Extended chains via hydrogen bond linkages of dinuclear copper(II) and cadmium(II) complexes with a new flexible disulfoxide ligand

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Abstract

A new flexible disulfoxide ligand 1,6-bis(benzylsulfinyl)hexane (**L**), which is a mixture of the *meso* and *rac* isomers, was treated with Cu^{II} or Cd^{II} nitrate and obtained dimeric complex $[Cu_2(\mathbf{L})_3(H_2O)_2(NO_3)_4]$ **2** or $[Cd_2(\mathbf{L})_3(H_2O)_2(NO_3)_4]$ **3**. In the reacting system the crystals of *meso* isomer **1** of **L** together with **2** or **3** were obtained. **2** and **3** have similar molecular structures. In the neutral dimer, three ligands present two kinds of coordination models: monodentate and bis-monodentate. The neutral dimeric units in **2** and **3** are linked by hydrogen bonds to yield a chain structure. Crystal structures of all three compounds were determined by single-crystal X-ray diffraction methods. Crystal data for **1**: monoclinic, space group Cc, $a = 41.95(2)$, $b = 5.132(2)$, $c = 8.660(4)$ Å, $\beta = 94.898(9)°$, $V = 1857.7(15)$ Å^3, $Z = 4$, final refinement $(I > 2\sigma(I))$: $R1 = 0.0659$, w$R2 = 0.1415$. Crystal data for **2**: triclinic, space group $P\bar{1}$, $a = 9.242(4)$, $b = 9.539(4)$, $c = 21.042(9)$ Å, $\alpha = 83.888(9)$, $\beta = 87.971(8)$, $\gamma = 74.177(9)°$, $V = 1774.6(13)$ Å^3, $Z = 2$, final refinement $(I > 2\sigma(I))$: $R1 = 0.0577$, w$R2 = 0.0954$. Crystal data for **3**: triclinic, space group $P\bar{1}$, $a = 9.203(4)$, $b = 9.831(3)$, $c = 20.860(7)$ Å, $\alpha = 84.313(6)$, $\beta = 86.432(7)$, $\gamma = 74.188(6)°$, $V = 1805.9(11)$ Å^3, $Z = 2$, final refinement $(I > 2\sigma(I))$: $R1 = 0.0548$, w$R2 = 0.1192$.
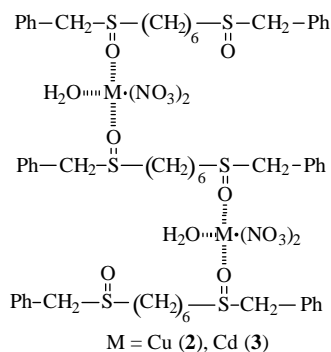
1. Introduction

A particularly active field of chemical research in recent years has been the design of extended molecular system [1]. Advances in this general area have employed a range of synthetic strategies and the products have taken a variety of forms [2]. An important goal in this developing field has been the rationalization of the structures of supramolecular crystals based on the structures of their component molecules [3]. Strong, selective, and directional hydrogen bonding has been noted as a most powerful organizing force in molecular assembly, and the vast majority of publications and reviews have been devoted to the self-organization of organic molecules into multi-dimensional hydrogen-bonded architectures [4]. By contrast, relatively less is known about hydrogen-bonding control of self-assembly of coordination compounds [5]. In addition, most of these materials are formed with rigid ligands, such as 4,4′-bipyridine and pyrazine [6], which can assist the design of predictable networks, simultaneously it frequently limits their ability to accommodate ionic or non-ionic species. Studies on flexible ligands are still relatively rare [7], and we are interested in coordination polymers containing flexible ligands such as disulfoxide, dithioether, and trithioether. We have used these flexible ligands to generate polymeric metal complexes, which possess unique lamellar square array [3–5] topological or pseudo-octahedral metal-organic frameworks, etc., and we have substantiated that the cavities of the coordination networks can be controlled by varying the chain length of the ligands [8]. As a continuation of our work to investigate the coordination chemistry of disulfoxide ligands and the architecture of their polymeric metal complexes, we synthesized a new flexible disulfoxide ligand 1,6-bis(benzylsulfinyl)hexane (**L**) which has a longer spacer than those previous reported. We expect that this ligand is more flexible and its metal complexes may display unprecedented structure.

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Ph—CH$_2$—S—(CH$_2$)$_6$—S—CH$_2$—Ph

O ‖ O ‖

H$_2$O''''M·(NO$_3$)$_2$

O ‖

Ph—CH$_2$—S—(CH$_2$)$_6$—S—CH$_2$-Ph

O ‖

H$_2$O''''M·(NO$_3$)$_2$

O ‖ O ‖

Ph—CH$_2$—S—(CH$_2$)$_6$—S—CH$_2$—Ph

M = Cu (**2**), Cd (**3**)

Chart 1. The chemical structures of complexes **2** and **3**.

The ligand **L** was treated with Cu(NO$_3$)$_2$ and Cd(NO$_3$)$_2$ to produce neutral dimeric [Cu$_2$(**L**)$_3$(H$_2$O)$_2$(NO$_3$)$_4$] **2** and [Cd$_2$(**L**)$_3$(H$_2$O)$_2$(NO$_3$)$_4$] **3** (Chart 1), self-assembled by hydrogen-bonding to form one-dimensional chain structure. Herein, we report the syntheses and crystal structures of the ligand and its two complexes.

2. Experimental

2.1. Materials and general methods

All the reagents and solvents employed were commercially available and used without further purification. The C, H and N analyses were performed on a Perkin-Elmer 240C analyzer. FT-IR spectra (KBr pellets) were taken on a FT-IR 170SX (Nicolet) spectrometer and ^{1}H NMR spectra were measured on a Bruker AC-P 200 spectrometer using TMS as the internal standard and CDCl$_3$ as the solvent.

2.2. Syntheses of ligand

The ligand was synthesized by a similar method according to the Ref. [9].

2.2.1. 1,6-Bis(benzylthio)hexane
Potassium hydroxide (80%, 7.2 g, 0.1 mol) and benzyl mercaptan (12.4 g, 0.1 mol) were dissolved in anhydrous ethanol (75 mL) at 70°C, then 1,6-dibromohexane (12.2 g, 0.05 mol) was added to the above solution with stirring over 1 h. The mixture was cooled to room temperature and filtrated to remove KBr precipitate. Then the solvent was removed under reduced pressure from above filtrate. The crude product was dissolved in chloroform (100 mL) and washed with 5% potassium hydroxide solution and distilled water, then dried over MgSO$_4$. The product was obtained after the solvent was evaporated. Yield: 92%.

2.2.2. 1,6-Bis(benzylsulfiny)hexane
To a vigorously stirred solution of 1,6-bis(benzylthio)-hexane (13.2 g, 0.04 mol) in benzene (50 mL) concentrated nitric acid (63%, 6 mL) was added drop-wise. After stirring for 24 h on ice bath, 15% sodium hydrogen carbonate solution was added to the resulting mixture to adjust the pH value to ca. 7 and the solid product was filtered, and washed with distilled water, ethanol and ether. Yield: 60%. FT-IR (cm^{-1}): 696 m, 761w, 1023 s, 1454 m. Anal. calcd for C$_{20}$H$_{26}$O$_2$S$_2$: C, 66.20; H, 2.78. Found: C, 66.28; H, 2.69%. ^{1}H NMR (300 MHz): δ1.394 (q, 4 H), 1.736 (t, 4 H), 2.529 (t, 4H), 3.975 (q, 4H), 7.258–7.375 (m, 10H). Colorless cubic crystals of **1** (mp: 181–183°C) were obtained together with those of **2** or **3** as described below, and also can be separated by fractional crystallization from methanol and chloroform from *rac* isomer (mp: 158–160°C).

2.3. Preparation of complexes

[Cu$_2$L$_3$(H$_2$O)$_2$(NO$_3$)$_4$] **2**. Diethoxyethane (2.5 mL) was added to the CHCl$_3$ solution (5 mL) of **L** (219 mg, 0.75 mmol), and the mixture was stirred for ca. 20 min. Then Cu(NO$_3$)$_2$·3H$_2$O (60 mg, 0.25 mmol) in anhydrous methanol (5 mL) was added to the above mixture and further stirred at 70–80°C for about 4 h. After the mixture was cooled to room temperature and filtered, the clear green filtrate was allowed to stand at room temperature for ca. 1 week, and blue flaky crystals suitable for X-ray investigation were obtained. Yield: 25%. Anal. calcd for C$_{30}$H$_{41}$CuN$_2$O$_{10}$S$_3$: C, 48.04; H, 5.51; N, 3.74. Found: C, 48.15; H, 5.44; N, 3.70%. FT-IR (cm^{-1}): 506m, 620m, 688s, 765m, 990w, 1025s, 1437m, 1383s, 1461m, 1496w, 2860m, 2920m and 3062w.

[Cd$_2$L$_3$(H$_2$O)$_2$(NO$_3$)$_4$] **3**. This complex was prepared using a similar procedure to that described for **2** but using Cd(NO$_3$)$_2$·4H$_2$O instead of Cu(NO$_3$)$_2$·3H$_2$O in 20% yield. Anal. calcd for C$_{30}$H$_{41}$CdN$_2$O$_{10}$S$_3$: C, 45.10; H, 5.18; N, 3.51. Found: C, 45.21; H, 5.04; N, 3.48%. FT-IR (cm^{-1}): 505m, 617m, 697s, 754m, 992w, 1026s, 1119s, 1245m, 1297m, 1324w, 1384s, 1460m, 1495w, 2855m, 2917m and 3061w.

2.4. Crystal structure determinations

Single crystals of **1**, **2** and **3** suitable for X-ray diffraction analysis with dimensions of 0.30 × 0.25 × 0.20, 0.30 × 0.25 × 0.30 and 0.25 × 0.40 × 0.30 mm^3, respectively, were selected and mounted on top of a glass fiber. Single-crystal X-ray diffraction measurements of **1–3** were carried out at 293(2) K on a Bruker Smart 1000 CCD area detector equipped with a graphite-monochromator situated in the incident beam for data collection. The determinations of unit cell parameters and data collections were performed with

Table 1
Crystal data and details of measurements for compounds **1**, **2** and **3**

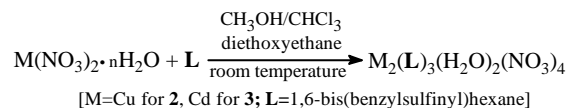|	**1**	**2**	**3**
Formula	$C_{20}H_{26}O_2S_2$	$[Cu(L)_{1.5}(H_2O)(NO_3)_2]_2$	$[Cd(L)_{1.5}(H_2O)(NO_3)_2]_2$
Mr	362.53	749.37	798.23
T(K)	293(2)	293(2)	293(2)
System	Monoclinic	Triclinic	Triclinic
Space group	Cc	$P-1$	$P-1$
a/Å	41.95(2)	9.242(4)	9.203(4)
b/Å	5.132(2)	9.539(4)	9.831(3)
c/Å	8.660(4)	21.042(9)	20.860(7)
α/degree		83.888(9)	84.313(6)
β/degree	94.898(9)	87.971(8)	86.432(7)
γ/degree		74.177(9)	74.188(6)
V/Å^3	1857.7(15)	1774.6(13)	1805.9(11)
D_c (g/cm^3)	1.296	1.402	1.468
Z	4	2	2
Min., max. transmission	0.9164, 0.9431	0.7853, 0.8490	0.8190, 0.8513
μ (Mo$K\alpha$) mm^{-1}	0.296	0.846	0.832
Measured reflections	3588	7319	7543
Unique reflections	2351	6223	6347
Refined parameters	217	415	415
Final $R1$,w$R2$ ($I>2\sigma(I)$)	0.0659, 0.1415	0.0577, 0.0954	0.0548, 0.1415
w$R2$ (F^2, all data)	0.1868	0.1508	0.1443

Note. $R1 = \sum||F_o|-|F_c||/\sum|F_o|$. w$R2 = \{\sum [w(F_o^2-F_c^2)^2]/\sum [w(F_o^2)^2]\}^{1/2}$.

Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). Unit cell dimensions were obtained with least-squares refinements and all the structures were solved by the direct methods using SHELXS-97 program [10]. The final refinements for the three structures were done by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2 [11]. The hydrogen atoms were added theoretically, and riding on the concerned atoms and refined with fixed thermal factors. Semi-empirical absorption correction was applied using the SADABS program [12]. Crystallographic data and the experimental details for structural analyses are summarized in Table 1. Molecular drawings were produced by the SHELXTL-XP program [13].

3. Results and discussion

3.1. Syntheses and general characterizations

The ligand was prepared by a similar method to our previous work [9]. When $M(NO_3)_2 \cdot nH_2O$ (M = Cu or Cd) was treated with the mixture ligand of *meso* and *rac* isomers, crystals of *meso* isomer of the ligand together with the crystals of **2** or **3** were isolated. The *meso* isomer of the ligand can also be separated from *rac* isomer by fractional crystallization in $CH_3OH/CHCl_3$. The complexes were prepared by the reaction of $M(NO_3)_2 \cdot nH_2O$ with the ligand in $CH_3OH/CHCl_3$ in the presence of diethoxyethane to dehydrate (Scheme 1). Both complexes are soluble in DMF and DMSO, and slightly

$$M(NO_3)_2 \cdot nH_2O + L \xrightarrow[\text{room temperature}]{\overset{\text{CH}_3\text{OH/CHCl}_3}{\text{diethoxyethane}}} M_2(L)_3(H_2O)_2(NO_3)_4$$

[M=Cu for **2**, Cd for **3**; L=1,6-bis(benzylsulfinyl)hexane]

Scheme 1.

soluble in CH_3OH and CH_3CN, and almost insoluble in H_2O and acetone. The IR spectrum of **1** shows a strong band at 1023 cm^{-1} assigned to $\nu_{S=O}$. The spectra of complexes **2** or **3** have a $\nu_{S=O}$ band at 1025 or 1026 cm^{-1} approximately identical to that of the free ligand, and a $\nu_{S=O}$ band at 990 or 992 cm^{-1} shifted to the frequency lower than that for the free ligand. It indicates that the ligand does not behave as a complete bidentate ligand but does coordinate, at least partially, as a monodentate ligand [14]. The existence of nitrate anions in the complexes was confirmed by IR spectra.

3.2. Description of the crystal structures

$C_{20}H_{26}O_2S_2$ **1**. The X-ray analysis of **1**, as shown in Fig. 1, has revealed that it corresponds to the *meso* diastereomer having an *R,S* conformation. All atoms between two S atoms, benzyl methene carbon atom C(14) and phenyl carbon atom C(15) lie almost on one plane, which form distinct dihedral angles of 68.0(2) and 143.6(3)° with two phenyl rings, respectively, and the dihedral angle between them is 76.3(4)°. Two S=O groups lie on the opposite sides of that plane with the distance of 9.157(5) Å for two O donors and their pseudo-torsion angle (S=O···S=O) is –160.5(4)°. The
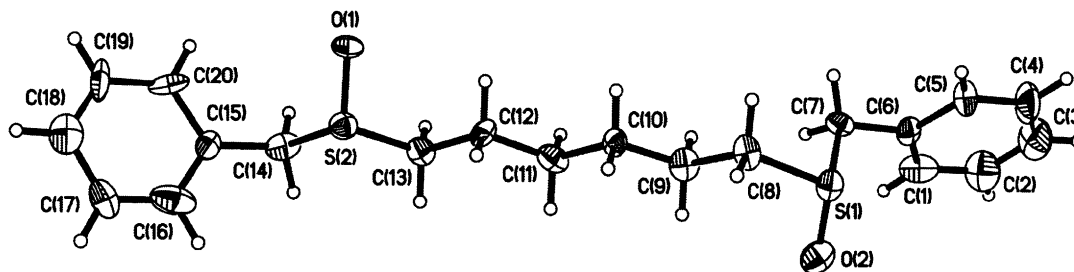
Fig. 1. An ORTEP view of **1**.

torsion angles of O(2)–S(1)–C(7)–C(6) and O(1)–S(2)–C(14)–C(15) are −76.8(2) and −83.5(3)°, respectively. Bond lengths and angles of the sulfinyl groups in **1,** with the average values of 1.475(5) Å for the S=O bond distance and 107.1(8)° for the O–S–C bond angle, are in agreement with the values reported for uncoordinated mono-sulfoxide (DMSO) (S=O, 1.48(1) Å O–S–C, 106.7(1)°), but the average value of 104.4(6)° for the C–S–C angle is larger than the reported value (96.4(2)°) [15].

[Cu₂(L)₃(H₂O)₂(NO₃)₄] **2**. An ORTEP view of **2** including the atomic numbering scheme is shown in Fig. 2a. The structure of **2** consists of a neutral [Cu₂(**L**)₃(H₂O)₂(NO₃)₄] dimer having an inversion center. Each Cu[II] ion is coordinated to two oxygen atoms from monodentate and bis-monodentate **L** molecules, two oxygen atoms of two nitrate ions and one water molecule, showing a distorted square pyramidal coordination geometry. The equatorial plane is built up by two oxygen atoms of two nitrates, one oxygen atom of water molecule and one oxygen atom of the ligand, and the apical site is occupied by another ligand oxygen atom. The two nitrate groups are almost coplanar. The Cu–O(disulfoxide) distances are 1.975(5) in equatorial plane and 2.254(5) Å in axial position, respectively being similar to those of other Cu[II] complexes of disulfoxide [16]. The Cu–O(water) distance is 2.000(5) Å in normal bond length range [17], and the average bond length of Cu–O(nitrate) is 1.979(6) Å.

[Cd₂(L)₃(H₂O)₂(NO₃)₄] **3**. The ORTEP structure of **3** with atom labeling is shown in Fig. 2b. The structure of **3** consists of a neutral [Cd₂(**L**)₃(H₂O)₂(NO₃)₄] molecule with inversion center. Each Cd[II] ion has hepta-coordinate geometry. Two oxygen atoms of the monodentate and bis-monodentate **L** molecules, four oxygen atoms of two bidentate nitrate ions and one water molecule surround each metal center to form a distorted pentagonal bipyramidal polyhedron. Two nitrate ions and a sulfoxide group are at the equatorial position, and an oxygen atom of water molecule and an oxygen atom of **L** at the apical position. The coordinated oxygen atoms at the equatorial position are almost coplanar, but the alignment of the apical oxygen

atoms is somewhat deviated from 180° [O(1)–Cd(1)–O(10), 178.3(2)°]. Two oxygen atoms of each nitrate ion coordinated to Cd[II] unequally with the average Cd–O(nitrate) bond lengths of 2.365(3) and 2.503(5) Å in equatorial plane, and these are different from those of {[Cd₂(μ-bet)₃](NO₃)₄} which are almost equal for Cd–O(nitrate) bond lengths but similar to {[Cd₂(μ-3,3′-pytz)₃(NO₃)₄](EtOH)} [18]. The Cd–O(**L**) distance is 2.285(4) Å in the equatorial plane and 2.238(4) Å in the apical position, and the bond length of Cd–O(water) is 2.269(4) Å which is shorter than other analogous apical position Cd–O(water) bond length [19].

In the dimeric complexes **2** and **3**, the ligands take two kinds of coordination modes on the coordination donors. One reserved as a bridge to link two adjacent metal ions by its two distinct O donors to form a dimer with two metal ions separated by 11.085(5) and 10.260(7) Å for **2** and **3**, and the other two ligands coordinate to two metal ions, respectively by one oxygen donor. As shown in Fig. 3a and b, the neutral dimeric units in **2** and **3** are bridged alternately by the hydrogen bonds formed by metal-coordinated water molecules of one complex unit, and nitrate oxygen atoms and uncoordinated O donors of **L** in the other complex molecule. The O···O(**L**) and O···O(nitrate) separations are 2.658(4) and 2.728(5) Å in **2** and 2.681(3) and 2.751(4) Å in **3,** falling into the normal range of the O···O separation for hydrogen bonding [20]. In complexes **2** and **3**, the bis-monodentate ligand has a symmetric center, and the quasi-torsion angle of O–S···S–O is 180°, and the S–O vectors are parallel to each other but pointing to opposite directions; however, the S–O vectors of the monodentate ligand form 91.3 and 98.8° angles, respectively. This may be due to the reason that one oxygen donor of the ligand coordinates to the metal center. The distances between two oxygen atoms in the bis-monodentate ligand are 10.048(3) and 9.457(3) Å, respectively, and the distances in the monodentate ligand are 11.206(3) and 8.400(6) Å for **2** and **3**, respectively. To our knowledge **3** is the first structurally determined cadmium(II) complex with flexible sulfoxide ligand.
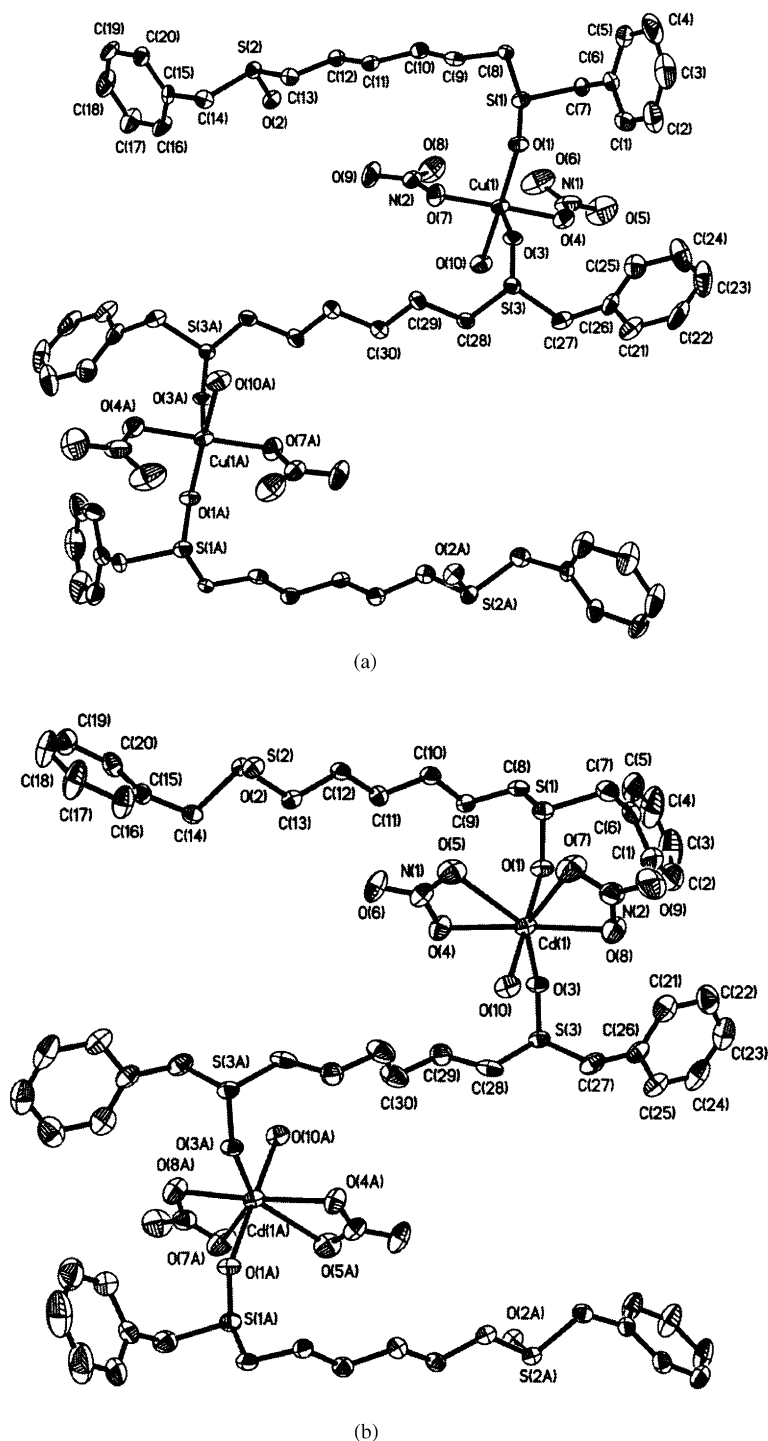
(a)

(b)

Fig. 2. The Z-shaped dimetric unit of (a) **2** and (b) **3**.

In summary, (a) only the *meso isomer* complexes were obtained when the starting ligand is a mixture of the *rac* and *meso* forms; (b) the binding of the ligands to Cu^{II} or Cd^{II} ions is in two kinds of coordination modes, i.e., monodentate and bis-monodentate. It is rare that two kinds of coordination modes present simultaneously in a complex molecule with disulfoxide; (c) in the complexes,

the chain structure is formed by hydrogen bonds. For free sulfoxide, the formation of hydrogen bonding is common phenomenon, but the chain structure of the metal complexes constructed by hydrogen bonds is less; (d) in both complexes, nitrate ions adopt different coordination modes, probably due to the result of a delicate balance between electronic and steric factors.
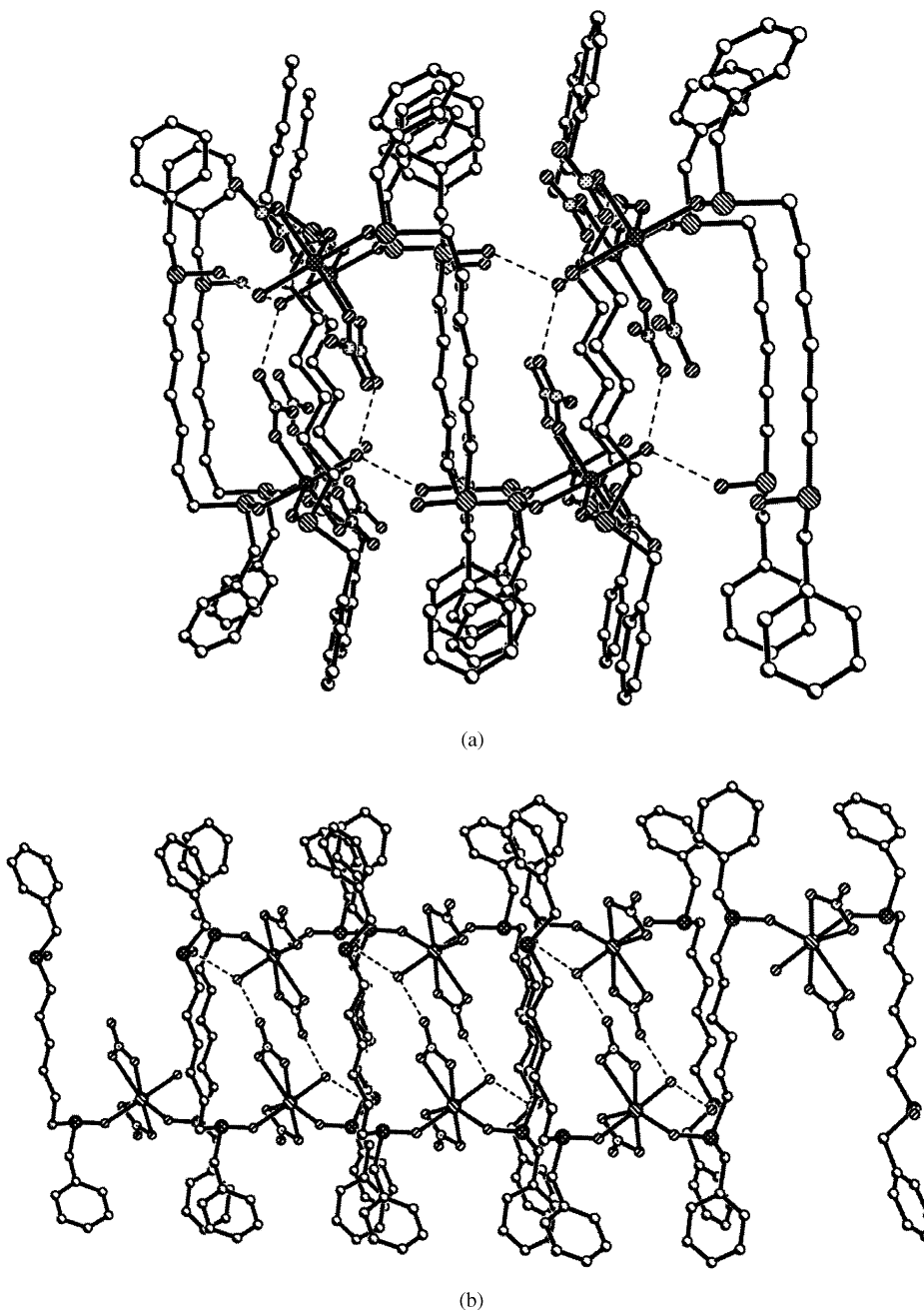
(a)

(b)

Fig. 3. Extended chain of (a) **2** and (b) **3** via hydrogen bond linkage.

References

[1] B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629.
[2] (a) G.F. Swiegers, T.J. Malefetse, Chem. Rev. 100 (2000) 3483.
    (b) S. Leininger, B. Olenyuk, P.J. Stang, Chem. Rev. 100 (2000) 853.
[3] (a) S.R. Batten, R. Roboson, Angew. Chem. Int. Ed. 37 (1998) 1460.
    (b) A.J. Blake, N.R. Champness, A.N. Khlobystov, S. Parsons, M. Schröder, Angew. Chem. Int. Ed. 39 (2000) 2317.
    (c) T.M. Reineke, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, Angew. Chem. Int. Ed. 38 (1999) 2590.
    (d) D.-L. Long, A.J. Blake, N.R. Champness, C. Wilson, M. Schröder, J. Am. Chem. Soc. 123 (2001) 3401.
    (e) T. Yamaguchi, F. Yamazaki, T. Ito, J. Am. Chem. Soc. 123 (2001) 743.
    (f) E. Lee, J. Kim, J. Heo, D. Wang, K. Kim, Angew. Chem. Int. Ed. 40 (2001) 399.
    (g) L.C. Tabares, J.A.R. Navarro, J.M. Salas, J. Am. Chem. Soc. 123 (2001) 383.

(h) Y.-H. Liu, C.-S. Lin, S.-Y. Chen, H.-L. Tsai, C.-H. Ueng, K.-L. Lu, J. Solid State Chem. 157 (2001) 166.

[4] (a) V.A. Russell, C.C. Evans, W.-J. Li, M.D. Ward, Science 276 (1997) 575.

(b) L. Brunsveld, B.J.B. Folmer, E.W. Meijer, R.P. Sijbesma, Chem. Rev. 101 (2001) 4071.

(c) D.C. Sherrington, K.A. Taskinen, Chem. Soc. Rev. 30 (2001) 83.

(d) S.N.G. Acharya, R.S. Gopalan, G.U. Kulkarni, K. Venkatesan, S. Bhattachar, Chem. Commun. (2000) 1351.

(e) P. Gangopadhyay, T.P. Radhakrishnan, Angew. Chem. Int. Ed. 40 (2001) 2451.

[5] (a) C. Schmuck, W. Wienad, Angew. Chem. Int. Ed. 40 (2001) 4363.

(b) C.V.K. Sharma, R.D. Rogers, Chem. Commun. (1999) 83.

(c) Z.-N. Chen, H.-X. Zhang, K.-B. Yu, K.-C. Zheng, H. Cai, B.-S. Kang, J. Chem. Soc., Dalton Trans. (1998) 1133.

(d) C.-Y. Su, B.-S. Kang, H.-Q. Liu, Q.-G. Wang, T.C.W. Mak, Chem. Commun. (1998) 1551.

(e) S.B. Copp, K.T. Holman, J.O.S. Sangster, S. Subramanian, M.J. Zaworotko, J. Chem. Soc., Dalton Trans. (1995) 2233.

(f) V.Y. Kukushkin, T. Nishioka, D. Tudela, I. Kinoshita, Inorg. Chem. 36 (1997) 6157.

[6] (a) Y.L. Cho, H. Uh, S.-Y. Chang, H.-Y. Chang, M.-G. Choi, I. Shin, K.-S. Jeong, J. Am. Chem. Soc. 123 (2001) 1258.

(b) S.R. Batten, B.F. Hoskins, R. Robson, New J. Chem. (1998) 173.

(c) L. Carlucci, G. Ciani, D.M. Proserpio, A. Sironi, Angew. Chem. Int. Ed. Engl. 34 (1995) 1895.

(d) M.-L. Tong, X.-M. Chen, X.-L. Yu, T.C.W. Mak, J. Chem. Soc., Dalton Trans. (1998) 5.

(e) A.S. Batsanov, M.J. Begley, P. Hubberstey, J. Stroud, J. Chem. Soc., Dalton Trans. (1996) 1947.

(f) M. Fujita, Y.J. Kwon, O. Sasaki, K. Yamaguchi, K. Ogura, J. Am. Chem. Soc. 117 (1995) 7287.

(g) T. Otieno, S.J. Rettig, R.C. Thompson, J. Trotter, Inorg. Chem. 32 (1993) 1607.

[7] (a) F.M. Tabellion, S.R. Seidel, A.M. Arif, P.J. Stang, Angew. Chem. Int. Ed. 40 (2001) 1529.

(b) M.-C. Brandys, R.J. Puddephatt, Chem. Commun. (2001) 1508.

(c) T.L. Hennigar, D.C. MacOuarrie, P. Losier, R.D. Rogers, M.J. Zaworotko, Angew. Chem. Int. Ed. 36 (1997) 972.

(d) P.C.M. Duncan, D.M.L. Goodgame, S. Menzer, D.J. Williams, Chem. Commun. (1996) 2172.

(e) A.J. Blake, N.R. Champness, M. Crew, L.R. Hanton, S. Parsons, M. Schröder, J. Chem. Soc., Dalton Trans. (1998) 1533.

[8] (a) X.-H. Bu, W. Chen, S.-L. Lu, R.-H. Zhang, D.-Z. Liao, W.-M. Bu, M. Shionoya, F. Brisse, J. Ribas, Angew. Chem. Int. Ed. 40 (2001) 3201.

(b) X.-H. Bu, W. Weng, J.-R. Li, W. Chen, R.-H. Zhang, Inorg. Chem. 41 (2002) 413.

(c) X.-H. Bu, W. Weng, M. Du, W. Chen, J.-R. Li, R.-H. Zhang, L.-J. Zhao, Inorg. Chem. 41 (2002) 1007.

(d) R.-H. Zhang, B.-Q. Ma, X.-H. Bu, H.-G. Wang, X.-K. Yao, Polyhedron 16 (1997) 1123–1787.

(e) X.-H. Bu, W. Chen, M. Du, R.-H. Zhang, Cryst. Eng. Commun. 30 (2001) 1.

[9] R.-H. Zhang, Y.-L. Zhan, J.-T. Chen, Synth. React. Inorg. Met-Org. Chem. 25 (1995) 283.

[10] G.M. Sheldrick, SHELXTL-97, Program for X-ray Crystal Structure Solution, University of Göttingen, Germany, 1997.

[11] G.M. Sheldrick, SHELXTL-97, Program for X-ray Crystal Structure Refinement, University of Göttingen, Germany, 1997.

[12] G.M. Sheldrick, SADABS Siemens Area Detector Absorption (and other) Correction, University of Göttingen, Germany, 1997.

[13] SHELXTL ver. 5.10, Reference Manual, Brucker Industrial Automation, Analytical Instrument, Madison, WI 53719, 1997.

[14] H.B. Kagan, B. Ronan, Rev. Heteroat. Chem. 7 (1992) 92.

[15] V.I. Baranovskii, Y.N. Kukushkin, N.S. Panina, A.I. Panin, Russian J. Inorg. Chem. 18 (1967) 844 (and references quoted therein).

[16] (a) S. Geremia, M. Calligaris, S. Mestroni, Inorg. Chim. Acta 292 (1999) 144.

(b) M. Calligaris, A. Melchior, S. Geremia, Inorg. Chim. Acta 323 (2001) 89.

[17] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, J. Chem. Soc., Dalton Trans. (1989) S1.

[18] (a) M. Fujita, Y.J. Kwon, M. Miyazawa, K. Ogura, J. Chem. Soc., Chem. Commun. (1994) 1977.

(b) M.A. Withersby, A.J. Blake, N.R. Champness, P.A. Cooke, P. Hubberstey, W.-S. Li, M. Shröder, Inorg. Chem. 38 (1999) 2259.

[19] G.-R. Angel, F. Juan J, R. Santiago, L.-L. Antonio, M. Elies, E. Enrique, B. Elisa, A. Gloria, B. Joaquin, C. Alfonso, Polyhedron 19 (2000) 991.

[20] G.H. Stout, L.H. Jensen, X-ray Structure Determination: A Practical Guide, MacMillan, New York, 1968.