

# Hydrothermal syntheses and single crystal structural characterization of $M(H_2O)_6(OPTA)_2$ [ $M = Co(II), Ni(II), Zn(II)$ ; $OPTA = 1\text{-oxopyridinium-2-thioacetato}$ ]

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**Abstract.** A new class of compounds of the family  $M(H_2O)_6(OPTA)_2$  (where  $M = Co(II), Ni(II),$  and  $Zn(II)$ ;  $OPTA = 1\text{-oxopyridinium-2-thioacetato}$ ) was prepared from the appropriate metal acetates, 1-oxopyridinium-2-thioacetic acid (OPTAH), and potassium hydroxide in hydrothermal media and structurally characterized. The structure is constructed from  $M(H_2O)_6^{2+}$  and two anions of OPTAH ( $C_7H_6NO_3S$ ) linked through hydrogen bonding into an extended network.

**Keywords.** Hydrothermal; ionic crystals; cobalt; nickel; zinc; 1-oxopyridinium-2-thioacetato.

## 1. Introduction

Hydrothermal methods<sup>1</sup> have been employed to obtain new materials, viz. microporous crystals,<sup>2–6</sup> phosphates,<sup>7–12</sup> complex oxide ceramics,<sup>13–15</sup> and luminescent materials,<sup>16,17</sup> with novel structures and interesting properties. In addition, hydrothermal synthesis finds an important role in guest exchange,<sup>18,19</sup> selective catalytic activity,<sup>20,21</sup> study of origin of life,<sup>22–24</sup> and environmental protection.<sup>25</sup>

Compounds containing N-oxides and sulphur possess important biological activity.<sup>26,27</sup> N-Hydroxypyridine-2-thione behaves as a source of  $\bullet OH$  radical upon irradiation<sup>28</sup>. Further, compounds containing sulphur, such as 2-mercaptopyridine, 2-mercaptopyridine-N-oxide, 2,2'-dithiodipyridine-1,1'-dioxide and related derivatives, as well as their metal complexes exhibit numerous biochemical applications.<sup>29–31</sup> 1-Oxopyridinium-2-thioacetic acid (OPTAH) has been known<sup>32</sup> for several years. However, its coordination chemistry remains relatively unexplored. Thus, we wanted to investigate the coordination ability of this N-oxide that contains N–O, C–S–C and –COOH as the donor entities, which could form stable chelates with various ions. Frequently, more

complex macrostructures can be attained by the incorporation of organic components to yield composite inorganic–organic hybrid materials providing a powerful synthetic approach. Herein, we report the syntheses and structural characterization of three compounds with the structure  $M(H_2O)_6(OPTA)_2$  [where  $M = Co(II), Ni(II), Zn(II)$ ;  $OPTA = 1\text{-oxopyridinium-2-thioacetato}$ ].

## 2. Experimental

### 2.1 Syntheses of complexes $M(H_2O)_6(OPTA)_2$ ( $M = Co, Ni, Zn$ ) (1–3)

N-Hydroxypyridine-2-thione sodium salt was obtained from E-Merck and used as received. Chloroacetic acid, cobalt acetate.4H<sub>2</sub>O, nickel acetate.4H<sub>2</sub>O, and zinc acetate.2H<sub>2</sub>O were of AR grade, purchased from Acros. Deionized water was used as the solvent. Infrared (IR) spectra were recorded on a Jasco FT-IR 410 spectrometer. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo Star<sup>c</sup>-850 system. Elemental analysis was obtained using Elementar Vario EL III Carlo Erba 1108.

In the general procedure for the preparation of complexes 1–3, the reagents were homogenized prior to being sealed in a 23 ml polyfluoroethylene-

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**Table 1.** Experimental details.

Millimolar ratio of reagents M(OAc) <sub>2</sub> : OPTAH : KOH : H <sub>2</sub> O	Time (h)	Product	Colour of the product	Yield (%)
0.123 : 0.248 : 0.250 : 138	72	<b>1</b>	Pink	82
0.123 : 0.248 : 0.250 : 138	72	<b>2</b>	Green	80
0.123 : 0.248 : 0.250 : 111	36	<b>3</b>	Colourless	84

lined stainless steel bomb. After heating in a programmable oven at the respective temperatures and autogenous pressures for the notified time scale, cooling was carried out on a ramp of 10°C/h to room temperature. The crystals were collected by filtration, washed with, deionized water followed by diethyl-ether and then air-dried. Table 1 gives the experimental details.

For **1**: m.p. 182°C (uncorrected). Anal. Calc. for C<sub>14</sub>H<sub>24</sub>N<sub>2</sub>O<sub>12</sub>S<sub>2</sub>Co: C, 31.29; H, 4.88; N, 5.21; S, 11.93%; Found: C, 32.04; H, 4.39; N, 5.60; S, 11.83%.

For **2**: m.p. 239°C (uncorrected). Anal. Calc. for C<sub>14</sub>H<sub>24</sub>N<sub>2</sub>O<sub>12</sub>S<sub>2</sub>Ni: C, 31.30; H, 4.88; N, 5.22; S, 11.94%; Found: C, 32.15; H, 4.41; N, 5.68; S, 12.14%.

For **3**: m.p. 239°C (uncorrected). Anal. Calc. for C<sub>14</sub>H<sub>24</sub>N<sub>2</sub>O<sub>12</sub>S<sub>2</sub>Zn: C, 30.92; H, 4.82; N, 5.15; S, 11.79%; Found: C, 31.24; H, 4.48; N, 5.31; S, 12.21%.

For **1–3**: Selected FT IR data (KBr, cm<sup>-1</sup>): 3440 (broad, OH<sub>str</sub>), 3076 (aromatic C–H), 2939 (aliphatic C–H), 1096 (*ν*<sub>N–O</sub>), and 826 (*d*<sub>N–O</sub>). Non-coordination of the ligand (OPTA) to the metal centres leads to similar stretching vibrations in these complexes.

### 3. Results and discussion

The structure of M(H<sub>2</sub>O)<sub>6</sub>(OPTA)<sub>2</sub> represents a simple ionic salt of M(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> and (OPTA)<sub>2</sub><sup>2-</sup>. There are no apparent bondings between these ions except simple electrostatic interactions. The free ligand (OPTAH) exhibits an IR absorption at 833 cm<sup>-1</sup> for *d*<sub>N–O</sub><sup>33</sup>. Nevertheless, a considerable change in *d*<sub>N–O</sub> (826 cm<sup>-1</sup>) for the three complexes indicates the involvement of this mode of vibration in the hydrogen bonding. As the ligand is not directly bonded to the metal ion, there are no significant variations among the *d*<sub>N–O</sub> of these three complexes.

Thermogravimetric analysis (TGA) was carried out under an inert atmosphere of dry nitrogen from room temperature to 1000°C. For all the three complexes, the first stage of the decomposition (100–180°C) corresponds to the loss of six coordinated water molecules. Whereas the cobalt complex (**1**)

loses two units of OPTA (≈210–220°C), the nickel and the zinc complexes (**2**) and (**3**) eliminate just a single unit of OPTA (≈240–260°C) in the second stage. The third stage is presumed to involve further decomposition leading to the formation of oxides and/or sulphides of cobalt, nickel, and zinc. Saturation temperature above which there is no obvious weight loss for the cobalt complex (**1**) occurs at ≈350°C, for the nickel complex (**2**) at ≈850°C; and for the zinc complex (**3**) at ≈500°C.

### 4. Experimental details of crystallography

Single crystals suitable for X-ray crystallographic measurements of (**1**) (pink, 0.40 × 0.20 × 0.20 mm), (**2**) (green, 0.20 × 0.20 × 0.20 mm), and (**3**) (colourless, 0.20 × 0.20 × 0.10 mm) were studied with a Bruker-AXS SMART APEX/CCD diffractometer, using Mo-K $\alpha$  radiation ( $I = 0.7107 \text{ \AA}$ ). Diffracted data were corrected for Lorentz and polarization effects and for absorption using the SADABS program.<sup>34</sup> The structure was solved by direct methods and the structure solution and refinement were based on  $I/I^2$ . All non-hydrogen atoms were refined with anisotropic displacement parameters whereas hydrogen atoms were placed in calculated positions, and given isotropic U values 1.2 times that of the atom to which they are bonded. To solve the structure, all crystallographic calculations were performed using the SHELXTL package.<sup>35</sup> A summary of the crystallographic data and structure refinements are listed in table 2.

### 5. Description of the complexes

The complexes M(H<sub>2</sub>O)<sub>6</sub>(OPTA)<sub>2</sub> crystallized in the centrosymmetric space group  $P2_1/c$  with half a molecule in the asymmetric unit. In hexaaquabis(1-oxopyridinium-2-thioacetato)metal(II), the metal cation is coordinated by six aqua ligands and associated with two 1-oxopyridinium-2-thioacetato ions through hydrogen bonds. Six water molecules are nearly octa-

**Table 2.** Crystal data and structure refinement for **1–3**.

Empirical formula	C <sub>14</sub> H <sub>24</sub> CoN <sub>2</sub> O <sub>12</sub> S <sub>2</sub> ( <b>1</b> )	C <sub>14</sub> H <sub>24</sub> NiN <sub>2</sub> O <sub>12</sub> S <sub>2</sub> ( <b>2</b> )	C <sub>14</sub> H <sub>24</sub> ZnN <sub>2</sub> O <sub>12</sub> S <sub>2</sub> ( <b>3</b> )
Formula weight	535.40	535.18	541.84
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P2(1)/c</i>	<i>P2(1)/c</i>	<i>P2(1)/c</i>
Temperature (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
<i>a</i> (Å)	7.2341(7)	7.2179(6)	7.2447(6)
<i>b</i> (Å)	6.9835(7)	6.9846(6)	6.9966(6)
<i>c</i> (Å)	20.431(2)	20.4230(16)	20.4352(16)
<i>a</i> (°)	90	90	90
<i>b</i> (°)	98.635(2)	98.8020(10)	98.7950(10)
<i>g</i> (°)	90	90	90
Volume (Å <sup>3</sup> )	1020.44(18)	1017.48(15)	1023.65(15)
<i>Z</i>	2	2	2
Density (calculated) (Mg/m <sup>3</sup> )	1.742	1.747	1.758
<i>F</i> (000)	554	556	560
Crystal size (mm <sup>3</sup> )	0.40 × 0.20 × 0.20	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.10
Theta range for data collection (°)	2.85 to 28.30	2.02 to 28.25	2.02 to 28.28
Index ranges	−5 < = <i>h</i> < = 9, −9 < = <i>k</i> < = 9, −26 < = <i>l</i> < = 26	−8 < = <i>h</i> < = 9, −9 < = <i>k</i> < = 7, −26 < = <i>l</i> < = 18	−9 < = <i>h</i> < = 9, −9 < = <i>k</i> < = 9, −26 < = <i>l</i> < = 17
Reflections collected	6298	5923	6175
Independent collections	2401	2382	2412
	[ <i>R</i> (int) = 0.0205]	[ <i>R</i> (int) = 0.0254]	[ <i>R</i> (int) = 0.0249]
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least- squares on <i>F</i> <sup>2</sup>
Data/restraint/parameters	2401/0/190	2382/0/190	2412/0/190
GOF on <i>F</i> <sup>2</sup>	1.058	1.056	1.052
Final <i>R</i> indices [ <i>I</i> > 2 <i>s</i> ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0254, <i>wR</i> <sub>2</sub> = 0.0651	<i>R</i> <sub>1</sub> = 0.0277, <i>WR</i> <sub>2</sub> = 0.0691	<i>R</i> <sub>1</sub> = 0.0276, <i>wR</i> <sub>2</sub> = 0.0717
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0267, <i>wR</i> <sub>2</sub> = 0.0658	<i>R</i> <sub>1</sub> = 0.0313, <i>wR</i> <sub>2</sub> = 0.0710	<i>R</i> <sub>1</sub> = 0.0296, <i>wR</i> <sub>2</sub> = 0.0730
Largest diff. peak and hole ( <i>e</i> Å <sup>−3</sup> )	0.335 and −0.348	0.468 and −0.347	0.472 and −0.328
Absorption correction	None	None	None
Maximum transmission	1.000	1.000	1.000
Minimum transmission	0.670	0.843	0.866

hedrally coordinated to the Co(II), Ni(II), and Zn(II) ions. The metal cation sits on a crystallographic centre of inversion that bridges the water molecules. The two organic anions form a non-bonded one-dimensional chain with the hexaaquametal moieties, mediated by a hydrogen bonded self-recognition interaction. Thus, the organic component serves both as a charge balancing counterion and a chemical spacer that participates in extensive hydrogen bonding. Stable [M(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> octahedral cations in several Co(II),<sup>36</sup> Ni(II),<sup>36</sup> Zn(II)<sup>37</sup> systems have been reported. From X-ray crystallographic analysis, we found that the structures of **1**, **2**, and **3** are isomorphic. Deviation from ideal octahedral coordination from the observed geometry (close to 90° or 180°) seems to be an

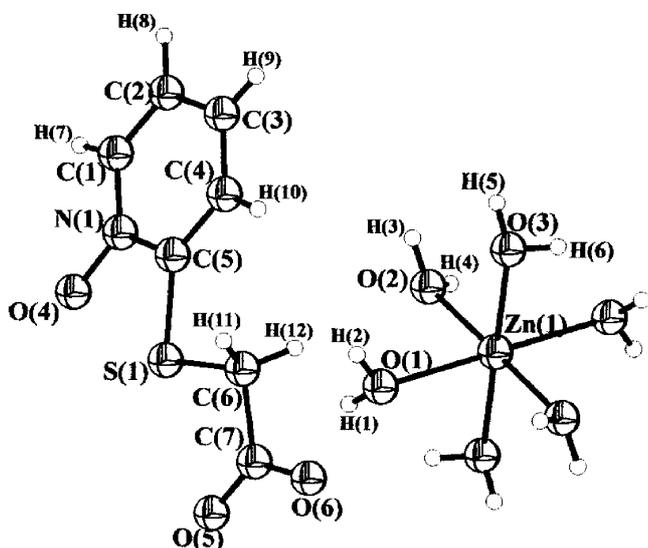
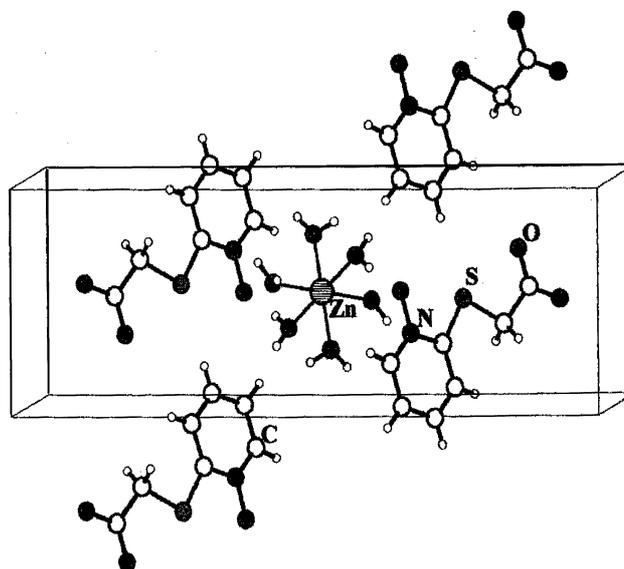
essential requirement to form better hydrogen bonds between coordinated water molecules and the ligand.<sup>38</sup> An ORTEP diagram of **3** is shown in figure 1 and the packing diagram is given in figure 2.

Selected bond lengths and bond angles of **1**, **2**, and **3** are given in table 3. The M–O<sub>w</sub> distances are 2.122–2.082 Å for **1**, 2.068–2.053 Å for **2**, and 2.081–2.103 Å for **3** respectively. These values agree well with the reported<sup>39</sup> M–O<sub>w</sub> distances in similar water octahedron systems.

The N–O bond distance [1.34103(17)–1.3398(17) Å] of OPTA is found to be elongated compared to the average N–O value [1.30(2) Å] of a typical non-coordinated N-oxide.<sup>40</sup> The bond lengths of C(7)–O(5) and C(7)–O(6) are 1.2702 Å and 1.2418 Å for

**Table 3.** Selected bond lengths and bond angles in **1**, **2**, and **3**.

(1)	(2)	(3)
<i>Bond length (Å)</i>		
C(7)–O(5) 1.2702	C(7)–O(5) 1.2448	C(7)–O(5) 1.2397
C(7)–O(6) 1.2418	C(7)–O(6) 1.272	C(7)–O(6) 1.273
N(1)–O(4) 1.3399	N(1)–O(4) 1.3403(17)	N(1)–O(4) 1.3398(17)
Co(1)–O(1) 2.0825	Ni(1)–O(1) 2.0537	Zn(1)–O(1) 2.1026(12)
<i>Bond angle (deg.)</i>		
C(5)–S(1)–C(6) 101.27(7)	C(5)–S(1)–C(6) 101.09(8)	C(5)–S(1)–C(6) 101.05(8)
O(5)–C(7)–O(6) 115.14(12)	O(5)–C(7)–O(6) 126.09(15)	O(5)–C(7)–O(6) 118.87
O(2)–Co(1)–O(2)#1 180.00(7)	O(2)–Ni(1)–O(2)#1 180.000(1)	O(2)#1–Zn(1)–O(2) 180.000(1)
O(1)–Co(1)–O(1)#1 180.00(7)	O(1)–Ni(1)–O(1)#1 180.0	O(1)#1–Zn(1)–O(1) 180.0
O(3)–Co(1)–O(1)#1 180.00(7)	O(3)–Ni(1)–O(3)#1 180.0	O(3)#1–Zn(1)–O(3) 180.0

**Figure 1.** An ORTEP diagram of **3** with the atomic numbering scheme shown. Thermal ellipsoids are drawn to 40% probability level.**Figure 2.** Packing diagram of **3**.

**1**, 1.2448 Å and 1.272 Å for **2**, and 1.2397 Å and 1.273 Å for **3** respectively, which are in agreement with the reported values.<sup>37</sup>

The O(4)–N(1)–C(5)–S(1) moiety of OPTA is found to be a part of a regular heterocyclic hexagon. The N(1)–C(5)–S(1) bond angle [112.32(11)°] shows a significant and unprecedented distortion from the expected value of 120° towards the pyridine N-oxide O atom.<sup>41</sup> According to the measured bond angles, the S atom is bent considerably towards the O atom of N-oxide. The N(1)–C(1) bond distance [1.351(2) Å] of OPTA is slightly shorter than that of the N(1)–C(5) [1.364(2) Å] while the average N–C bond length in the pyridine ring is 1.36(2) Å.

Complexes **1**, **2**, and **3** display both intermolecular and intramolecular H-bonding interactions (figure

**3**). Selected H-bonding interactions for the complexes **1–3** are given in tables 4–6. Intramolecular hydrogen bond distances of O(1)–H(1)⋯O(6), and O(2)–H(3)⋯O(6) are found to be 2.817(2) Å and 2.784(2) Å respectively in complex **3**. Intermolecular hydrogen bond distances of O(1)–H(2)⋯O(4)<sup>i</sup>, O(3)–H(5)⋯N(1)<sup>iii</sup>, and C(3)–H(9)⋯S(1)<sup>iv</sup> are found to be 2.695(2) Å, 3.222(2) Å and 2.75(3) Å respectively for the zinc complex **3**. Similar interactions are also observed for the complexes **1** and **2**.

## 6. Supplementary material

Crystallographic data for the complexes **1–3** have been deposited with the Cambridge Crystallographic

**Table 4.** Selected intramolecular and intermolecular hydrogen bond distances in **1**.

Interactions	D–H	H⋯A	D⋯A	D–H⋯A
<i>Intramolecular</i>				
O(2)–H(4)⋯O(6)	0.83(2)	1.86(2)	2.692(2)	174(2)
O(3)–H(5)⋯O(5)	0.83(2)	1.86(2)	2.688(2)	171(2)
<i>Intermolecular</i>				
O(1)–H(1)⋯O(5) <sup>i</sup>	0.84(2)	2.01(2)	2.800(2)	156(2)
O(1)–H(2)⋯O(4) <sup>ii</sup>	0.78(2)	1.91(2)	2.6826(2)	173(2)
O(2)–H(3)⋯O(4) <sup>iii</sup>	0.80(2)	1.93(2)	2.715(2)	168(2)
O(2)–H(3)⋯N(1) <sup>iii</sup>	0.80(2)	2.55(2)	3.208(2)	141(2)
O(3)–H(6)⋯O(5) <sup>iv</sup>	0.85(2)	1.95(2)	2.788(2)	166(2)
C(1)–H(7)⋯O(1) <sup>v</sup>	0.90(2)	2.54(2)	3.414(2)	165(2)
C(2)–H(8)⋯O(3) <sup>vi</sup>	0.99(2)	2.56(2)	3.396(2)	142(2)
C(3)–H(9)⋯S(1) <sup>vii</sup>	0.87(2)	2.74(2)	3.554(2)	158(2)

D – donor, A – acceptor

*Symmetry transformations used to generate equivalent atoms*#1  $-x + 1, -y, -z$ *Symmetry codes*i.  $x, -1 + y, z$ ii.  $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$ iii.  $2 - x, -\frac{1}{2} + y, \frac{1}{2} - z$ iv.  $1 - x, 1 - y, -z$ v.  $1 + x, \frac{1}{2} - y, \frac{1}{2} - z$ vi.  $1 + x, \frac{3}{2} - y, \frac{1}{2} + z$ vii.  $x, 1 + y, z$ **Table 5.** Selected intramolecular and intermolecular hydrogen bond distances in **2**.

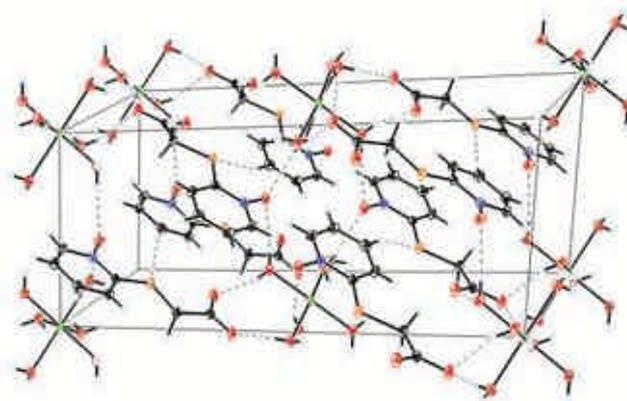
Interactions	D–H	H⋯A	D⋯A	D–H⋯A
<i>Intramolecular</i>				
O(3)–H(5)⋯O(4)	0.76(2)	1.94(2)	2.698(2)	172(2)
<i>Intermolecular</i>				
O(1)–H(1)⋯O(5) <sup>i</sup>	0.82(3)	1.89(3)	2.702(2)	170(2)
O(1)–H(2)⋯O(4) <sup>ii</sup>	0.78(3)	1.95(3)	2.727(2)	169(3)
O(1)–H(2)⋯N(1) <sup>ii</sup>	0.78(3)	2.56(3)	3.229(2)	143(2)
O(2)–H(3)⋯O(6) <sup>i</sup>	0.84(3)	1.85(3)	2.689(2)	170(3)
O(2)–H(4)⋯O(6) <sup>iii</sup>	0.78(2)	2.02(2)	2.785(2)	164(2)
O(3)–H(6)⋯O(6) <sup>iv</sup>	0.88(3)	1.98(3)	2.818(2)	157(2)
C(1)–H(7)⋯O(3) <sup>v</sup>	0.94(2)	2.48(2)	3.386(2)	163(2)
C(2)–H(8)⋯O(2) <sup>vi</sup>	1.00(2)	2.58(2)	3.422(2)	142(2)
C(3)–H(9)⋯S(1) <sup>vii</sup>	0.88(2)	2.71(2)	3.544(2)	157(2)

D – donor, A – acceptor

*Symmetry transformations used to generate equivalent atoms*#1  $-x, -y + 2, -z + 1$ *Symmetry codes*i.  $-x, -\frac{1}{2} + y, \frac{1}{2} - z$ ii.  $-1 + x, y, z$ iii.  $x, \frac{3}{2} - y, \frac{1}{2} + z$ iv.  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ v.  $1 - x, 2 - y, 1 - z$ vi.  $1 - x, 1 - y, 1 - z$ vii.  $x, -1 + y, z$ **Table 6.** Selected intramolecular and intermolecular hydrogen bond distances in **3**.

Interactions	D–H	H⋯A	D⋯A	D–H⋯A
<i>Intramolecular</i>				
O(1)–H(1)⋯O(6)	0.82(2)	2.04(2)	2.817(2)	158(2)
O(2)–H(3)⋯O(6)	0.81(3)	2.00(3)	2.784(2)	164(3)
<i>Intermolecular</i>				
O(1)–H(2)⋯O(4) <sup>i</sup>	0.77(2)	1.92(2)	2.695(2)	173(2)
O(2)–H(4)⋯O(6) <sup>ii</sup>	0.82(3)	1.87(3)	2.683(2)	173(3)
O(3)–H(5)⋯O(4) <sup>iii</sup>	0.77(3)	1.95(3)	2.719(2)	173(3)
O(3)–H(5)⋯N(1) <sup>iii</sup>	0.77(3)	2.57(3)	3.222(2)	144(2)
O(3)–H(6)⋯O(5) <sup>iv</sup>	0.85(3)	1.85(3)	2.698(2)	173(2)
C(1)–H(7)⋯O(1) <sup>v</sup>	0.89(2)	2.53(2)	3.390(2)	163(2)
C(2)–H(8)⋯O(2) <sup>iii</sup>	0.98(2)	2.59(2)	3.418(2)	142(2)
C(3)–H(9)⋯S(1) <sup>iv</sup>	0.85(3)	2.75(3)	3.559(2)	158(2)

D – donor, A – acceptor

*Symmetry transformations used to generate equivalent atoms*#1  $-x + 1, -y + 1, -z + 1$ *Symmetry codes*i.  $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ii.  $1 - x, 2 - y, 1 - z$ iii.  $-x, -\frac{1}{2} + y, \frac{1}{2} - z$ iv.  $x, -1 + y, z$ v.  $-1 + x, \frac{3}{2} - y, -\frac{1}{2} + z$ 

Green = Zinc  
 Blue = Nitrogen  
 Red = Oxygen  
 Light blue = Hydrogen  
 Yellow = Sulphur

**Figure 3.** H-bonding interactions in **3**.

Data Centre (CCDC), deposition numbers are 226216, 226217, and 226215 for the complexes (**1**), (**2**), and (**3**) respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033, email: deposit@ccdc.cam.ac.uk).

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