DALTON
FULL PAPER

A novel supramolecular synthon for H-bonded coordination networks: syntheses and structures of extended 2-dimensional cadmium(II) arenedisulfonates

Jiwen Cai,* Cai-Hong Chen, Xiao-Long Feng, Cheng-Zhu Liao 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 26th March 2001, Accepted 11th June 2001
First published as an Advance Article on the web 31st July 2001

Four cadmium(II) arenedisulfonate polymers, namely [Cd(N,N′-meen)$_2$](2,6nds) (**1**), [Cd(N,N′-meen)$_2$](1,5nds) (**2**), [Cd(N,N′-meen)$_2$](bpds) (**3**), and [Cd(N-meen)$_2$](2,6nds)·2H$_2$O (**4**), where nds = naphthalenedisulfonate, bpds = 4,4′-biphenyldisulfonate, N,N′-meen = *N*,*N*′-dimethylethylenediamine and N-meen = *N*-methylethylenediamine, have been synthesized in aqueous solution and structurally characterized by X-ray single crystal diffraction and IR spectroscopy. In all four crystalline materials, the arenedisulfonate anions act as bifunctional spacers to coordinate the CdN_4 complex cations, generating stepwise 1-dimensional strings. Due to the inherent multiple H-bonding donors/acceptors on their neutral polymeric backbones the same pattern of inter-chain H-bonding interactions described as $C(6)R_2^2(12)$ are formed by the amino H-atoms and sulfonate O-atoms. Hence, the driving forces for the assembly of these 1-dimensional polymers into 2-dimensional networks have been rationalized and a unique supramolecular synthon identified. It represents a novel strategy that leads to predictable 2-dimensional coordination networks sustained by direct H-bonding interactions between the 1-dimensional polymeric backbones.

Introduction

Traditionally, networks sustained either by directional non-covalent interactions in organic systems[1] or by coordinate covalent bonds in coordination polymers[2] represent the two primary classes of crystal engineering which have mainly been developed separately.[3] However, the ability to design and control the assembly of coordination networks through both coordination and H-bonding interactions has been of great interest in recent years.[4–6] By employing organic ligands with H-bonding functionalities combined with coordination sites for transition metals, bridges have been built between the two main streams of crystal engineering.[7] Crystalline materials have been constructed by linear polymeric $[M(L^1L^2)]_n$ chains mediated by neutral ligands L^1 (where L^1 = 4,4′-bipy,[8] 4,4′-azopyridine;[9] $L^2 = H_2O$) *via* H-bonding interactions between $[M(L^1L^2)]_n$ and ligand L^1. This strategy was aimed at creating larger cavities and non-square grids.[9] One common feature of these systems is that only pyridine-based rigid bifunctional spacers were employed whose coordination behaviors are well-established and predictable.

In our previous study, we reported 1-dimensional polymers, with diverse topologies, constructed by amino-coordinated copper(II) and arenedisulfonates through weak coordination.[10] Herein we present another novel family of 1-dimensional coordination polymers, namely [Cd(N,N′-meen)$_2$](2,6nds) (**1**), [Cd(N,N′-meen)$_2$](1,5nds) (**2**), [Cd(N,N′-meen)$_2$](bpds) (**3**) and [Cd(N-meen)$_2$](2,6nds)·2H$_2$O (**4**), where nds = naphthalenedisulfonate, bpds = 4,4′-biphenyldisulfonate, N,N′-meen = *N*,*N*′-dimethylethylenediamine and N-meen = *N*-methylethylenediamine. It is noteworthy that the bridging ligands (spacers) we employed here are flexible sulfonates. Both the S–C and central C–C bonds of biphenyl can rotate freely and engender conformational freedom, which makes the assembly process less predictable, in contrast to the rigid bridging ligands typically employed for crystal engineering with coordination compounds.[11] However, similar packing arrangements are observed in these title compounds. Due to the inherent multiple H-bonding donors/acceptors along their neutral polymeric backbones, complementary inter-backbone H-bonds are formed by the amino H-atoms and sulfonate O-atoms. As far as we are aware, there are only a few existing examples of 2-dimensional networks sustained by direct H-bonding interactions between 1-dimensional backbones.[12] All of them are copper complexes containing ligands with a metal-coordinated site and a self-complementary H-bond moiety, such as methyl-substituted nicotinic acid,[12a] pyridinealdoxime, isonicotinamide[12b] and isonicotinic acid.[12c]

Results and discussion

Coordination modes of arenedisulfonates toward $[CdN_4]^{2+}$

Fig.1 shows the coordination environments of the Cd^{2+} cations in compounds **1**–**4**. Selected bond lengths and angles are listed in Table 1. In all structures, Cd^{2+} is six-coordinated equatorially by four N-atoms from the amine ligands and axially by two O-atoms from the monodentate SO_3^- groups. The Cd–O distances are in the range 2.3504(19)–2.4324(13) Å, longer than the reported Cd–O (2.304(5) Å in the structure of $\{[Cd(4,4'\text{-bipy})(CF_3SO_3)_2(H_2O)_2](4,4'\text{-bipy})\}_n$.[13] There are no comparable Cd–O distances recorded for arenesulfonate in the Cambridge Structural Database.[14] The Cd–N distances are in the range 2.2961(18)–2.363(2) Å. The CdN_4O_2 chromophores are all centrosymmetric. The naphthalenedisulfonate and biphenyldisulfonate anions behave as bifunctional spacers coordinating the adjacent Cd^{2+} complex centers, resulting in 1-dimensional chains propagating in a stepwise fashion.

The coordination chemistry of transition metal sulfonates is not well explored and rationalized,[10,15] in comparison with the well-studied metal phosphates.[16,17] Due to the weak coordination strength of the sulfonate toward transition metal ions, most of the reported transition metal sulfonates prepared in aqueous solution were all caused by segregation of aquametal

 DOI: 10.1039/b102729h

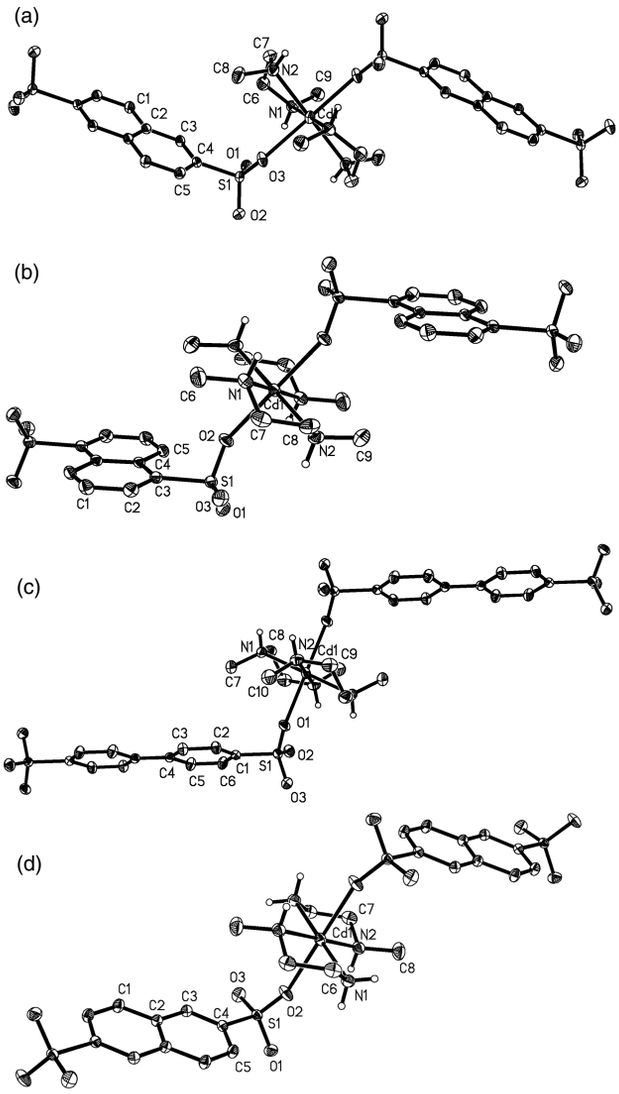


Fig. 1 (a)–(d) Coordination envronment of Cd^{2+} in **1**–**4**, respectively, with 30% probability displacement ellipsoids.

complex cations and sulfonate anions.[18] In our preceding paper,[10] we reported that, by tailoring the chemical environment of Cu^{2+} with organic ligands, such as amines, the SO_3^- oxygen can compete with water molecules and coordinate to Cu^{2+}. Compared with Cu^{2+}, the SO_3^- group shows stronger coordinative strength toward Cd^{2+} under the same reaction conditions, as indicated by the comparable and consistent Cd–O and Cd–N bond distances. The diversities in the coordination modes and topologies of the 1-dimensional chains of Cu^{2+} arenedisulfonates have also been discussed.[10] Herein, we employ the same geometric parameters to rationalize the coordination modes of this series of complexes. $\theta 1$ is the torsion angle C–S–O–Cd for the coordinated sulfonate oxygen, and $\theta 2$ is the dihedral angle formed between the equatorial plane of $[CdN_4]^{2+}$ and the naphthalene or phenyl rings. $\theta 1$ and $\theta 2$, together with other geometric parameters of **1**–**4** associated with their different coordination modes are listed in Table 2. In contrast with that reported for the Cu^{2+} analogues, the coordination modes of the sulfonate groups toward the Cd^{2+} centers vary to a much smaller extent. This observation is in line with the similar stepwise 1-dimensional structures observed in all four compounds.

Description of the extended 2-dimensional structures

Remarkably, despite the differences in both the components and the lattices they adopt, the four polymers arrange in a very similar pattern of extended 2-dimensional networks, as

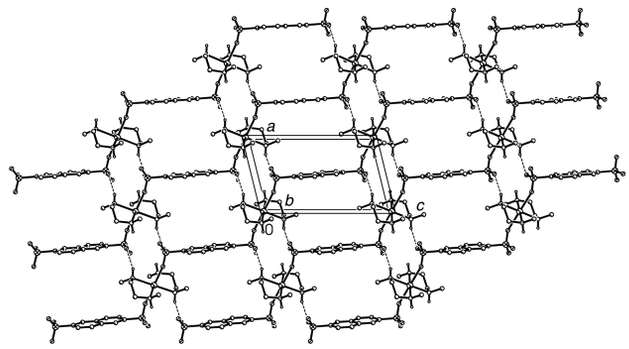


Fig. 2 Packing arrangement of compound **1** on the *ac* plane. Note that there are grids constructed by the two adjacent naphthalene rings along the *a* axis and the corresponding CdN_4 units. Grids of the adjacent layers shift half the cell unit along the *a* axis.

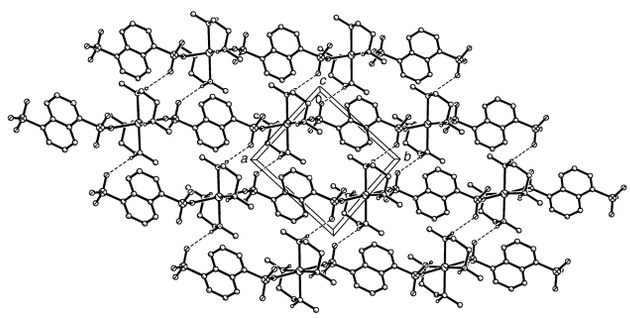


Fig. 3 Packing arrangement of compound **2** on the *ab* plane. Note that the N-substituted methyl groups occupy the grid areas constructed by naphthalene rings and CdN_4 units.

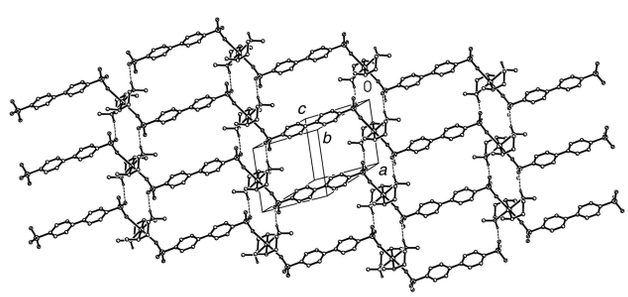
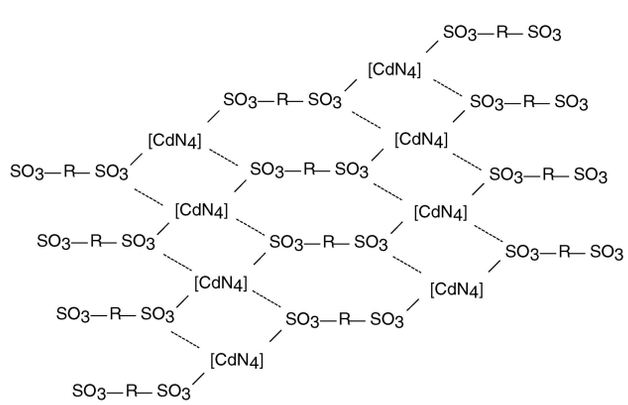


Fig. 4 Packing arrangement of compound **3** on the *ab* plane.



Scheme 1

illustrated in Scheme 1, through H-bonding interactions between adjacent chains. In all cases, both the $[CdN_4]^{2+}$ fragments and the naphthalene/biphenyl rings align along the crystallographic *a* axis. And the *a* length of the cell is equal to the separation between the two adjacent naphthalene/biphenyl rings, which is 7.6548(12) and 7.6031(10) Å for **1** and **3**, 8.4306(14) and 8.4953(11) Å for **2** and **4**, respectively. As shown in Figs. 2–5, the secondary amino H-atoms point up and down

Table 1 Selected bond distances (in Å) and angles (in °) for compounds **1**–**4**

[Cd(N,N′-meen)$_2$](2,6nds) (**1**)			
Cd(1)–N(1)	2.3356(16)	S(1)–O(1)	1.4507(15)
Cd(1)–N(2)	2.3106(17)	S(1)–O(2)	1.4473(15)
Cd(1)–O(3)	2.4324(13)	S(1)–O(3)	1.4649(13)
S(1)–C(4)	1.7828(17)		
N(1)–Cd(1)–N(2)	78.75(6)	O(1)–S(1)–O(2)	114.13(9)
N(2)–Cd(1)–N(1)	101.25(6)	O(1)–S(1)–O(3)	112.60(8)
N(1)–Cd(1)–O(3)	88.76(5)	O(2)–S(1)–O(3)	112.21(9)
N(1)–Cd(1)–O(3)	91.24(5)	O(1)–S(1)–C(4)	106.36(8)
N(2)–Cd(1)–O(3)	93.44(6)	O(2)–S(1)–C(4)	105.92(8)
N(2)–Cd(1)–O(3)^{i}	86.56(6)	O(3)–S(1)–C(4)	104.73(8)
[Cd(N,N′-meen)$_2$](1,5nds) (**2**)			
Cd(1)–N(1)	2.363(2)	S(1)–O(1)	1.450(2)
Cd(1)–N(2)	2.354(2)	S(1)–O(2)	1.460(2)
Cd(1)–O(2)	2.3504(19)	S(1)–O(3)	1.446(2)
S(1)–C(3)	1.794(2)		
N(1)–Cd(1)–N(2)	77.42(9)	O(1)–S(1)–O(2)	112.30(15)
N(2)–Cd(1)–N(1)^{i}	102.58(9)	O(1)–S(1)–O(3)	113.88(14)
N(1)–Cd(1)–O(2)^{i}	87.38(8)	O(2)–S(1)–O(3)	112.66(14)
N(1)–Cd(1)–O(2)	92.62(8)	O(1)–S(1)–C(3)	106.03(12)
N(2)–Cd(1)–O(2)	93.46(8)	O(2)–S(1)–C(3)	104.40(11)
N(2)–Cd(1)–O(2)^{i}	86.54(8)	O(3)–S(1)–C(3)	106.69(13)
[Cd(N,N′-meen)$_2$](bpds) (**3**)			
Cd(1)–N(1)	2.315(2)	S(1)–O(1)	1.4622(16)
Cd(1)–N(2)	2.3554(19)	S(1)–O(2)	1.4546(17)
Cd(1)–O(1)	2.4018(16)	S(1)–O(3)	1.4514(17)
S(1)–C(1)	1.779(2)		
N(1)–Cd(1)–N(2)	101.40(8)	O(1)–S(1)–O(2)	113.22(10)
N(2)–Cd(1)–N(1)^{i}	78.60(8)	O(1)–S(1)–O(3)	112.45(11)
N(1)–Cd(1)–O(1)	96.61(7)	O(2)–S(1)–O(3)	113.28(11)
N(1)–Cd(1)–O(1)^{i}	83.39(7)	O(1)–S(1)–C(1)	104.80(10)
N(2)–Cd(1)–O(1)	89.67(7)	O(2)–S(1)–C(1)	106.04(10)
N(2)–Cd(1)–O(1)^{i}	90.33(7)	O(3)–S(1)–C(1)	106.18(10)
[Cd(N-meen)$_2$](2,6nds)·2H$_2$O (**4**)			
Cd(1)–N(1)	2.2961(18)	S(1)–O(1)	1.4512(15)
Cd(1)–N(2)	2.3497(18)	S(1)–O(2)	1.4537(15)
Cd(1)–O(2)	2.4245(15)	S(1)–O(3)	1.4509(15)
S(1)–C(4)	1.7673(17)		
N(1)–Cd(1)–N(2)	102.20(7)	O(1)–S(1)–O(2)	111.58(11)
N(2)–Cd(1)–N(1)	77.80(7)	O(1)–S(1)–O(3)	113.21(10)
N(1)–Cd(1)–O(2)	87.31(6)	O(2)–S(1)–O(3)	113.33(11)
N(1)–Cd(1)–O(2)	92.69(6)	O(1)–S(1)–C(4)	105.19(9)
N(2)–Cd(1)–O(2)	85.40(6)	O(2)–S(1)–C(4)	105.72(9)
N(2)–Cd(1)–O(2)	94.60(6)	O(3)–S(1)–C(4)	107.06(9)

Symmetry code for **1**: ^{i} $-x, -y + 1, -z$. Symmetry code for **2**: ^{i} $-x + 1, -y + 2, -z + 1$. Symmetry code for **3**: ^{i} $-x + 1, -y + 2, -z + 2$. Symmetry code for **4**: ^{i} $-x, -y, -z + 1$.

Table 2 Comparison of the coordination parameters of compounds **1**–**4** (distances in Å and angles in °)

	1	**2**	**3**	**4**
Dihedral angle ($\theta 2$)	38.8	37.8	31.6	19.1
Torsion angle C–S–O–Cd ($\theta 1$)	−116.5	138.0	−108.4	−80.1
Cd–O	2.4324(13)	2.3504(19)	2.4018(16)	2.4245(15)
Cu–O–S	137.2	144.4	140.1	160.9

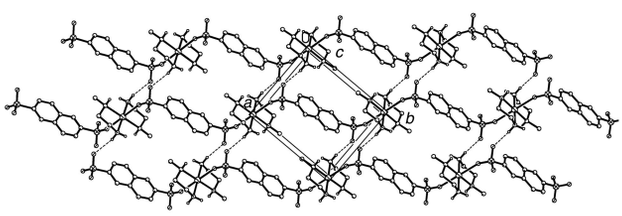


Fig. 5 Packing arrangement of compound **4** on the *ab* plane. Water molecules are omitted for clarity.

the equatorial CdN_4 planes, catching the sulfonate oxygen atoms of adjacent chains. There are two strong or moderate intermolecular H-bonds for each repeating unit, described as $R_2^2(12)$ according to the graph set notation.[19] The infinite H-bonding patterns can be described as C(6). There are one or two other weaker H-bonds (indicated as less favored N–H···O angle and/or longer N···O distance) formed by the other amino H-atoms as listed in Table 3. The overall 2-dimensional structures can be described as inorganic layers pillared by organic groups, reminiscent of the well-studied lamellar metal

Table 3 Selected hydrogen bonds (Å, °)

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
[Cd(N,N′-meen)$_2$](2,6nds) (**1**)				
N(1)–H(1A)···O(1)	0.91	2.26	3.013(2)	140.3
N(2)–H(2A)···O(1)^{i}	0.91	2.17	3.042(2)	160.4
[Cd(N,N′-meen)$_2$](1,5nds) (**2**)				
N(1)–H(1A)···O(1)^{i}	0.91	2.32	3.118(3)	146.2
N(2)–H(2A)···O(3)^{ii}	0.91	2.63	3.237(3)	124.8
[Cd(N,N′-meen)$_2$](bpds) (**3**)				
N(1)–H(1A)···O(2)^{ii}	0.91	2.21	3.090(3)	163.9
N(2)–H(2A)···O(2)^{i}	0.91	2.43	3.126(3)	133.6
N(2)–H(2A)···O(3)^{ii}	0.91	2.52	3.164(3)	128.6
[Cd(N′-meen)$_2$](2,6nds)·2H$_2$O (**4**)				
N(1)–H(1B)···O(1)^{i}	0.90	2.30	3.078(2)	144.2
N(1)–H(1C)···O(1W)^{ii}	0.90	2.10	2.963(3)	161.6
N(2)–H(2A)···O(3)^{iii}	0.91	2.53	3.285(2)	141.3

Symmetry codes for **1**: ^{i} $x-1, y, z$. Symmetry codes for **2**: ^{i} $x-1, y, z$. ^{ii} $-x+1, -y+2, -z+2$. Symmetry codes for **3**: ^{i} $-x+1, -y+2, -z+2$. ^{ii} $x-1, y, z$. Symmetry codes for **4**: ^{i} $-x+1, -y, -z+1$. ^{ii} $-x+1, -y+1, -z+1$. ^{iii} $-x+1/2, y+1/2, -z+1/2$.

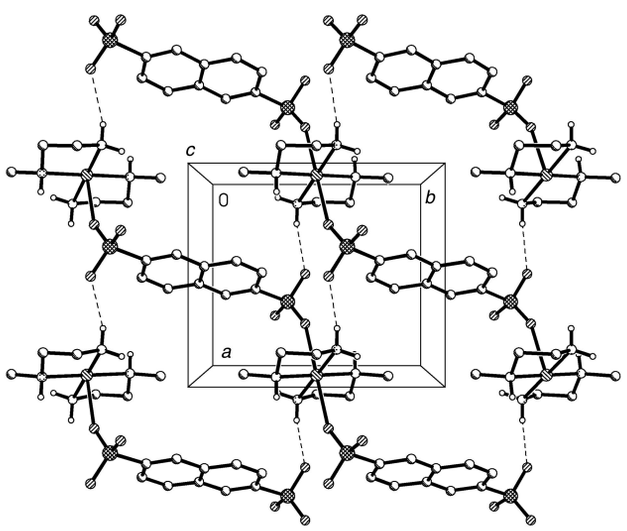


Fig. 6 Packing arrangement of compound Cu(N-meen)$_2$(2,6nds)·2H$_2$O on the *ab* plane, for comparison with that of the Cd analogue (compound **4**).

phosphates.[16] In compounds **1**–**3**, there is no contact between the stacking 2-dimensional networks. While in the case of compound **4**, due to the extra amino H-atoms available, there are inter-layer H-bonds present which extend the 2-dimensional structure further into a 3-dimensional array.

One of the unique features about crystal engineering with inorganic compounds is that the role of metal atoms can be evaluated.[4] Together with the previous structure of the copper(II) analogue,[10] we have a good opportunity to compare the role of the metal ion (with the same charge) in the assembly process of the polymeric $[M(N_4)(nds/bpds)]_n$ chains. Despite the differences in the coordination geometries (elongated *vs.* regular octahedral MN_4O_2 chromophores, Cu–N = 2.029(2) and 2.068(2) Å, Cu–O = 2.496(2) Å *vs.* Cd–N = 2.2961(18) and 2.3497(18) Å, Cd–O = 2.4245(15) Å), compounds Cu(N-meen)$_2$(2,6nds)·2H$_2$O and Cd(N-meen)$_2$(2,6nds)·2H$_2$O (**4**) are isostructural. As shown in Figs. 5 and 6, the packing arrangements of these two compounds are very similar. The inter-chain H-bonding strength is weaker in the copper(II) analogue (N···O 3.142(4) Å, N–H···O 134.6° *vs.* N···O 3.078(2) Å, N–H···O 144.2°). Interestingly, there is one crystalline water molecule present per asymmetric unit in both materials. The water molecule occupies the same lattice position between the 2-dimensional layers and forms strong H-bonds with the backbone sulfonate O-atoms. This is not observed in the other Cd^{2+} analogues **1**–**3**, probably because of the second substitution of the methyl group on the N-atom. Therefore, the metal center plays a minor role in the assembly process of these 1-dimensional polymers.

Finally, such types of 2-dimensional array are only observed for polymers with stepwise or wave-like topology, for the linear Cu(en)$_2$(1,5nds)·2H$_2$O, Cu(cyclam)(1,5nds)(cyclam = 1,4,8,11-tetraazacyclotetradecane), and the castellated Cu(dpn)$_2$(bpds)·H$_2$O, different arrangements are adopted.[10]

Spectral characterization and thermal analyses

In all these compounds, only compound **4** has broad and strong absorptions at 3450–3505 cm^{-1} corresponding to the presence of water molecules. The N–H stretching frequencies of the amino groups were recorded in the regions 3320–3330 cm^{-1} and 3370–3440 cm^{-1}. The aromatic C–H stretching extends through the region 2800–3000 cm^{-1}. The well-resolved frequencies of the aromatic rings span over 500–1000 cm^{-1} and 1240–1600 cm^{-1}. Those frequencies characteristic of the fundamental and split ν_3 S–O stretching modes are observed in the range 1000–1240 cm^{-1}.[10]

TGA analyses showed that the first weight losses were recorded at 231, 289 and 284 °C for compounds **1**, **2** and **3**, respectively. The release of water molecules in compound **4** was at 103 °C, followed by another weight loss at 230 °C.

Concluding remarks

N–H···O types of H-bonds formed by guanidinium and sulfonate have been used in organic crystal engineering.[20] However, the properties of the N–H···O H-bonds to the sulfonate and the effect of metal coordination have not been discussed.[21] Herein, we have identified a novel supramolecular synthon,[1] namely the N–H···O H-bonds formed by the metal-coordinated amino H-atoms and ionic sulfonate O-atoms, which provides the driving force for the assembly of 1-dimensional metal arenedisulfonates. The most significant feature about this synthon is its flexibility. Even though the inter-chain H-bonding pattern C(6)R$_2^2$(12) is persistent in all the structures studied here and also in the Cu^{2+} analogue of **4** it is flexible enough to adapt to certain variations introduced by different coordination modes of the disulfonate toward the metal center, the nature of the organic group (naphthalene *vs.*

Table 4 Crystal data for compounds **1**–**4**

	1	**2**	**3**	**4**
Empirical formula	$C_{18}H_{30}O_6N_4S_2Cd$	$C_{18}H_{30}O_6N_4S_2Cd$	$C_{20}H_{32}O_6N_4S_2Cd$	$C_{16}H_{30}O_8N_4S_2Cd$
Formula weight	574.98	574.98	601.02	582.96
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	7.6548(12)	8.4306(14)	7.6031(10)	8.4953(11)
b/Å	11.9968(18)	8.5243(14)	9.0127(12)	9.6732(13)
c/Å	12.832(2)	8.5607(14)	9.5933(13)	14.0313(18)
α/°	90	87.652(3)	73.237(2)	90
β/°	103.836(3)	67.476(2)	84.119(2)	90.412(2)
γ/°	90	88.910(3)	72.192(2)	90
V/Å^3	1144.2(3)	567.80(16)	599.21(14)	1153.0(3)
Z	2	1	2	2
D_c/g cm^{-3}	1.669	1.682	1.666	1.668
μ/mm^{-1}	1.179	1.188	1.129	1.177
F(000)	588	588	616	588
Reflections collected/unique	8020/3256	4608/3130	4330/3319	8052/3286
Observed reflections ($I > 2\sigma(I)$)	2731	2903	3096	2892
$R(F)$; $R_w(F)$ ($I > 2\sigma(I)$)	0.0255; 0.0710	0.0371; 0.0914	0.0324; 0.0862	0.0286; 0.0787

biphenyldisulfonate) and the amino ligand (N,N′-meen *vs.* N-meen), clathration of water molecules, as well as different metal cations with the same charge.

Experimental

Materials and methods

All reagents were commercially available and used as received. Elemental analyses were carried out with a Perkin-Elmer 240 elemental analyzer. FTIR spectra were obtained on a Bruker EQUINOX 55 FTIR spectrometer as KBr pellets. TGA was performed using a Netzsch TG 209 analyzer in flowing nitrogen.

Synthesis and characterization

[Cd(N,N′-meen)$_2$](2,6nds) (1). N,N′-meen (0.18 g, 2 mmol) was added with stirring to an aqueous solution of Cd(CH$_3$COO)$_2$·2H$_2$O (0.27 g, 1 mmol). The solution was then treated with Na$_2$(2,6nds) (0.33 g, 1 mmol). Colorless crystals of **1** were collected after 4 days (63% yield based on Cd). Found: C 36.99, H 5.35, N 9.60. $C_{18}H_{30}O_6N_4S_2Cd$ requires C 37.60, H 5.26, N 9.74%. IR (cm^{-1}, KBr): 3374.0(w), 3290.5(s), 3265.2(s), 2976.4(m), 2918.6(m), 2810.1(m), 1581.6(m), 1484.3(m), 1453.1(m), 1421.6(m), 1357.0(m), 1280.1(m), 1237.5(s), 1176.6(s), 1142.8(m), 1084.2(s), 1025.1(s), 921.8(s), 843.0(m), 659.1(s), 617.0(s), 543.9(m).

The same procedure was used to synthesize compounds **2**–**4**, using the corresponding arenedisulfonates.

[Cd(N,N′-meen)$_2$](1,5nds) (2). (80% yield based on Cd) Found: C 36.80, H 5.33, N, 9.54. $C_{18}H_{30}O_6N_4S_2Cd$ requires C 37.60, H 5.26, N 9.74% IR (cm^{-1}, KBr): 3380.0(w), 3284.7(m), 3260.3(s), 2965.5(w), 2885.5(m), 2814.4(w), 1586.4(w), 1484.8(m), 1453.2(m), 1247.0(s), 1218.3(s), 1195.0(s), 1078.1(m), 1029.0(s), 955.6(s), 849.9(m), 816.0(s), 760.8(s), 608.9(s), 563.2(m), 527.7(m).

[Cd(N,N′-meen)$_2$](bpds) (3). (50% yield based on Cd) Found: C 39.52, H 5.49, N 9.17. $C_{20}H_{32}O_6N_4S_2Cd$ requires C 39.97, H 5.37, N 9.32%. IR (cm^{-1}, KBr): 3440.0(w), 3292.0(s), 3270.0(s), 2974.9(m), 2913.0(m), 2859.0(m), 2804.1(m), 1595.5(w), 1478.7(s), 1414.8(m), 1354.0(m), 1238.1(s), 1189.2(s), 1124.4(s), 1067.4(w), 1032.6(s), 995.0(s), 925.7(s), 830.6(s), 718.1(s), 606.2(s), 563.2(s).

[Cd(N-meen)$_2$](2,6nds)·2H$_2$O (4). (71% yield based on Cd) Found: C 32.58, H 5.24, N 9.39. $C_{16}H_{30}O_8N_4S_2Cd$ requires C 32.97, H 5.19, N 9.61%. IR (cm^{-1}, KBr): 3505.3(s), 3473.0(s), 3386.2(m), 3321.1(s), 3258.4(m), 2967.1(w), 2935.6(w), 2881.7(w), 1658.7(m), 1608.6(m), 1479.0(w), 1441.2(w), 1215.5(s), 1190.0(s), 1145.2(m), 1090.9(s), 1033.5(s), 942.0(m), 828.6(m), 665.1(s), 625.4(s), 562.0(m), 523.1(m).

X-Ray crystallography

Experimental details of the X-ray analyses are provided in Table 4. 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[22] and processed by SAINT+.[23] Absorption corrections were applied by SADABS.[24] Space groups of these compounds were determined from systematic absences and further justified by the refinement results. In all cases, the structures were solved by direct methods and refined using full-matrix least-squares/difference Fourier techniques using SHELX.[25,26] 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. The H-atoms of water were located from the difference Fourier map at the final state of refinement.

CCDC reference numbers 162417–162420.

See http://www.rsc.org/suppdata/dt/b1/b102729h/ 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)

References

1 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311.
2 G. F. Swiegers and T. J. Malefetse, *Chem. Rev.*, 2000, **100**, 3483.
3 M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 1998, **37**, 1211.
4 D. Braga, F. Grepioni and G. R. Desiraju, *Acc. Chem. Res.*, 2000, **33**, 601.
5 D. Braga and F. Grepioni, *Chem. Rev.*, 1998, **98**, 1375.
6 J. C. MacDonald, P. C. Dorrestein, M. M. Oilley, M. M. Foote, J. L. Lundburg, R. W. Henning, A. J. Schultz and J. L. Manson, *J. Am. Chem. Soc.*, 2000, **122**, 11692; M. Munakata, L. P. Wu, M. Yamamoto, T. Kuroda-Sowa and M. Maekawa, *J. Am. Chem. Soc.*, 1996, **118**, 3117; A. D. Burrows, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1996, 97; J. C. M. Rivas and L. Brammer, *New J. Chem.*, 1998, **22**, 1315.
7 Y.-B. Dong, M. D. Smith, R. C. Layland and H.-C. Z. Loye, *J. Chem. Soc., Dalton Trans.*, 2000, 775.

8 M.-L. Tong, J. Cai, X.-L. Yu, X.-M. Chen, S. W. Ng and T. C. K. Mak, *Aust. J. Chem.*, 1998, **51**, 637; X.-M. Chen, M.-L. Tong, Y.-J. Luo and Z.-N. Chen, *Aust. J. Chem.*, 1996, **49**, 835; A. J. Blake, S. J. Hill, P. Hubberstey and W. S. Li, *J. Chem Soc., Dalton Trans.*, 1997, 913; L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem Soc., Dalton Trans.*, 1997, 1801.
9 S.-I. Nora, M. Kondo, T. Ishii, S. Kitagawa and H. Matsuzaka, *J. Chem. Soc., Dalton Trans.*, 1999, 1569.
10 J. Cai, C.-H. Chen, C.-Z. Liao, J.-H. Yao, X.-P. Hu and X.-M. Chen, *J. Chem. Soc., Dalton. Trans.*, 2001, 1137.
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 (*a*) C. B. Aakeröy, A. M. Beatty and K. R. Lorimer, *J. Chem. Soc., Dalton Trans.*, 2000, 3869; (*b*) C. B. Aakeröy, A. M. Beatty, D. S. Leinen and K. R. Lorimer, *Chem. Commun.*, 2000, 935; (*c*) M. A. S. Goher and T. C. W. Mak, *Inorg. Chim. Acta*, 1985, **101**, L27.
13 R.-G. Xiong, C.-M. Liu, J.-L. Zuo and X.-Z. You, *Inorg. Chem. Commun.*, 1999, **2**, 292.
14 F. H. Allen and O. Kennard, *Chem. Des. Automat. News*, 1993, **8**, 1; F. H. Allen and O. Kennard, *Chem. Des. Automat. News*, 1993, **8**, 31.
15 N. S. Hüsgen, G. A. Luinstra, F. Schaper and K. Schmidt, *Inorg. Chem.*, 1998, **37**, 3471.
16 M. E. Thompson, *Chem. Mater.*, 1994, **6**, 1168.
17 D. Grohol, F. Ging and A. Clearfield, *Inorg. Chem.*, 1999, **38**, 751 and references therein; 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.
18 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.
19 M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120; J. Bernstein, R. E. Davis, L. Shimoni and N.-L. Chang, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1555.
20 V. A. Russell, C. C. Evans, W. Li and M. D. Ward, *Science*, 1997, **276**, 575; J. A. Swift, A. M. Pivovar, A. M. Reynolds and M. D. Ward, *J. Am. Chem. Soc.*, 1998, **120**, 5887.
21 A. Onoda, Y. Yamada, M. Doi, T.-A. Okamura and N. Ueyama, *Inorg. Chem.*, 2001, **40**, 516.
22 Bruker AXS, SMART, Version 5.0, Bruker AXS, Madison, WI, USA, 1998.
23 Bruker AXS, SAINT+, Version 6.0, Bruker AXS, Madison, WI, USA, 1999.
24 R. Blessing, *Acta Crystallogr., Sect. A*, 1995, **51**, 33.
25 Bruker AXS, SHELXTL, Version 5.1, Bruker AXS, Madison, WI, USA, 1998.
26 G. M. Sheldrick, SHELX97, Program for X-Ray Crystal Structure Solution and Refinement, Göttingen University, Germany, 1997.