DALTON
FULL PAPER

Variation in the coordination mode of arenedisulfonates to copper(II): synthesis and structural characterization of six copper(II) arenedisulfonate complexes

Jiwen Cai,* Cai-Hong Chen, Cheng-Zhu Liao, Jun-Hua Yao, Xiao-Peng Hu and Xiao-Ming Chen

Instrumentation Analysis and Research Center & Department of Chemistry, Zhongshan University, Guangzhou 510275, P. R. China. E-mail: puscjw@zsu.edu.cn

Received 8th December 2000, Accepted 9th February 2001
First published as an Advance Article on the web 14th March 2001

Six copper(II) arenedisulfonate complexes with the general formula $Cu(N_4)(nds/bpds)\cdot nH_2O$ (nds = naphthalenedisulfonate, bpds = biphenyldisulfonate) have been synthesized in aqueous solution and structurally characterized by X-ray single crystal diffraction, IR and UV spectroscopies, TGA and DSC. In $Cu(en)_2(1,5nds)\cdot 2H_2O$ **1**, $Cu(N\text{-}meen)_2(2,6nds)\cdot 2H_2O$ **2** (N-meen = *N*-methylethylenediamine), $Cu(dpn)_2(bpds)$ **3** (dpn = 2,3-diaminopropane), and Cu(cylam)(1,5nds) **4** the SO_3^- group coordinates monodentately to the axial position of Cu^{2+} which is equatorially coordinated by four amino nitrogens. In **1** and **4** intramolecular hydrogen bonds are formed between the SO_3^- oxygens and amino hydrogens which reinforce interaction between the SO_3^- group and Cu^{2+} complex cation. In $Cu(dpn)_2(1,5nds)\cdot 2H_2O$ **5** and $Cu(N,N'\text{-}meen)_2(1,5nds)\cdot 3H_2O$ **6** (N,N′-meen = *N*,*N*′-dimethylethylenediamine), due to the steric hindrance caused by the methyl substitution of the amino ligands and the rigidity of the naphthalene ring, water molecules, instead of the bulky SO_3^- group, coordinate to the axial position of Cu^{2+}. Structures **1**–**4** represent the first synthesis and structural characterization of polymeric 1-dimensional structures constructed by arenedisulfonates and divalent transition metals. Also, **1** crystallizes in the enantiomorphic space group $P4_12_12$ and displays interesting chiral grids constructed by ionic hydrogen bonds. The coordination geometries of Cu^{2+}, as well as the coordination modes of arenedisulfonates, are discussed in detail.

Introduction

The coordination chemistry of transition metal sulfonates is not well explored and/or rationalized, in comparison with the well studied metal phosphates.[1–3] Also, lamellar inorganic–organic systems employing sulfonates are virtually unknown.[4] Owing to the weak coordination strength of sulfonate toward transition metal ions, most of the reported transition metal sulfonates prepared in aqueous solution were formed by segregation of aquametal complex cations and sulfonate anions.[5] There have been only two crystal structures reported containing aromatic sulfonate, namely *p*-toluenesulfonate, coordinated to the divalent transition metal Cu^{2+} as a monodentate ligand.[6,7]

In our preceding paper we demonstrated systematically the coordination chemistry of IA and Group IIA metal cations toward 1,5-naphthalenedisulfonate.[1] In this study we have synthesized and structurally characterized Cu^{2+} arenedisulfonates with the general formula $Cu(N_4)(nds/bpds)\cdot nH_2O$ (nds = naphthalenedisulfonate, bpds = biphenyldisulfonate), where N_4 represents two bidentate ligands, such as ethylenediamine (en), *N*-methylethylenediamine (N-meen), 2,3-diaminopropane (dpn), *N*,*N*′-dimethylethylenediamine (N,N′-meen), or one tetradentate ligand, namely 1,4,8,11-tetraazacyclotetradecane (cyclam). The purpose was to document the coordination chemistry of arenesulfonates toward divalent transition metal ions, as well as the nature of inorganic–organic lamellar materials derived from metal disulfonates. These structures demonstrate that by incorporating organic ligands, such as amines, at the divalent transition metal center the SO_3^- oxygen can compete with water molecules and coordinate to Cu^{2+}. They also represent the first syntheses and structural characterization of 1-dimensional coordination networks constructed by arenedisulfonates and amino-coordinated transition metals in the presence of water molecules.[8]

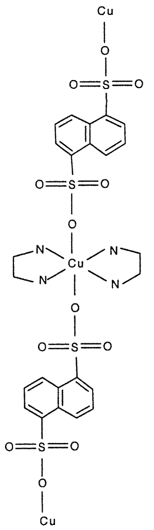
Results and discussion

Description of the structures

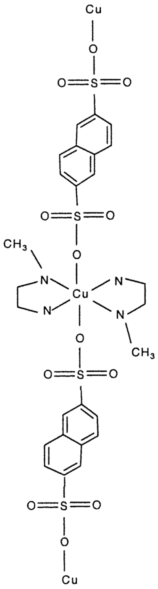
In all the structures Cu^{2+} is 6-coordinated equatorially by four nitrogen atoms from the amine ligands and axially by two oxygen atoms of the monodentate SO_3^- groups (compounds **1**–**4**) or of water molecules (**5**, **6**). The CuN_4O_2 chromophores are tetragonally elongated to different extents along the axial positions. Except for **1**, which crystallizes in an enantiomorphic space group, all CuN_4O_2 chromophores in **2**–**6** are centrosymmetric. In **1**–**4** each SO_3^- coordinates to Cu^{2+} monodentately, and the naphthalenedisulfonate and biphenyldisulfonate behave as bifunctional spacers, bringing the complex cations into infinite, 1-dimensional strings.

$Cu(en)_2(1,5nds)\cdot 2H_2O$ **1** crystallizes in the enantiomorphic space group $P4_12_12$. Both the coordinated copper cation and the naphthalenedisulfonate anion are located on crystallographic 2-fold axes. Fig. 1(a) shows the coordination environment of the Cu^{2+} cation. The Cu–N distances are 1.9897(16) and 1.9978(15) Å, respectively. The distance between the Cu^{2+} and the sulfonate oxygen is 2.8128(13) Å, a value which could be considered to be too long to indicate meaningful coordination.[6] However, coupling with a weak hydrogen bond formed between the amino hydrogen of the en ligand and one oxygen of the SO_3^- group (N1 ··· O3 3.139(2) Å, N1–H ··· O3 137.16°), the SO_3^- group displaces the water molecules from the coordination sphere of Cu^{2+}. The interaction between the Cu^{2+} and SO_3^- group is directing and strong enough to order the $[Cu(en)_2]^{2+}$ cations into 1-dimensional chains, as shown in Fig. 1(b). Adjacent chains are linked by water molecules which form strong hydrogen bonds with sulfonate oxygens from adjacent chains (Ow ··· O 2.7977(19) and 2.890(2) Å, Ow–Hw ··· O 170.6 and 162.1° for O3 and O1, respectively), giving rise to a 2-dimensional network.

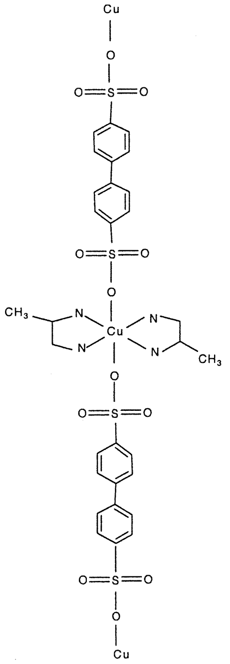
DOI: 10.1039/b009851p



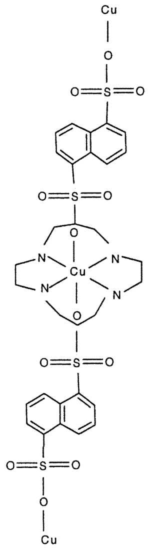
1



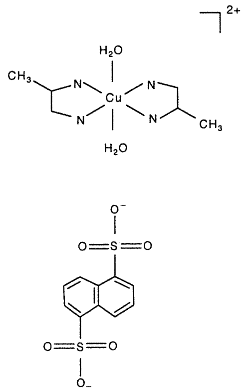
2



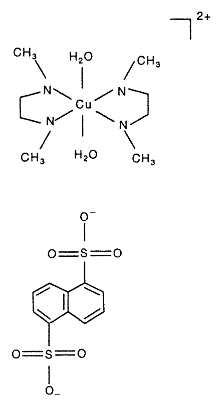
3



4



5



6

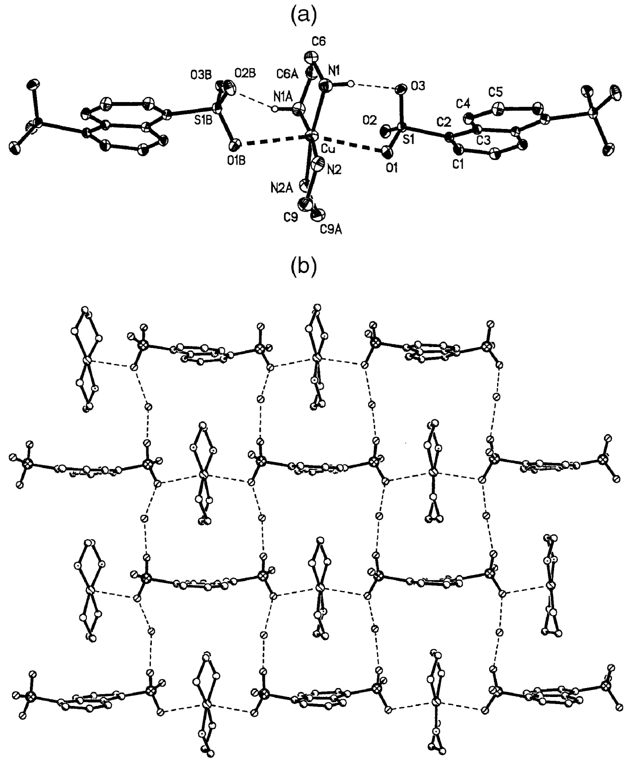


Fig. 1 (a) Coordination environment of Cu^{2+} in complex **1** with 30% probability displacement ellipsoids (as in all structures shown). Cu–O contacts are represented by thick dashed lines, hydrogen bonds as thin dashed lines. (b) 2-Dimensional network constructed by hydrogen bonds and weak $SO_3\cdots Cu$ contacts.

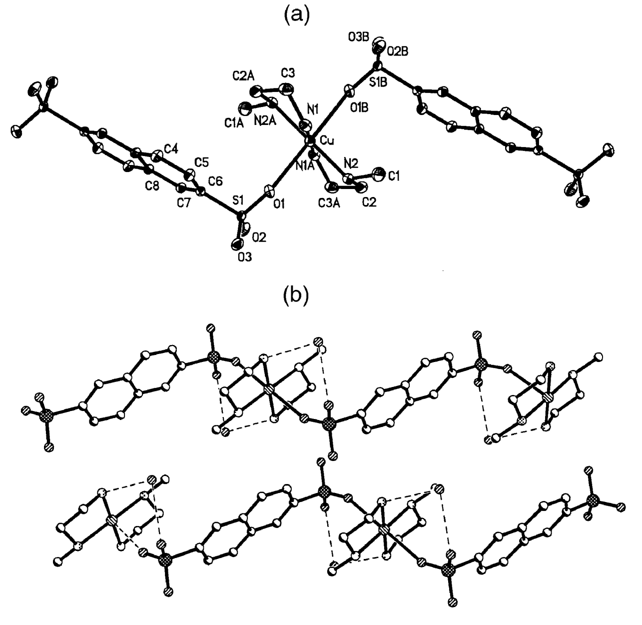


Fig. 2 (a) Coordination environment of Cu^{2+} in complex **2**. (b) Wave like 1-dimensional strings observed in **2**.

The fact that compound **1** crystallizes in an enantiomorphic space group reveals another interesting feature about naphthalenedisulfonate anion acting as a linking spacer. Namely, the chirality of the structure itself arises from the fact that two of the sulfonate oxygens (O1 and O3) form strong, ionic hydrogen bonds with water molecules, while O1 is weakly coordinated to the copper ion. These non-covalent interactions make the sulfur atom a chiral center upon assembly of the compound, and the naphthalenedisulfonate anion a potential useful chiral linking group capable of creating non-centrosymmetric packing motifs.

Cu(N-meen)$_2$(2,6nds)·2H_2O **2** crystallizes in the centrosymmetric space group $P2_1/n$. Both the copper complex cation and the naphthalenedisulfonate anion sit on crystallographic inversion centers. The same chain structure is constructed, with different coordination geometry for Cu^{2+} (Cu–N 2.029(2) and 2.068(2) Å, Cu–O1 2.496(2) Å), as shown in Fig. 2(a). The distance between the copper atom and sulfonate oxygen is much shorter, compared with that observed in compound **1**. Water molecules form strong intermolecular hydrogen bonds with sulfonate oxygens (Ow···O 2.831(3) and 2.880(3) Å, Ow–Hw···O 176.2 and 177.5° for O3 and O2, respectively). The 1-dimensional chain propagates in a wave-like fashion, as shown in Fig. 2(b).

In Cu(dpn)$_2$(bpds) **3**, the Cu^{2+} is located at an inversion center, while the biphenyldisulfonate group is located on a 2-fold axis. As shown in Fig. 3(a), the Cu^{2+} cation is 6-coordinated by four nitrogen atoms from two dpn groups with distances of 1.9992(18) and 2.0147(17) Å, and two SO_3^- groups from two different bpds ligands with distance of 2.5946(16) Å. The phenyl rings bend toward two Cu^{2+} cations for better coordination by the two SO_3^- groups, and form a dihedral angle of 6.4°. The chain propagates in a castellated

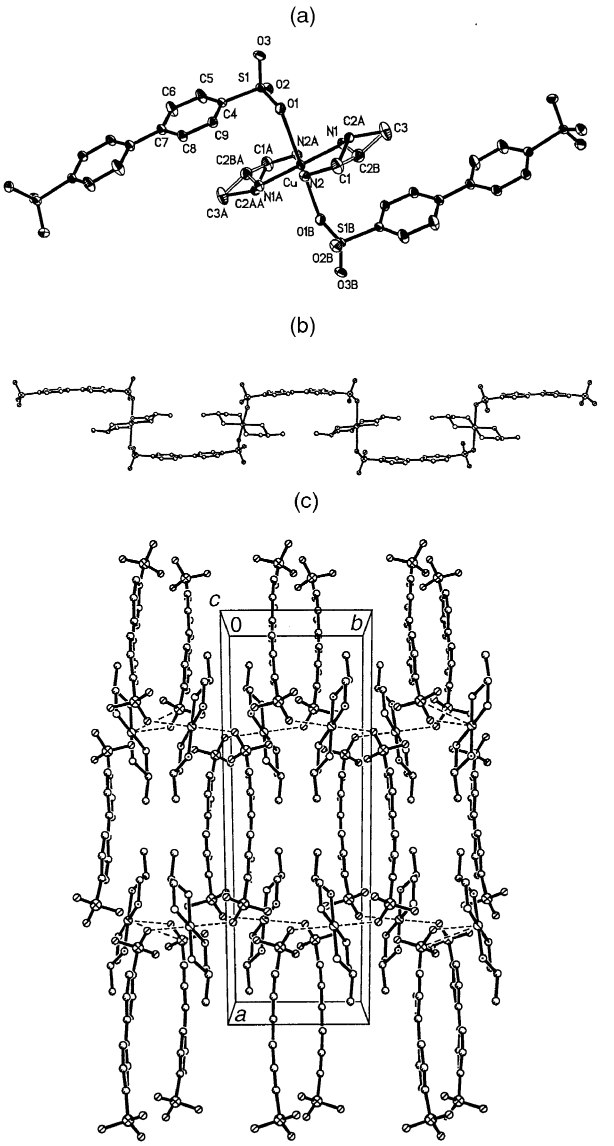


Fig. 3 (a) Coordination environment of Cu^{2+} in complex **3**. Note that C2 was disordered and refined over two positions. (b) The 1-dimensional castellated chain. (c) Packing arrangement looking down along the *c* axis showing the inorganic–organic layered structure.

fashion, in which the cations are sandwiched between two anions and located on the same level, along the *a* axis, as indicated in Fig. 3(b). The packing arrangement in Fig. 3(c) shows that the bpds ligands align along the *a* axis, with the two adjacent ones bending away from each other. This arrangement creates a structure similar to the so-called lamellar "inorganic–organic" network[4] wherein Cu^{2+} cations and SO_3^- groups constitute inorganic layers parallel to the *bc* plane, while the biphenyl groups form the organic layers. The bpds behave as pillars supporting the inorganic layers, while the dpn ligands occupy the void space formed between the two long pillars. This is different from **1** and **2**. The two oxygen atoms (O1 and O2), which are not bonded to Cu^{2+}, form hydrogen bonds with the amino hydrogen atoms of the dpn group and are anchored in the inorganic network.

In Cu(cyclam)(1,5nds) **4** both the complex cation and 1,5nds group are located at crystallographic inversion centers. The coordination sphere of Cu^{2+} is shown in Fig. 4(a). The Cu–N distances are 2.000(9) and 2.014(8) Å, while the shortest distance between Cu^{2+} and SO_3^- is 2.509(7) Å. There are two moderate intramolecular hydrogen bonds between the amino hydrogens and SO_3^- oxygens (N1 ··· O3 3.046(10) Å, N1–H ··· O3 159.75°; N2 ··· O2 2.992(11) Å, N2–H ··· O 161.58°).

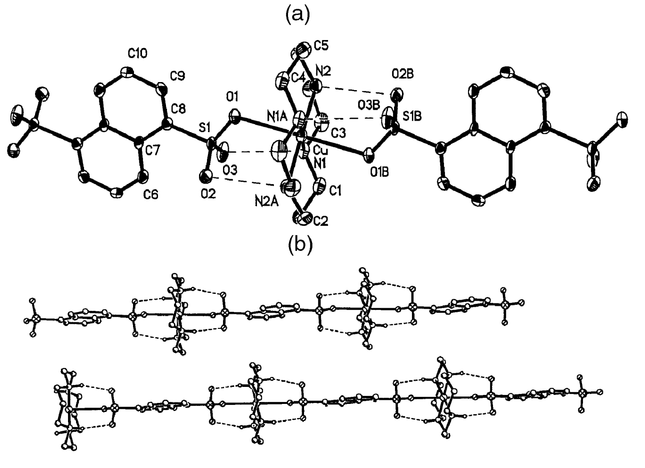


Fig. 4 (a) Coordination environment of Cu^{2+} in complex **4**. Hydrogen bonds are represented as dashed lines. (b) Linear 1-dimensional chains constructed by **4**.

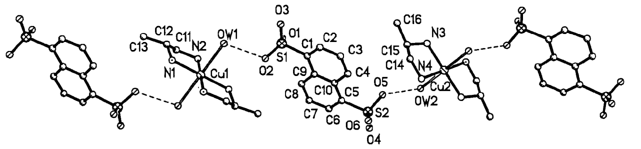


Fig. 5 1-Dimensional string constructed by hydrogen bonds and weak coordination between H_2O and Cu^{2+} in complex **5**.

The SO_3^- groups and the N_4 equatorial plane adopt a face-to-face coordination mode. This arrangement was not observed in previous structures. In comparison with the conformation adopted by the two bidentate ligands after coordination to Cu^{2+}, the cyclam ring is more planar. This feature makes the amino hydrogen atoms more accessible to the oxygens of bulky SO_3^- groups, thus forming more effective intramolecular hydrogen bonds. As shown in Fig. 4(b), the 1-dimensional string is almost linear, and comparable to that observed in compound **1**. Interestingly, there are no significant inter-string hydrogen bonded interactions.

In the asymmetric unit of $Cu(dpn)_2(1,5nds)\cdot 2H_2O$ **5**, there are two halves of copper complex cations (related to each other by an inversion center), one organic anion, and two water molecules. As illustrated in Fig. 5, the Cu^{2+} cation is coordinated by four amino nitrogen atoms from two dpn groups with Cu–N distances ranging from 1.995(2) to 2.018(3) Å. The two water molecules are at distances of 2.605(2) and 2.630(3) Å, respectively. There is no direct coordination between the SO_3^- group and Cu^{2+}. The coordinated water forms strong hydrogen bonds with oxygens of the SO_3^- group. Therefore, the 1,5-naphthalenedisulfonate anion, water molecule, Cu^{2+} complex cation, and water molecule alternate positions along a line, giving rise to a 1-dimensional chain running along the *b* axis. SO_3^- groups are also involved in extensive hydrogen bonding both with amino groups and water molecules.

Finally, in $Cu(N,N'\text{-meen})_2(1,5nds)\cdot 3H_2O$ **6**, as was the case in **5**, there are no direct interactions between Cu^{2+} and SO_3^- groups; instead, they are mediated by the water molecules coordinated to Cu^{2+}. As a result, an interesting 2-dimensional hydrogen bonding network is constructed, as shown in Fig. 6. Here, one coordinated water molecule, Cu–Ow 2.4921(17) Å, forms another two strong hydrogen bonds with two SO_3^- groups (Ow1 ··· O1 = 2.761(3) Å, Ow1–Hw1 ··· O1 176.2°, and Ow1 ··· O2 2.795(3) Å, Ow1–Hw2 ··· O2 152.5°). The second water molecule, located between two SO_3^- groups, is disordered. The overall structure can be described as stacking of 2-dimensional networks, held together by inter-layered hydrogen bonds between amino hydrogen atoms and SO_3^- groups.

Table 1 Comparison of coordination parameters of compounds **1**–**4** (distances in Å and angles in degree)

	1	**2**	**3**	**4**
Dihedral angle (θ_2)	87.9	19.3	22.3	90.3
Torsion angle				
C–S–O1–Cu (θ_1)	178.9	70.4	75.2	179.1
C–S–O2–Cu	−63.9	46.7	−39.2	64.2
C–S–O3–Cu	64.1	176.28	−168.1	−64.2
Cu–O	2.8128(13)	2.496(2)	2.5946(16)	2.509(7)
Cu–O–S	109.21(7)	156.92(9)	131.22(10)	115.7(4)

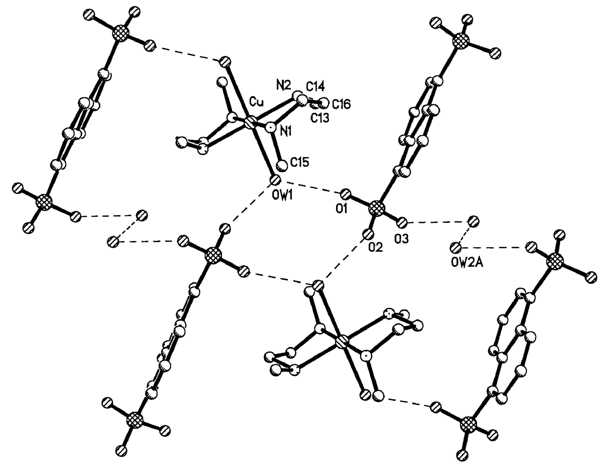


Fig. 6 2-Dimensional network constructed by hydrogen bonds in complex **6**.

Coordination mode and structural aspects of CuN_4O_2 in complexes 1–4

We find it confusing and not appropriate to use the terms *syn* and *anti*,[6] a definition adapted from the description of the coordination mode of metal carboxylates,[9] to describe the coordination geometry of copper arenedisulfonates for the following reasons: first of all the carboxylate group is planar, while the sulfonate group is tetrahedral; secondly, the arenedisulfonate behaves as a bifunctional spacer coordinated to two metal centers. Therefore, it imposes some geometrical restraints on the relative orientation of the aromatic rings of the sulfonate as regards the copper center. Herein, we use two parameters to describe and compare the coordination geometry of this series of compounds. θ_1 is the torsion angle of C–S–O–Cu for the coordinated sulfonate oxygen, and θ_2 the dihedral angle formed between the equatorial plane of $[CuN_4]^{2+}$ and the naphthalene or phenyl rings. θ_1 and θ_2, together with other geometric parameters of **1**–**4**, are listed in Table 1, which shows the diverse geometrical range, similar to the coordination modes of arene sulfonates to zirconocene.[10] Despite the much longer Cu–O distance observed in **1**, where the C–S and Cu–O bonds are close to collinear, the aromatic ring and the equatorial plane of the Cu^{2+} complex cation tend to be perpendicular to each other, as observed in **1** and **4**. Complexes **2** and **3** display another coordination geometry, in which the C–S and Cu–O bonds are close to being perpendicular to each other and the two least squares planes of the cation and anion tend to be coplanar. Therefore, there seems to exist a correlation between the collinearity of the Cu–O–S–C fragments and the co-planarity of the two least squares planes of the cation and anion. The homogeneity of the torsion angles of C–S–O2–Cu and C–S–O3–Cu, observed in **1** and **4**, is consistent with a closer approach of SO_3^- oxygens toward the Cu^{2+} core in order to facilitate intramolecular hydrogen bonding. Concomitantly with this observation, the different geometries of the coordination sphere, as well as the free rotation of about the S–C bond, produce variant topologies for the 1-dimensional chains; in **1** and **4** they are almost linear, as indicated by the θ_1 value close to be 180°, while **2** forms a wave-like structure. In **3** the serrated profile of a castellation is formed. Such conformational freedom engenders various topologies, a phenomenon which is structurally less predictable and explored in coordination polymers,[11] as compared with the readily predictable architectures employing linear and rigid linking groups, such as 4,4′-bipyridine.[12]

It is also interesting that, in complexes **5** and **6**, the axial positions of the Cu^{2+} are coordinated by water molecules, instead of sulfonate groups. In **5** the amino ligand is methyl substituted on one carbon atom; in **6** both N atoms are methyl substituted. In both cases, steric hindrance prevents the effective approach of the bulky SO_3^- group to Cu^{2+}. Compounds **3** and **5** share the same $[Cu(dpn)_2]^{2+}$ cation. However, bpds in **3** coordinates to Cu^{2+}, but not 1,5nds in **5**. The bpds ligand is much more flexible than the naphthalene ring because, in the former, the central C–C bond is able to rotate in order to promote better anion–cation interaction. This is the steric effect responsible for the difference in the coordination modes observed in **3** and **5**.

DSC and TGA studies

In order to characterize more fully the compounds in terms of thermal stability, and considering the fact that water molecules coordinate to Cu^{2+} with distances comparable with those of the sulfonate group in **5** and **6**, we examined **1**–**3**, **5** and **6** using DSC and TGA. Compound **1** shows an obvious endothermic event at 301 °C ($\Delta H = 48.6$ kJ mol^{-1}), corresponding to the decomposition of organic ligands, starting at 287 °C. In comparison, the endothermic event was recorded at 121 °C ($\Delta H = 126.8$ kJ mol^{-1}) for **2**, in accord with the weight loss of water molecules recorded at 102–202 °C. **3** shows an ill defined phase transition, with the first endothermic event at 61.3 °C, and the second and third at 176 and 203 °C, respectively. The endothermic event is observed at 96 ($\Delta H = 100.7$) and 121 °C ($\Delta H = 157.8$ kJ mol^{-1}) in **5** and **6**, respectively, corresponding to the weight loss of the first water molecules recorded at 78–91 °C for **5** and 96–113 °C for **6**. Therefore, for water-coordinated compounds **5** and **6**, and sulfonate-coordinated compounds **2** and **3**, similar thermal stability is observed. Thus, **1** shows abnormally high thermal stability when compared with that of the other compounds. The condensed 2-dimensional network constructed by strong hydrogen bonds, which is not present in the other species, is the only structural feature capable of accounting for this extra thermal stability. The condensed packing arrangement of compound **1** is also consistent with the much higher calculated density of 1.706 g cm^{-3}, compared with that of 1.55–1.58 g cm^{-3} for **2**–**6**.

Spectral characterization

The UV spectra display broad bands at wavelength longer than 540 nm, corresponding to the characteristic band of coordinated Cu^{2+}. λ_{max} shifts to lower energies as the number of N-substituted groups of the amine ligands increases.[13] The characteristic absorptions of the naphthalene rings are observed in the regions 221–230, 264–287 and 312–326 nm, which are split in different patterns corresponding to the different substituent changes. Those for the diphenyl ring are observed as broadened bands at 247 nm.

All compounds have absorptions at 3400–3500 cm^{-1} in their IR spectra, corresponding to the presence of water molecules. For **3** the single crystal analysis shows no water molecule in the structure. However, a broad band at 3429 cm^{-1} indicates the presence of water molecules, weakly bonded, in the batch material. The presence of water molecules is further verified by the TGA and elemental analysis result. This observation suggests that the water molecule exits discretely in the structure. The N–H stretching frequencies of the amino groups were recorded in the region 3060–3370 cm^{-1} as strong bands, which show different absorption patterns corresponding to their different chemical environments (primary and secondary) and the strength of hydrogen bonds involved. The aromatic C–H stretching is recorded at 2870–2980 cm^{-1}. The well resolved frequencies of aromatic rings span over the regions 600–930 and 1240–1630 cm^{-1}. Bands characteristic of the fundamental and split v_3 S–O stretching modes are observed in the range 1000 to 1240 cm^{-1}.[1,14]

Concluding remarks

Previous studies of the structures of metal naphthalenesulfonate salts have revealed that the divalent, first row, transition metal ions show no tendency to coordinate to sulfonate anions in the presence of water molecules.[5] The crystal structure of $[Cu(H_2O)_6][1,5nds]$ studied in this group also reveals a layered structure composed exclusively of inorganic and organic components, without any direct interaction between the sulfonate and Cu^{2+}.[15] Herein, we have demonstrated that the coordination behavior of Cu^{2+} toward SO_3^- can be tailored chemically, and that naphthalenedisulfonate can compete with water molecules and coordinate with Cu^{2+}, with bond distances comparable to those of methylbenzenesulfonato complexes.[6] This study also represents the first synthesis and structural characterization of 1-dimensional structures constructed by arenedisulfonates and transition metals in the presence of water molecules.

Experimental

Material and methods

All materials were commercially available and used as received. FTIR spectra were obtained on a Bruker EQUINOX 55 FTIR spectrometer with KBr pellets, UV-VIS spectra on a Shimadzu UV-2501pc spectrometer. TGA was performed using a Netzsch TG 209 analyzer in flowing nitrogen. DSC data were obtained using a Netzsch DSC 204 analyzer. Elemental analyses were carried out with a Perkin-Elmer 240 elemental analyzer.

Synthesis and characterization

$Cu(en)_2(1,5nds)\cdot 2H_2O$ 1. Ethylenediamine (0.12 g, 2mmol) was added to an aqueous solution (20 ml) of $CuCl_2\cdot 2H_2O$ (0.17 g, 1 mmol). The solution was then treated with disodium 1,5-naphthalenedisulfonate (0.33 g, 1 mmol). Purple-brown crystals of complex **1** were collected after 6 days (52% yield based on Cu). Found: C, 33.75; H, 4.84; N, 11.75; S, 12.85. $C_{14}H_{26}CuN_4O_8S_2$ requires C, 33.23; H, 5.18; N, 11.07; S, 12.67%. IR (cm^{-1}, KBr): 3374.0(s), 3298.3(s), 3229.5(s), 3133.0(s), 2936.9(s), 2887.9(s), 1591.6(s), 1495.8(s), 1454.5(s), 1239.9(s), 1215.4(s), 1184.0(s), 1032.1(s), 980.5(s), 792.2(s), 765.0(s), 723.6(s), 611.1(s), 568.1(s), 531.1(s) and 470.7(s). UV (nm, water): 231, 277, 287, 298, 319 and 543.

$Cu(N\text{-meen})_2(2,6nds)\cdot 2H_2O$ 2. *N*-Methylethylenediamine (0.15 g, 2 mmol) was added with constant stirring to an aqueous solution (20 ml) of $CuCl_2\cdot 2H_2O$ (0.17 g, 1 mmol). The solution was then treated with disodium 2,6-naphthalenedisulfonate (0.33 g, 1 mmol). Blue crystals of complex **2** were collected after 2 days (68% yield based on Cu). Found: C, 35.74; H, 5.44; N, 10.35; S, 12.20. $C_{16}H_{30}CuN_4O_8S_2$ requires C, 35.98; H, 5.66; N, 10.49; S, 12.01%. IR (cm^{-1}, KBr): 3494.8(s), 3462.0(s), 3303.9(s), 3243.7(s), 3210.0(s), 3166.0(s), 3118.8(s), 2930.0(m), 1657.9(s), 1598.7(s), 1473.7(s), 1436.8(s), 1315.2(m), 1203.7(s), 1143.7(s), 1094.8(s), 1033.9(s), 965.6(s), 913.7(s), 839.8(s), 665.7(s), 625.6(s), 543.1(s) and 482.0(s). UV (nm, water): 230, 264, 312, 326 and 557.

$Cu(dpn)_2(bpds)\cdot H_2O$ 3. 2,3-Diaminopropane (0.15 g, 2 mmol) was added with constant stirring to an aqueous solution (20 ml) of $CuCl_2\cdot 2H_2O$ (0.17 g, 1 mmol). The solution was then treated with disodium 4,4′-biphenyldisulfonate (0.36 g, 1 mmol). Purple crystals of complex **3** were collected after 8 days (50% yield based on Cu). Found: C, 39.78; H, 5.41; N, 10.66; S, 12.09. $C_{18}H_{30}CuN_4O_7S_2$ requires C, 39.88; H, 5.58; N, 10.33; S, 11.83%. IR (cm^{-1}, KBr): 3429.0(br), 3305.0(s), 3245.6(s), 3131.5(s), 3060.3(s), 2875.0–2967.2(m), 1591.7(s), 1461.6(s), 1379.3(s), 1225.1(s), 1193.2(s), 1123.5(s) 1063.3(s), 1030.5(s), 994.8(s), 840.5(s), 814.9(s), 718.6(s), 612.6(s), 564.3(s), 498.0(s) and 440.7(s). UV (nm, water): 247.5 and 542.

Cu(cyclam)(1,5nds) 4. The aqueous solution (20 ml) of $CuCl_2\cdot 2H_2O$ (0.09 g, 0.5 mmol) was treated slowly with 1,4,8,11-tetraazacyclotetradecane (0.10 g, 0.5 mmol) in MeOH with constant stirring. Disodium 1,5-naphthalenedisulfonate (0.17 g, 0.5 mmol) was dissolved in distilled water. Slow diffusion of the two solutions into a U-tube containing agar gel produced deep purple crystals after 5 days (10% yield based on Cu). Found: C, 43.18; H, 5.68; N, 10.14. $C_{20}H_{30}CuN_4O_6S_2$ requires C, 43.66; H, 5.50; N, 10.18%.

$Cu(dpn)_2(1,5nds)\cdot 2H_2O$ 5. 2,3-Diaminopropane (0.15 g, 2 mmol) was added with constant stirring to an aqueous solution (20 ml) of $CuCl_2\cdot 2H_2O$ (0.17 g, 1 mmol). The solution was then treated with disodium 1,5-naphthalenedisulfonate (0.33 g, 1 mmol). Purple crystals of complex **5** were collected after 1 day (52% yield based on Cu). Found: C, 35.14; H, 5.90; N, 10.64; S, 11.75. $C_{16}H_{30}CuN_4O_8S_2$ requires C, 35.98; H, 5.66; N, 10.49; S, 12.01%. IR (cm^{-1}, KBr): 3435.7(br), 3283.9(m), 3157.8(s), 2935.0(m), 1595.0(s), 1498.7(s), 1462.3(s), 1194.1(m), 1065.9(s), 1032.3(s), 931.8(s), 833.0(s), 798.1(s), 763.7(s), 666.1(s), 608.5(s), 564.8(s), 531.0(s) and 493.6(s). UV (nm, water): 232, 276, 287, 298, 319 and 542.

$Cu(N,N'\text{-meen})_2(1,5nds)\cdot 3H_2O$ 6. *N*,*N*′-Dimethylethylenediamine (0.18 g, 2 mmol) was added with constant stirring to an aqueous solution (20 ml) of $CuCl_2\cdot 2H_2O$ (0.17 g, 1 mmol). The solution was then treated with disodium 1,5-naphthalenedisulfonate (0.33 g, 1 mmol). Blue crystals of complex **6** were collected after 1 day (72% yield based on Cu). Found: C, 37.31; H, 6.04; N, 9.85; S, 11.56. $C_{18}H_{36}CuN_4O_9S_2$ requires C, 37.26; H, 6.25; N, 9.66; S, 11.05%. IR (cm^{-1}, KBr): 3493.4(s), 3413.0(br), 3276.7(s), 3203.9(s), 2820.0–2979.0(m), 1638.3(s), 1497.3(s), 1463.2(s), 1220.4(s), 1184.0(s), 1160.5(s), 1033.9(s), 967.4(m), 861.8(s), 803.2(s), 764.8(s), 611.3(s), 569.4(s), 534.9(s) and 462.6(s). UV (nm, water): 225, 276, 287, 319 and 570.

X-Ray crystallography

Experimental details of the X-ray analyses are provided in Table 2. All diffraction data were collected on a Bruker Smart 1000 CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature, using the program SMART[16] and processed by SAINT+.[17] Absorption corrections were applied using SADABS.[18] Space groups of these compounds were determined from systematic absences

Table 2 Crystallographic data for compounds **1**–**6**

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_{14}H_{26}CuN_4O_8S_2$	$C_{16}H_{30}CuN_4O_8S_2$	$C_{18}H_{28}CuN_4O_6S_2$	$C_{20}H_{30}CuN_4O_6S_2$	$C_{16}H_{30}CuN_4O_8S_2$	$C_{18}H_{36}CuN_4O_9S_2$
Formula weight	506.05	534.10	524.10	550.14	534.10	580.17
Crystal system	Tetragonal	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P4_12_12$	$P2_1/n$	$C2/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a/Å	9.4371(9)	8.390(9)	23.486(2)	8.568(6)	10.3699(8)	8.4923(7)
b/Å	9.4371(9)	9.631(10)	7.9921(7)	10.521(8)	9.1849(7)	8.7434(7)
c/Å	22.129(3)	14.001(15)	12.3656(11)	12.839(9)	23.8804(18)	9.1900(7)
α/°						92.314(2)
β/°		90.00(2)	106.839(2)	91.869(15)	96.6430(10)	94.938(2)
γ/°						113.5570(10)
V/Å^3	1970.7(4)	1131(2)	2221.6(4)	1156.8(15)	2259.3(3)	621.09(9)
Z	4	2	4	2	4	1
μ/mm^{-1}	1.372	1.199	1.214	1.170	1.201	1.107
Reflections collected/ unique	18533/2146	7791/3241	7499/3168	6658/2332	15624/6453	4404/3393
Observed reflections ($I > 2\sigma(I)$)	2096	2519	2715	1704	3817	3113
$R(F)$; $R_w(F)$ ($I > 2\sigma(I)$)	0.0195; 0.0544	0.0290; 0.0771	0.0379; 0.1007	0.1181; 0.3564	0.0542; 0.1538	0.0489; 0.1469

and further justified by the results of refinement. In all cases the structures were solved by direct methods and refined using full-matrix least-squares/Fourier difference techniques using SHELXTL.[19,20] All non-hydrogen atoms were refined with anisotropic displacement parameters. After that all hydrogen atoms of the ligands were placed at idealized positions and refined as riding atoms with the relative isotropic parameters of the heavy atoms to which they are attached. Hydrogen atoms of water were located from the Fourier difference map at the final state of refinement. For compound **4** the crystals obtained were of poor quality, as indicated by the high $R_{\text{int}} = 0.0924$. However, the structure was solved and shows reasonable geometries and standard deviations.

CCDC reference numbers 145435 and 157237–157240.

See http://www.rsc.org/suppdata/dt/b0/b009851p/ for crystallographic data in CIF or other electronic format.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (Grant No. 29801006) and Guangdong Provincial Natural Science Foundation of China (No.990208).

References

1 J. Cai, C.-H. Chen, C.-Z. Liao, X.-L. Feng and X.-M. Chen, *J. Chem. Soc., Dalton Trans.*, unpublished work.

2 M. E. Thompson, *Chem. Mater.*, 1994, **6**, 1168; D. Grohol, F. Ging and A. Clearfield, *Inorg. Chem.*, 1999, **38**, 751 and the references cited therein.

3 D. M. Poojary, B. Zhang and A. Clearfield, *J. Am. Chem. Soc.*, 1997, **119**, 12550 and references cited therein; D. M. Poojary, B. Zhang, P. Bellinghausen and A. Clearfield, *Inorg. Chem.*, 1996, **35**, 4942.

4 G. K. H. Shimizu, G. D. Enright, C. I. Ratcliffe, K. F. Preston, J. L. Reid and J. A. Ripmeester, *Chem. Commun.*, 1999, 1485; G. K. H. Shimizu, G. D. Enright, C. I. Ratcliffe, G. S. Rego, J. L. Reid and J. A. Ripmeester, *Chem. Mater.*, 1998, **10**, 3282; G. K. H. Shimizu, G. D. Enright, C. I. Ratcliffe and J. A. Ripmeester, *Chem. Commun.*, 1999, 461.

5 E. J. Kosnic, E. Lynn McClymont, R. A. Hodder and P. J. Squattrito, *Inorg. Chim. Acta*, 1992, **201**, 143; A. J. Shubnell, E. J. Kosnic and P. J. Squattrito, *Inorg. Chim. Acta*, 1994, **216**, 101; B. J. Gunderman, I. D. Kabell, P. J. Squattrito and S. N. Dubey, *Inorg. Chim. Acta.*, 1997, **258**, 237.

6 M. R. Sundberg and R. Sillanpää, *Acta Chem. Scand.*, 1993, **47**, 1173.

7 I. Murase, G. Vuckovic, M. Kodera, H. Harada, N. Matsumoto and S. Kida, *Inorg. Chem.*, 1991, **30**, 728.

8 As far as we are aware, the only 1-dimensional polymeric structure constructed by a metal arenedisulfonate is $\{Ag(1,5nds)(MeCN)_2(H_3O)(H_2O)_2\}_\infty$ obtained in organic solvent, reported by G. Shimizu, G. D. Enright, G. S. Rego and J. A. Ripmeester, *Can. J. Chem.*, 1999, **77**, 313.

9 C. J. Carrell, H. L. Carrell, J. Erlebacher and J. P. Glusker, *J. Am. Chem. Soc.*, 1988, **110**, 8651.

10 N. S. Hüsgen, G. A. Luinstra, F. Schaper and K. Schmidt, *Inorg. Chem.*, 1998, **37**, 3471.

11 T. L. Hennigar, D. C. MacQuarrie, P. Losier, R. D. Rogers and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 972.

12 M.-L. Tong, B.-H. Ye, J. Cai, X.-M. Chen and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 2645.

13 D. W. Meek and S. A. Ehrhardt, *Inorg. Chem.*1965, **4**, 584.

14 G. Smith, B. A. Cloutt, D. E. Lynth, K. A. Byriel and C. H. L. Kennard, *Inorg. Chem.*, 1998, 37, 3236; Y. Ohki, Y. Suzuki, M. Nakamura, M. Shimoi and A. Ouchi, *Bull. Chem. Soc. Jpn.*, 1985, 2968.

15 $[Cu(H_2O)_6][1,5nds]$ crystallizes in space group $P2_1/c$, with $a = 13.3086(18)$, $b = 6.5806(9)$, $c = 9.7781(13)$ Å, $\beta = 93.405(2)$°. Cu–H_2O 1.9539(12)–2.3418(10) Å.

16 Bruker AXS, SMART, Version 5.0, Bruker AXS, Madison, WI, 1998.

17 Bruker AXS, SAINT+, Version 6.0, Bruker AXS, Madison, WI, 1999.

18 R. Blessing, *Acta Crystallogr., Sect. A*, 1995, **51**, 33.

19 Bruker AXS, SHELXTL, Version 5.1, Bruker AXS, Madison, WI, 1998.

20 G. M. Sheldrick, SHELX 97, Program for Crystal Structure Solution and Refinement, Göttingen University, 1997.