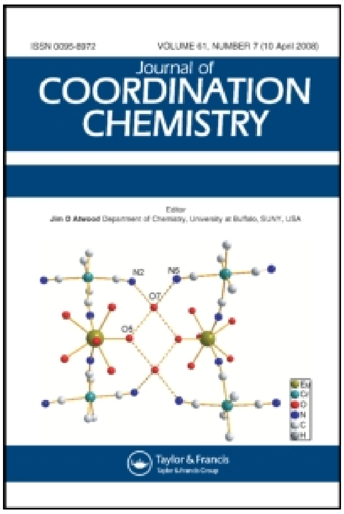

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Hydrogen-bond networks of 1,3-imidazolidine-2-thione: synthesis and structures of complexes of silver(I), copper(I), cadmium(II) and zinc(II)

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Solution reactions of silver(I), copper(I), cadmium(II) and zinc(II) salts with 1,3-imidazolidine-2-thione (imdt) under diverse conditions yielded four complexes: $[Cd(SC_3H_6N_2)_2(Ac)_2]$ (**1**), $[Zn(SC_3H_6N_2)_2(Ac)_2]$ (**2**), $[Cu_2(SC_3H_6N_2)_6]SO_4$ (**3**) and $[Ag_2(SC_3H_6N_2)_6]SO_4$ (**4**). Complexes **1** and **2** are 1D and 2D hydrogen-bond aggregations. Complexes **3** and **4** are isostructural 3D hydrogen-bond networks. The diverse coordination modes of imdt and different anions are the major factors for three distinct hydrogen-bond structures.

Keywords: 1,3-Imidazolidine-2-thione; Hydrogen-bond networks; Structure

1. Introduction

Organosulfur compounds in chemical processes has been extensively studied for many years [1] with current attention directed to heterocyclic thioamides, due to their similarity to many biological molecules [2]. For instance, Methimazole is the most commonly employed drug for treating hyperthyroidism [3]. Heterocyclic thioamide ligands and their heteroleptic phosphine derivatives are used as effective antiarthritic and antitumor drugs.

1,3-Imidazolidine-2-thione (imdt) is one of the simplest prototypes of heterocyclic thioamides with complexes such as $[Au(imdt)_2]Cl \cdot H_2O$ reported as early as 1928 [4]. Recently, imdt was found to induce DNA damage to the liver, lungs, spleen, and kidneys in mice [5]. Our interests are mainly on neutral imdt for two reasons. First, the exocyclic sulfur is capable of coordinating metals via η_1-S [6], μ_2-S [7], μ_3-S [8] and μ_4-S [9] bonding modes (chart 1). This versatility of imdt is attributed to the large size of the S atom. Secondly, the C=S bond can attach to a metal center at a variety of angles to form helix or nonplanar structures for different configurations [10].

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Furthermore, the endocyclic N–H moieties are capable of forming hydrogen-bonded aggregations [11, 12].

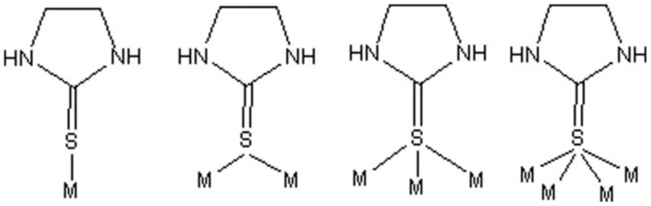

Chart 1. Four different coordination modes for S of imdt.

Herein, we report a systematic study of the reaction of imdt with transition metal ions. By changing the experimental conditions, four supramolecular complexes with 1D, 2D and 3D hydrogen-bond networks are obtained. Noticeably, in these complexes metal only coordinates to S of imdt ligand. The versatility of S is the key to the four different structures.

2. Experimental

2.1. *Materials and instrumentation*

Reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with a Vario EL elemental analyzer. The FT–IR spectra were recorded from KBr pellets in the range 400–4000 $\mathrm{cm^{-1}}$ on a Bruker-EQUINOX 55 FT–IR spectrometer. Thermogravimetric (TG) data were collected on a Netzsch TG-209 analyzer in nitrogen at a heating rate of 10°C $\mathrm{min^{-1}}$.

2.2. *Synthesis of [Cd(imdt)$_2$(Ac)$_2$] (1)*

A mixture of $Cd(Ac)_2 \cdot 2H_2O$ (0.1333 g, 0.5 mmol) (Ac = acetate) and imdt (0.1022 g, 1 mmol) was placed into a test tube containing ethanol (10 mL). Then the test tube was placed into a glass bottle containing ethanol (10 mL) and Et_3N (3 mL). The bottle was sealed and kept at −2°C in a refrigerator for one month to yield colorless crystals of **1**. The crystals were collected by filtration and dried at room temperature (Yield: 70% on the basis of cadmium). Anal. Calcd ($C_{10}H_{18}CdN_4O_4S_2$): N, 12.9; C, 27.6; H, 4.17. Found: N, 12.5; C, 27.9; H, 4.14%. FT–IR (KBr, $\mathrm{cm^{-1}}$): υ(C–S) 1089s, 910m, υ(N–H) 3176m, υ(C–N) 1540s.

2.3. *Synthesis of [Zn(imdt)$_2$(Ac)$_2$] (2)*

Complex **2** was prepared in the same way as for **1** using $Zn(Ac)_2 \cdot 2H_2O$ (0.1098 g, 0.5 mmol) in place of $Cd(Ac)_2 \cdot 2H_2O$. The resulting solution yielded colorless crystals of **2** (Yield: 72% on the basis of zinc). Anal. Calcd ($C_{10}H_{18}ZnN_4O_4S_2$): N, 14.4; C, 31.0; H, 4.68. Found: N, 14.2; C, 31.3; H, 4.71%. FT–IR (KBr, $\mathrm{cm^{-1}}$): υ(C–S) 1090s, 910m, υ(N–H) 3184m, υ(C–N) 1523s.

Table 1. Crystal and structure refinement data for **1**–**4**.

	1	**2**	**3**	**4**
Formula	$C_{10}H_{18}N_4O_4S_2Cd$	$C_{10}H_{18}N_4O_4S_2Zn$	$C_{18}H_{36}N_{12}O_4S_7Cu_2$	$C_{18}H_{36}N_{12}O_4S_7Ag_2$
Formula weight	434.83	387.48	836.18	924.82
Crystal system	Monoclinic	Orthorhombic	Trigonal	Trigonal
Space group	Cc	*Pbcn*	*R3c*	*R3c*
Unit cell dimensions (Å, °)				
a	12.440(3)	9.408(5)	12.7509(8)	12.967(3)
b	9.2702(19)	12.548(6)	12.7509(8)	12.967(3)
c	14.065(3)	13.577(7)	35.747(7)	35.37(2)
α	90	90	90	90
β	90.42(3)	90	90	90
γ	90	90	120	120
V (Å^3)	1622.0(6)	1602.6(14)	5033.3(11)	5150(3)
Z	10	10	6	6
D_{Calcd} (Mg m^{-3})	2.36	1.902	1.655	1.789
Reflections collected	4835	9156	7838	9973
Reflections unique	3058	2010	1953	2586
R_1^a	0.0345	0.0288	0.0284	0.0285
wR_2^a	0.0969	0.0969	0.0746	0.0638

${}^{a}R_1 = \Sigma\|F_o| - |F_c\|/|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

2.4. *Synthesis of [Cu_2(imdt)$_6$]SO_4 (3) [13]*

A mixture of $Cu(Ac)_2 \cdot H_2O$ (0.1000 g, 0.5 mmol), imdt (1 mmol, 0.1022 g) and ethanol (10 mL) was sealed in a teflon-lined autoclave and heated at 90°C for 3 days, followed by slow cooling to room temperature. The resulting brown, block crystals of **3** were obtained and washed with ethanol (Yield: 33% on the basis of copper). Anal. Calcd ($C_{18}H_{36}Cu_2N_{12}O_4S_7$): C, 25.86; N, 20.11; H, 4.34. Found: C, 25.28; N, 20.63; H, 4.13%. FT–IR (KBr, cm^{-1}): υ(C–S) 1095s, 910m, υ(N–H) 3230m, υ(C–N) 1602s.

2.5. *Synthesis of [Ag_2(imdt)$_6$]SO_4 (4)*

A mixture of AgBr (0.0939 g, 0.5 mmol) and imdt (0.1022 g, 1 mmol) was placed into a test tube containing DEF (*N*,*N*-diethylformamide, 8 mL). The test tube was placed into a glass bottle containing Et_3N (10 mL). The bottle was sealed and kept at −2°C in a refrigerator for one month yielding colorless crystals of **4** (Yield: 8% on the basis of silver). The crystals were collected by filtration and dried at room temperature. Anal. Calcd ($C_{18}H_{36}Ag_2N_{12}O_4S_7$): C, 23.38; N, 18.18; H, 3.92. Found: C, 22.76; N, 18.85; H, 3.67%. FT–IR (KBr, cm^{-1}): υ(C–S) 1085s, υ(N–H) 3225m, υ(C–N) 1592s.

2.6. *X-ray crystallography*

Diffraction data for **1**–**4** were collected on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied using SADABS [14]. Structures were solved by direct methods and refined with a full-matrix least-squares technique using SHELXS-97 and SHELXL-97 [15]. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically

Table 2. Selected bond lengths (Å) and angles (°) for **1**–**4**.

1			
Cd1–O2	2.191(12)	O(1)–Cd(1)–S(3)	122.0(3)
Cd1–O3	2.180(12)	O(2)–Cd(1)–S(2)	125.3(3)
Cd1–S2	2.507(4)	O(1)–Cd(1)–S(2)	98.3(3)
Cd1–S3	2.523(5)	S(3)–Cd(1)–S(2)	117.19(5)
S(2)–C(6)	1.782(10)	C(6)–S(2)–Cd(1)	94.8(5)
S(3)–C(3)	1.772(16)	C(3)–S(3)–Cd(1)	92.6(5)
O(2)–Cd(1)–O(1)	96.96(15)	C(9)–O(2)–Cd(1)	114.6(9)
O(2)–Cd(1)–S(3)	97.3(4)	C(10)–O(1)–Cd(1)	114.0(10)
2[a]			
Zn(1)–S(1)#1	2.3380(9)	O(2)–Zn(1)–S(1)	104.86(5)
Zn(1)–S(1)	2.3380(8)	O(2)#1–Zn(1)–S(1)#1	104.86(5)
Zn(1)–O(2)	1.9641(15)	O(2)–Zn(1)–S(1)#1	113.90(6)
Zn(1)–O(2)#1	1.9641(15)	S(1)–Zn(1)–S(1)#1	103.20(4)
S(1)–C(5)	1.709(2)	C(5)–S(1)–Zn(1)	102.33(7)
O(2)#1–Zn(1)–O(2)	115.63(9)	C(4)–O(2)–Zn(1)	118.32(13)
O(2)#1–Zn(1)–S(1)	113.90(6)		
3[b]			
Cu(1)–S(2)	2.2715(9)	Cu(2)–S(3)	2.2494(11)
Cu(1)–S(2)#1	2.2715(9)	Cu(2)–S(3)#3	2.2494(11)
Cu(1)–S(2)#2	2.2715(9)	Cu(2)–S(3)#4	2.2494(11)
S(3)–C(1)	1.714(4)	S(3)#3–Cu(2)–S(3)#4	119.999(1)
S(2)#2–Cu(1)–S(2)#1	119.704(7)	S(3)#3–Cu(2)–S(3)	119.999(1)
S(2)#2–Cu(1)–S(2)	119.703(7)	S(3)#3–Cu(2)–S(3)	119.999(1)
S(2)#1–Cu(1)–S(2)	119.704(7)		
4[c]			
Ag(1)–S(1)#1	2.5045(11)	S(1)#1–Ag(1)–S(1)	119.885(4)
Ag(1)–S(1)#2	2.5045(11)	S(1)#2–Ag(1)–S(1)	119.885(4)
Ag(1)–S(1)	2.5045(11)	S(2)–Ag(2)–S(2)#3	119.888(4)
Ag(2)–S(2)	2.4657(12)	S(2)–Ag(2)–S(2)#4	119.888(4)
Ag(2)–S(2)#3	2.4657(13)	S(2)#3–Ag(2)–S(2)#4	119.888(4)
Ag(2)–S(2)#4	2.4657(12)	C(1)–S(1)–Ag(1)	103.12(12)
S(1)–C(1)	1.705(4)	C(4)–S(2)–Ag(2)	105.86(12)
S(1)#1–Ag(1)–S(1)#2	119.885(4)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z+1/2$.

[b] Symmetry codes: #1 $-x+y+1, -x+1, z$; #2 $-y+1, x-y, z$; #3 $-y, x-y, z$; #4 $-x+y, -x, z$.

[c] Symmetry transformations used to generate equivalent atoms: #1 $-y+2, x-y, z$; #2 $-x+y+2, -x+2, z$; #3 $-x+y+3, -x+3, z$; #4 $-y+3, x-y, z$.

(C–H 0.96 Å and N–H 0.86 Å). Crystal data as well as details of data collection and refinement for the complexes are summarized in table 1. Selected bond lengths and angles are listed in table 2. The hydrogen bonding parameters are shown in table 3.

3. Results and discussion

3.1. *Crystal structures*

3.1.1. [Cd(imdt)$_2$(Ac)$_2$] (1) and [Zn(imdt)$_2$(Ac)$_2$] (2). X-ray analysis shows that the two compounds are both isolated clusters connected by hydrogen bonds to form aggregations. Metal ions in **1** and **2** are in the same coordination environment. Each Cd(II) or Zn(II) is situated in a distorted tetrahedral configuration, coordinating

Table 3. Hydrogen bonding interactions in **1**, **2**, **3** and **4** (Å, °).

1[a]				
D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N(4)–H(4A)···O(4)#1	0.86	2.35	3.21(2)	174.7
N(3)–H(3A)···O(4)	0.86	2.25	3.11(2)	177.2
N(1)–H(1A)···O(3)	0.86	2.2	3.06(4)	178.9
2[b]				
D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N(2)–H(2A)···O(1)#1	0.86	2.05(6)	2.91(6)	178.04
N(1)–H(1A)···O(1)#2	0.86	1.98(9)	2.84(5)	173.51
3				
D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N(1)–H(1A)···O(2)	0.88	1.92	2.795(4)	172
N(4)–H(4A)···O(2)	0.88	2.01	2.846(4)	157.9
N(3)–H(3C)···O(1)	0.88	2.25	3.003(4)	143.6
4				
D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N(1)–H(4A)···O(2)	0.86	1.94	2.795(6)	177.3
N(4)–H(1A)···O(2)	0.86	2.05	2.863(4)	164.7
N(3)–H(2C)···O(1)	0.86	2.28	3.049(4)	157.4

[a] Symmetry codes for 1: #1 $x, -y+1, z+1/2$.

[b] Symmetry codes for 2: #1 $-x, y, -z+1/2$; #2 $x+1/2, y+1/2, -z+1/2$.

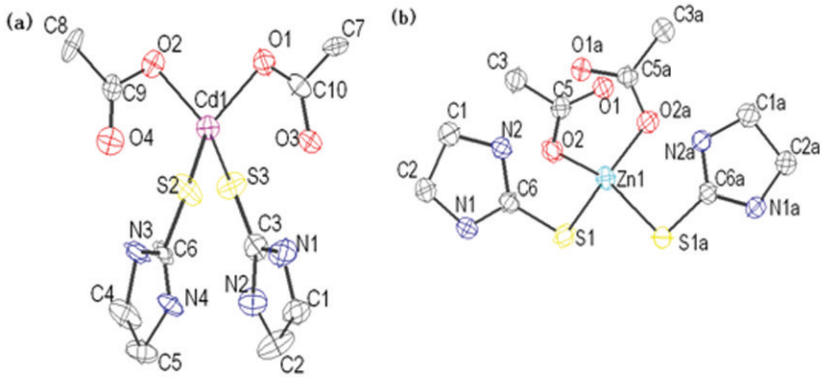

Figure 1. (a) Molecular structure of **1** with thermal ellipsoids at 50% probability. (b) Molecular structure of **2** with thermal ellipsoids at 50% probability.

two S atoms from two monodentate imdt molecules and two O atoms of two acetate molecules (figure 1).

The two complexes, which are somewhat structurally analogous, can be easily distinguished by bond lengths and angles. In **1**, the bond lengths of Cd–S and Cd–O vary from 2.586(5) Å to 2.174(1) Å. But in **2**, Zn–S and Zn–O lengths from 2.338(1) Å to 1.964(1) Å are shorter. O1–Cd–O2 angle in **1** is smaller than O1–Zn–O1a angle in **2** (96.96(42)° in **1** and 115.63(6)° in **2**), but S2–Cd–S3 angle in **1** is larger than S1–Zn–S1a angle in **2** (123.69(30)° in **1** and 103.21(2)° in **2**).

There are two kinds of hydrogen bonds in **1** and **2**, both attributed to the uncoordinated O atoms of acetate anions and protonated amino groups of imdt ligands, which act as hydrogen accepter and donor, respectively. Complex **1** is a 1D

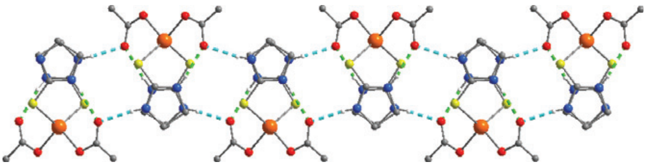

Figure 2. View of the hydrogen-bond 1D chain of **1** down the c axis (online: orange, Cd; red, O; blue, N; yellow, S; gray, C).

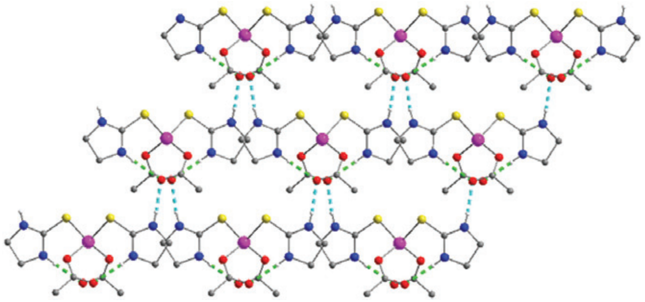

Figure 3. View of the hydrogen-bond 2D network of **2** down the *b* axis (online: purple, Zn; red, O; blue, N; yellow, S; gray, C). Intramolecular and intermolecular hydrogen bonds are illustrated in green and cyan dot-bond, respectively.

hydrogen-bond zigzag chain running along the *c* axis (figure 2). Every two adjacent Cd clusters are connected by a pair of parallel intramolecular N–H···O bonds (average 2.915(17) Å). Inside the cluster, two uncoordinated O atoms of acetate form two intermolecular N–H···O bonds (average 2.958(17) Å) with two protonated N atoms from imdt. Complex **2** is a 2D aggregation expanded along ***a*** and ***c*** axes (figure 3). Every Zn cluster links to four neighboring ones with four intermolecular N–H···O bonds (2.845(3) Å). Because the two moieties of the Zn cluster are symmetric, intramolecular N–H···O bonds of **2** are equal at 2.916(2) Å. The intramolecular and intermolecular hydrogen bonds stabilize the two aggregations. In **2**, the hydrogen bonding interactions appear to be more significant, somewhat stronger than those in **1**. Comparable N–H···O distances are found in $[Ag(imdt)_2]ClO_4$ [16]. This 2D supramolecular structure is a result of a dense H-bonded network.

3.1.2. $[Cu_2(imdt)_6]SO_4$ (3) and $[Ag_2(imdt)_6]SO_4$ (4). X-ray analysis showed that **3** and **4** are isostructural, consisting of isolated $[M(imdt)_3]^+$ (M = AgI, CuI) cations and SO_4^{2-} anions (figure 4). The presence of Cu(I) in **3** was established by bond valence sum (BVS) calculation [17]. Interestingly, SO_4^{2-} anions are not included in starting materials, but derived from oxidation of S of imdt ligands. The S=C bond is not stable at high temperature nor in low-temperature DEF solvent. Copper(II) is the likely oxidizing agent to make **3**, while ambient oxygen or the DEF solvent is the oxidizing agent in formation of **4**. Metal ions are situated in a triangular plane of MS_3 configuration [18], and S–M–S angles are nearly 120°. The three S are from three imdt ligands, with two kinds of S–Cu bonds in **3** with bond lengths of 2.271(5) Å and 2.249(1) Å. Similarly, in **4**, two S–Ag bonds are 2.504(1) Å and 2.466(1) Å.

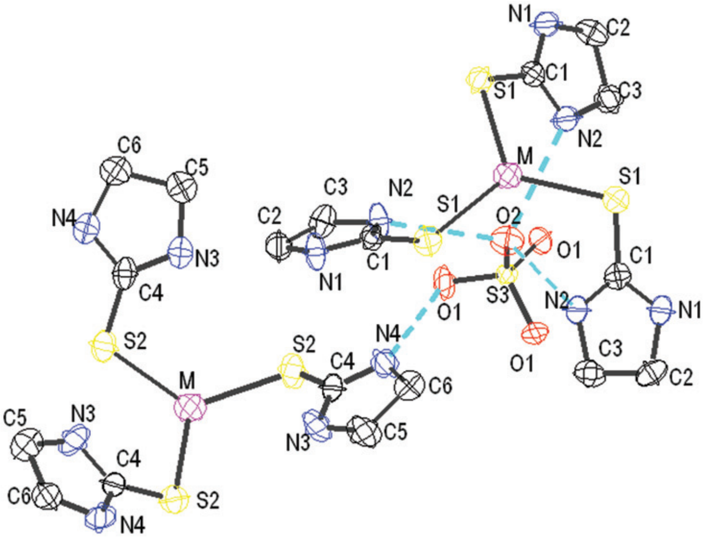

Figure 4. ORTEP representation of the isostructural **3** and **4** (M = CuI or AgI). Hydrogen bonds are emphasized in cyan online.

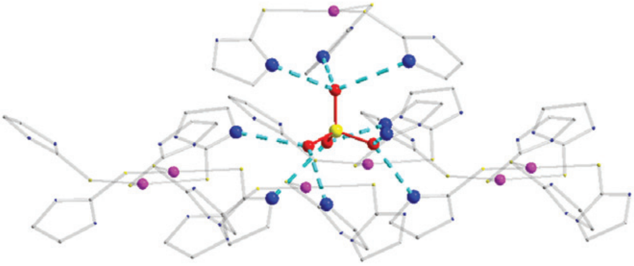

Figure 5. Hydrogen bond environment of SO_4^{2-} in **4**.

To discuss this structure in detail, we take **4** as an example. Every SO_4^{2-} anion is encapsulated in a hexagonal-based pyramid, with six $[Ag(imdt)_3]^+$ units at the bottom forming a hexagon and one $[Ag(imdt)_3]^+$ at the top. The O2 atoms of SO_4^{2-} connect three N atoms of one $[Ag(imdt)_3]^+$ on the top forming three N–H $\cdots$ O bonds (3.049(4) Å) perpendicular to the plane of the hexagon. The three O1 atoms connect two N atoms of two $[Ag(imdt)_3]^+$ at the bottom, with N–H $\cdots$ O bond lengths of 2.863(5) Å and 2.795(6) Å (figure 4, figure 5). One layer of $[Ag(imdt)_3]^+$ and one layer of SO_4^{2-} alternately stack to expand the 3D structure cemented by N–H $\cdots$ O bonds (figure 6). The distance between two $[Ag(imdt)_3]^+$ layers is 5.899(1) Å.

3.2. *Thermogravimetry*

Thermal analyses were performed on **1**, **2** and **3**. For **4**, due to the very low yields, thermal analysis was not carried out. Figure 7 shows the TGA data of **1** and **2**. For **1**, weight loss starts at ca 148–220°C to give loss of ca 27.6%, corresponding to loss of one

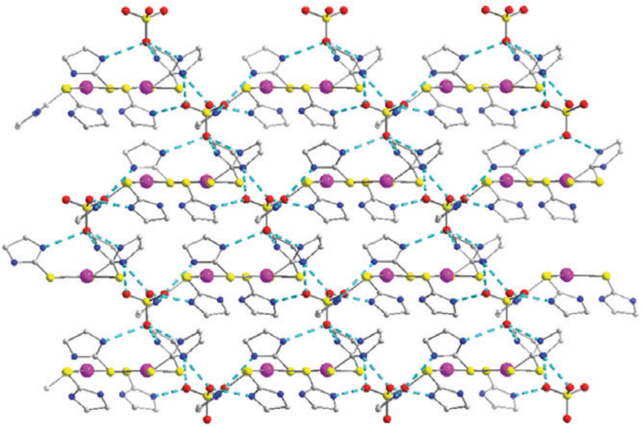

Figure 6. View of hydrogen-bond 3D network of **4** down the *c* axis (online: purple, Ag; red, O; blue, N; yellow, S; gray, C). Hydrogen bonds are emphasized in cyan.

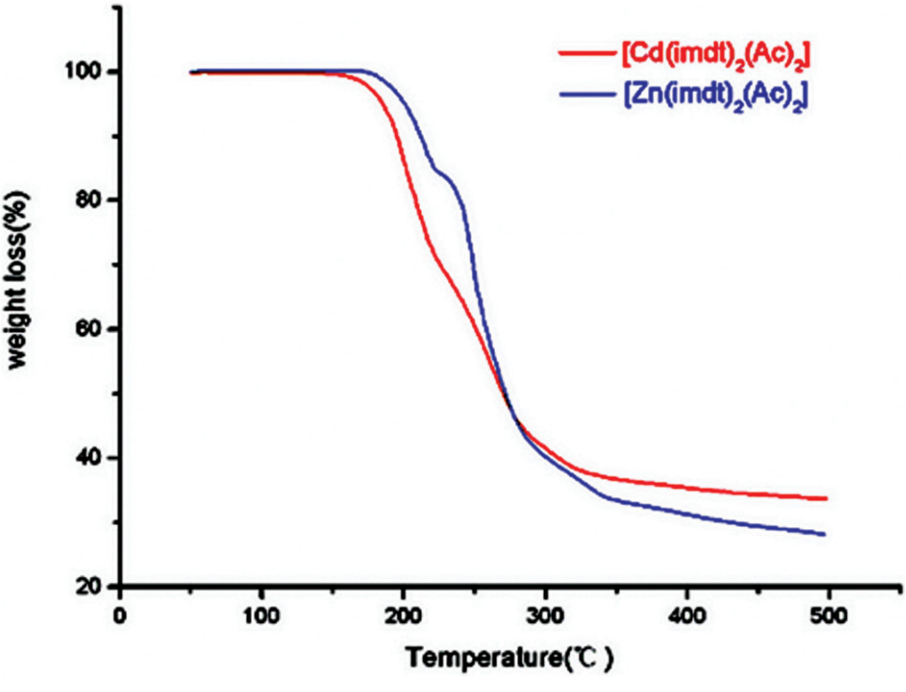

Figure 7. TGA curves of **1** (red) and **2** (blue) (color online only).

imdt molecule per formula unit. Another imdt and one acetate anion removal starts at ca 220–345°C to give loss of ca 35.5%. The final pyrolysis was completed at 345°C, giving $CdCO_3$ powder. For **2**, the TGA curve indicates two obvious weight losses, the first at ca 173–220°C to give loss of ca 15.92%, corresponding to loss of one acetate per formula unit. The second from ca 220–381°C gives a loss of ca 52%, corresponding to loss of two imdt molecules per formula unit, confirming that the hydrogen-bond

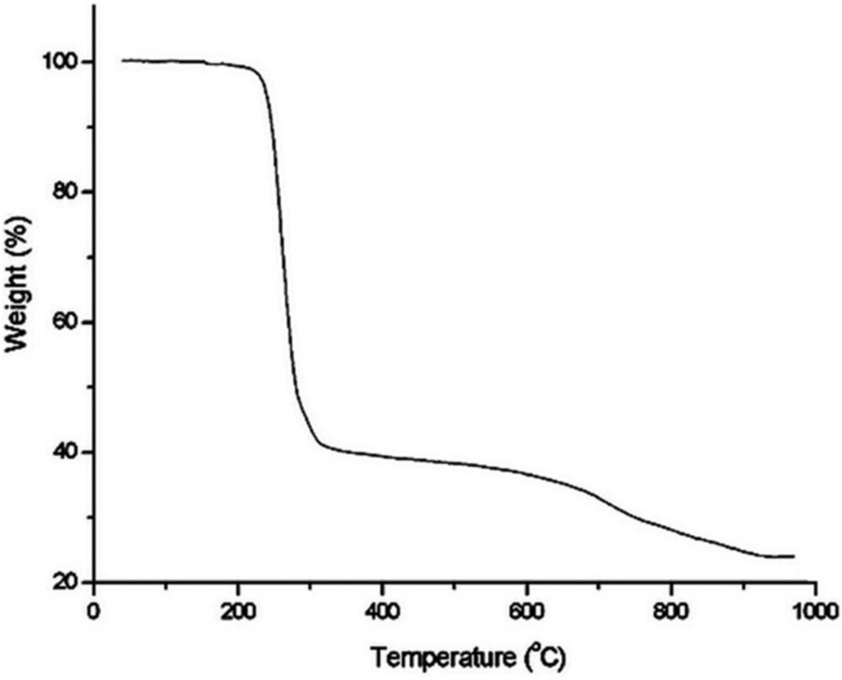

Figure 8. TGA curves of **3**.

aggregation of **2** is more stable. The final pyrolysis was completed at 381°C, giving $ZnCO_3$. The TGA curve of **3** (figure 8) shows weight loss starting at ca 246–293°C to give a total loss of ca 59.93%, corresponding to loss of imdt.

4. Conclusion

By changing reaction conditions and using different metal ions with imdt, we obtained supermolecular hydrogen-bonded networks of 1D (**1**), 2D (**2**) and 3D (**3** and **4**). Complexes **1** and **2** are similar in coordination environment, but the different metal ions (Cd^{II} in **1** and Zn^{II} in **2**) directly influence the degree of distortion from a tetrahedral configuration, making the hydrogen-bond system distinct. Complexes **3** and **4** are isostructural with trigonal planar coordination of Cu(I) and Ag(I), and the only difference in the structures is in the bond lengths with **3** just a ‘zoomed-out’ version of **4**.

Supplementary material

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Center as deposition no. CCDC 605501, 605502, 609373 and 609374. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 lEZ UK (Fax: +44-1223-336 033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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