reduced molar magnetization ($M/N\beta$). With the decreasing of temperature, the observed $\chi_M T$ values of **4** are constant until around 15 K, (0.433 $cm^3 mol^{-1} K$, typical for Cu^{II}). At very low temperature, $\chi_M T$ decreases, characteristic of a system with a net weak antiferromagnetic interaction;[6a] the behavior of **5** and **6** was similar. The susceptibility data were fitted by the expansion series of Lines[6b] for an $S = ½$ antiferromagnetic quadratic layer, assuming only one J value. The best fit is given by the superexchange parameter $J = -0.012\ cm^{-1}$, $g = 2.13$ ($R = 2.6 \times 10^{-5}$). The curve of the reduced magnetization versus H (Figure 6, insert) at 2 K follows the Brillouin formula. At

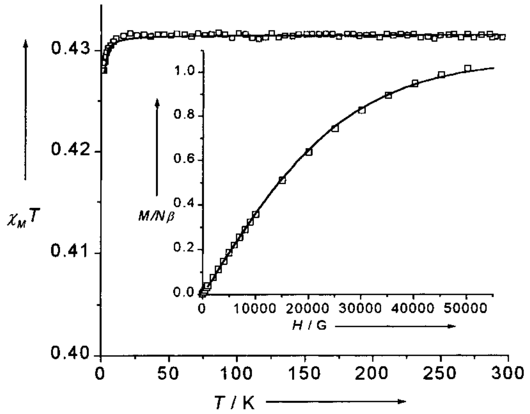

Figure 6. Temperature dependence of $\chi_M T$ [cm^{3}mol^{-1}K] for **4** (**5** and **6** have similar patterns). Insert: Field dependence for the reduced magnetization at 2 K ($M/N\beta$, number of electrons per formula unit).

50000 G, the $M/N\beta$ value tends to the saturation value (one electron, $S = \frac{1}{2}$). This feature corroborates the weak antiferromagnetic character shown in the $\chi_M T$ curve. Evidently, there is a possible interlayer contribution, the J value of which is impossible to calculate because of the features of the experimental curves.

In conclusion, **4**–**6** are rare examples of pseudo-octahedral metal organic frameworks which are noninterpenetrating and made up of macrometallacyclic arrays with controllable cavity sizes. The presence of the ligand phenyl groups and the need for counterions may play a key role in the generation of such noninterpenetrating structures. This implies that the interpenetration of coordination polymers might be controlled by ligand modification. Although **1**–**3** are very similar in structure, they form quite different metal–organic networks. This suggests that subtle variations of the ligands may result in quite different networks. The lattice dimensions in **4**–**6** are rather large, however, the ligand phenyl groups and counterions occupy the major parts of their voids. As *meso* ligands with *R*,*S* configurations were used, the networks of **4**–**6** are all mesomeric. Studies using *S*,*S* or *R*,*R* bis(sulfinyl) for construction chiral networks and systematic studies on such ligands by further varying their backbones are under way.

Experimental Section

4: A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (1 mmol) in acetone (10 mL), DMF (0.5 mL), and diethoxyethane (10 mL) was heated at reflux for 15 min, and stirred at 40 °C for further 1.5 h. Then **1** (3 mmol) dissolved in $CHCl_3$ (10 mL) was added to the solution and heated at reflux for 2 h. After cooling to room temperature, the solution was filtered and the filtrate was allowed to slowly evaporate to obtain the single crystals of **4** in about 30 % yield. **5** and **6** were prepared in the same manner. IR (KBr pellet) $\tilde{\nu}$ = **4**: 2924, 1444, 1092, 1035, 998, 966, 751, 691, 623 cm^{-1}; **5**: 2947, 1444, 1085, 1042, 996, 959, 744, 690, 624 cm^{-1}; **6**: 2956, 1479, 1092, 1072, 999, 972, 759, 695, 624 cm^{-1}.

Magnetic susceptibility data were collected with a Quantum Design SQUID magnetometer between 2–300 K. From room temperature to 4 K, these measurements were repeated with a pendulum-like MANICS-DMS8 susceptometer. The results were the same. The output data were corrected for the diamagnetism of the samples and holder. Magnetization measurements were performed at 2 K in the ±5 T range.

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[1] For examples: a) G. B. Gardner, D. Venkataraman, J. S. Moore, S. Lee, *Nature* **1995**, *374*, 792; b) H. O. Stumpt, L. Ouahab, Y. Pei, D. Grandjean, O. Kahn, *Science* **1993**, *261*, 447; c) O. M. Yaghi, G. Li, H. Li, *Nature* **1995**, *378*, 703; d) A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Withersby, M. Schröder, *Coord. Chem. Rev.* **1999**, *183*, 117; e) S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148; f) M. J. Zaworotko, *Angew. Chem.* **2000**, *112*, 3180; *Angew. Chem. Int. Ed.* **2000**, *39*, 3052, and references therein.

[2] For example: a) S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1558; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460, and references therein; b) M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151, and references therein; c) C. V. K. Sharma, G. A. Broker, J. G. Huddleston, J. W. Baldwin, R. M. Metzger, R. D. Rogers, *J. Am. Chem. Soc.* **1999**, *121*, 1137, and references therein.

[3] For examples: D. M. L. Goodgame, D. A. Grachvogel, I. Hussain, A. J. P. White, D. J. Williams, *Inorg. Chem.* **1999**, *38*, 2057, and references therein.

[4] R. H. Zhang, Y. Zhan, J. Chen, *Synth. React. Inorg. Met.-Org. Chem.* **1995**, *25*, 283.

[5] H. B. Kagan, B. Ronan, *Rev. Heteroat. Chem.* **1992**, *7*, 92.

[6] a) O. Kahn, *Molecular Magnetism*, VCH, New York, **1993**; b) M. E. Lines, *J. Phys. Chem. Solids* **1970**, *31*, 101.

[7] Crystal data for **4**: $C_{28}H_{28}Cl_2CuO_{12}S_4$, light green, $M_r = 819.18$, $0.30 \times 0.25 \times 0.20$ mm^3, triclinic, space group $P\bar{1}$, $a = 8.0447(16)$, $b = 9.1568(19)$, $c = 12.854(3)$ Å, $\alpha = 82.898(4)$, $\beta = 72.031(4)$, $\gamma = 67.553(4)°$, $V = 832.4(3)$ Å^3, $F(000) = 838$, $Z = 2$, $\mu = 2.257$ mm^{-1}, $\rho = 3.268$ g cm^{-3}, $\theta_{max} = 26.42°$, $T = 298$ K. Of 3730 measured data 3230 were unique (R_{int} 0.0216) with $I > 2\sigma(I)$. Final R, Rw, and S values are 0.0667, 0.1713, and 1.028, respectively. For **5**: $C_{45}H_{48}Cl_2CuO_{14}S_6$, light blue, $0.30 \times 0.20 \times 0.10$ mm^3, $M_r = 1139.6$, triclinic, space group $P\bar{1}$, $a = 9.4375(7)$, $b = 15.2188(11)$, $c = 18.9663(15)$ Å, $\alpha = 78.966(2)$, $\beta = 84.350(2)$, $\gamma = 80.514(2)°$, $V = 2630.9(3)$ Å^3, $F(000) = 1178$, $Z = 2$, $\mu = 0.816$ mm^{-1}, $\varrho = 1.439$ g cm^{-3}, $\theta_{max} = 25.03°$, $T = 298$ K. Of 11059 measured data 9259 were unique (R_{int} 0.0277) with $I > 2\sigma(I)$. Final R, Rw, and S values are 0.0506, 0.1374, and 1.034, respectively. Bruker Smart 1000 CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). SADABS absorption corrections were applied. The structures were solved by direct methods using SHELXS 97 program,[9a] and the refinements were performed with the full-matrix least-squares method on F^2. The largest residual peak and hole are 0.914 and -0.568 e Å^{-3}, respectively, for **4**; and 0.722 and -0.484 e Å^{-3}, respectively, for **5**.

[8] Crystal data for **6**: $C_{48}H_{54}Cl_2CuO_{14}S_6$, green, $M_r = 1181.71$, $0.50 \times 0.40 \times 0.37$ mm^3, triclinic, space group $P\bar{1}$, $a = 11.191(3)$, $b = 11.750(4)$, $c = 11.802(3)$ Å, $\alpha = 86.92(3)$, $\beta = 82.65(2)$, $\gamma = 62.90(2)°$, $V = 1370.1(6)$ Å^3, $F(000) = 613$, $Z = 1$, $\mu = 0.79$ mm^{-1}, $\rho = 1.432$ g cm^{-3}, $T = 293$ K, $\theta_{max} = 25.00°$ Of 5596 measured data 4789 were observed (R_{int} 0.0409) with $I > 2\sigma(I)$. Final R, Rw, and S are 0.0401, 0.0507, and 1.066, respectively. The largest residual peak and hole are 0.897 and -0.619 e Å^{-3}, respectively. Semi-empirical absorption correction. Siemens P4 diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods using the SHELXS 94 program.[9b] Crystallographic data (excluding structure factors) for the structures **4**–**6** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149507–149509. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[9] a) G. M. Sheldrick, SHELXS 97, Program for Crystal Structure Solution, Universitat Göttingen, **1997**; b) G. M. Sheldrick, SHELXS 94, Program for Crystal Structure Solution, Universitat Göttingen, **1994**.