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Two isomorphous transition metal complexes displaying a coordinated tetrathionate unit: bis(4,4'-dimethyl-2,2'-bipyridine- κ^2N,N')(tetrathionato- κ^2S,S')cadmium(II) dimethylformamide disolvate and the zinc(II) analogue

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Two isomorphous transition metal complexes displaying a coordinated tetrathionate unit: bis(4,4'-dimethyl-2,2'-bipyridine- κ^2N,N')(tetrathionato- κ^2S,S')cadmium(II) dimethylformamide disolvate and the zinc(II) analogue

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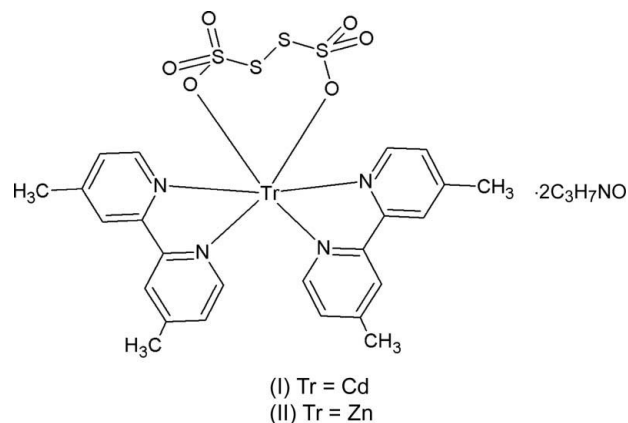
Accepted 13 June 2013

The isomorphous title compounds, $[\text{Tr}(\text{S}_4\text{O}_6)(\text{C}_{12}\text{H}_{12}\text{N}_2)_2] \cdot 2\text{C}_3\text{H}_7\text{NO}$ ($\text{Tr} = \text{Cd}^{\text{II}}$ and Zn^{II}), consist of metal centres to which one tetrathionate and two 4,4'-dimethyl-2,2'-bipyridine chelating ligands bind. The structures are completed by two symmetry-related dimethylformamide solvent molecules. Each metal-centred complex is bisected by a twofold axis running through the metal centre and halving the chelating tetrathionate dianion through the central S—S bond. The ancillary symmetry-related 4,4'-dimethyl-2,2'-bipyridine ligands act as chelates. This results in a distorted six-coordinate geometry, with similar $\text{Tr}-\text{O}/\text{N}$ distances but central angles differing substantially from 90 and 180°. Both ligands are basically featureless from a geometric point of view, with torsion angles in both coordinated tetrathionate groups suggesting a trend linking metal size (covalent radius) and ligand 'openness'. Packing is directed by $(\text{C}-\text{H})_{\text{aromatic}} \cdots \text{O}$ bridges and $\pi-\pi$ offset stacked interactions defining chains along [001], further linked by weaker $(\text{C}-\text{H})_{\text{methyl}} \cdots \text{O}$ bridges, some of them mediated by the dimethylformamide solvent molecules.

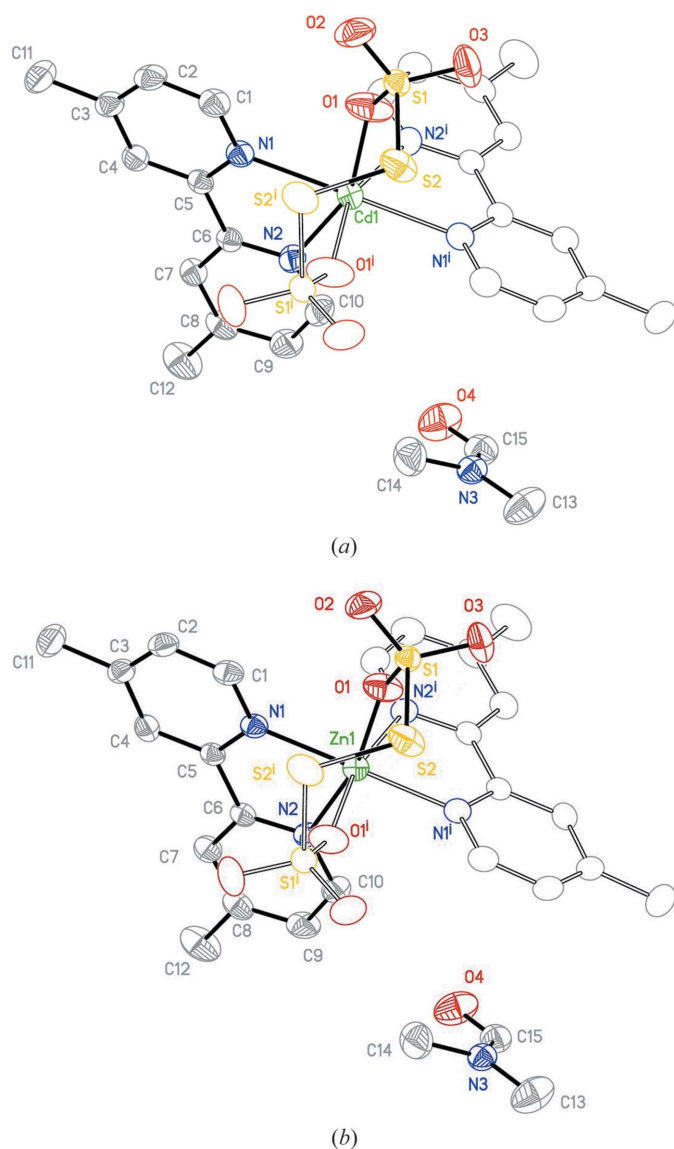
Comment

For an extended period of 40 years [*viz.* those between the reports of Baggio & Baggio (1973) and Suarez *et al.* (2013)], our group has been interested in the coordination affinity towards transition metals of a variety of different sulfur oxoanions (sulfate, sulfite, thiosulfate, peroxodisulfate, di/tri/tetra/

pentathionate *etc.*) in organic-inorganic coordination compounds. Even though many of them show a remarkable coordination tendency (SO_4^{2-} , SSO_3^{2-} *etc.*), others, in particular the latter 'thionate' family, present extremely poor binding abilities. This is readily confirmed by a search of the Cambridge Structural Database (CSD, Version 5.33; Allen, 2002), comparing for each ligand the total number of entries (m) with the number of entries involving the coordinated ligand (n), represented as (m,n) : dithionate (125,13), trithionate (4,1), tetrathionate (19,2) and pentathionate (8,0). The case of tetrathionate is particularly interesting; only two out of 19 structures in the CSD show the anion acting in a coordinating mode [Freire *et al.* (1998) showed it bridging Cu atoms and Freire *et al.* (2001) showed it chelating an Mn atom], and in both cases the ligand had been generated serendipitously during the synthesis procedure as an oxidation product of $\text{S}_2\text{O}_3^{2-}$, which thus acted unexpectedly as a precursor. In summary, no direct synthesis starting from any $\text{S}_4\text{O}_6^{2-}$ derivative has so far resulted in any transition metal complex with a coordinated tetrathionate group. In order to explore this puzzling situation further, we tried to 'fine tune' the synthesis and crystallization of different $\text{S}_4\text{O}_6^{2-}$ transition metal compounds (see *Experimental* section for details). We present herein the first two successful results of these attempts, the isomorphous Cd and Zn title complexes, namely bis(4,4'-dimethyl-2,2'-bipyridine- κ^2N,N')(tetrathionato- κ^2S,S')cadmium(II) dimethylformamide disolvate, $[\text{Cd}(\text{tth})(\text{dmbpy})_2] \cdot 2\text{DMF}$, (I) (Fig. 1a), and the zinc(II) analogue, $[\text{Zn}(\text{tth})(\text{dmbpy})_2(\text{tth})] \cdot 2\text{DMF}$, (II) (Fig. 1b), where dmbpy is 4,4'-dimethyl-2,2'-bipyridine, tth is the tetrathionate anion and DMF is dimethylformamide.



The molecules of both isomorphs consist of a d -block metal (Tr) cation [$\text{Tr} = \text{Cd}^{\text{II}}$ for (I) and $\text{Tr} = \text{Zn}^{\text{II}}$ for (II)], to which one tth and two dmbpy chelating ligands bind. The structures are completed by two symmetry-related DMF solvent molecules. Each complex molecule is bisected by a twofold axis running through the metal centre and halving the chelating tth anion through the central S—S bond. The ancillary symmetry-related dmbpy ligands also act as chelates. The metal cations present a 2+2+2 N_4O_2 environment. As expected, this results in a distorted six-coordinate geometry, with similar $\text{Tr}-\text{O}/\text{N}$ distances (Tables 1 and 2), but with the central angles differing substantially from 90 and 180° [90 ± 18.78 (6) and


Figure 1

Molecular views of (a) (I) and (b) (II), showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 30% probability level. Shaded ellipsoids and solid bonds represent the independent part of the molecule. [Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$]

180 ± 22.44 (7) $^\circ$ for (I), and 90 ± 12.80 (10) and 180 ± 13.27 (9) $^\circ$ for (II)].

The dmbpy units are planar, with maximum deviations of -0.033 (2) and 0.032 (2) \AA for (I), and -0.030 (2) and 0.018 (2) \AA for (II), corresponding in both cases to the terminal methyl groups.

The tth ligands chelate the metals in a similar manner to that found in the Mn–bipyridine analogue (Freire *et al.*, 2001). They present standard metric features, with clearly differentiated outer and central S–S bond lengths [2.1011 (10) versus 2.0169 (15) \AA for (I) and 2.1056 (13) versus 2.016 (2) \AA for (II)], as well as S=O and S–O bond lengths [1.403 (2)–1.4165 (18) versus 1.4297 (19) \AA in (I) and 1.417 (2)–1.424 (2) versus 1.442 (2) \AA in (II)], and they seem to adjust their flexible spatial conformation to the different metal sizes; the

O1–S1–S2–S2ⁱ and S1–S2–S2ⁱ–S1ⁱ torsion angles [symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$] along the anion ‘backbone’ are -55.99 (11) and 105.22 (5) $^\circ$ for (I), and -59.05 (12) and 99.48 (6) $^\circ$ for (II), respectively. Given that in an A–B–C–D torsion angle a 90° value corresponds to perpendicular ABC/BCD planes and a 0 or 180° value to parallel planes, a smaller or larger departure from 90° can be indicative of a more ‘closed/open’ character of the tth anionic group. It transpires (perhaps expectedly) that this case appears more ‘open’, with large departures from 90° . Similar results are obtained by comparing the S1⋯S1ⁱ distances in the coordinated anions, *viz.* 4.428 (2) \AA for (I) and 4.331 (2) \AA for (II).

As stated above, the donor atoms in (I) and (II) cannot fit in any regular polyhedron, but the three chelate ligands abide by the vector bond-valence postulate of the vectorial bond-valence model [for details on the theory, see Harvey *et al.* (2006)]. The three ligand vectors, as defined therein, lie in a planar trigonal geometry, with the sum of the angles being 360.0 (2) $^\circ$ for both (I) and (II) (ideal = 360°), and with resultant vector moduli of 0.085 valence units (v.u.) for (I) and 0.049 v.u. for (II) (ideal = 0.00 v.u.). The usual bond-valence sums (BVS; Brown, 2002) are 2.00 v.u. for Zn and 2.17 v.u. for Cd¹.

In spite of the lack of good hydrogen-bond donors, which weakens the interactions between monomers, packing indices [as calculated by PLATON (Spek, 2009), following Kitajgorodskij (1973)] are very near the expected average of *ca* 65% [66.15% for (I) and 67.4% for (II)].

Tables 3 and 4 present relevant C–H⋯O hydrogen bonds, while Table 5 gives information on the π – π interactions. The first three entries in Tables 3 and 4 correspond to the more active (C–H)_{aromatic} group, and in fact these have a definite structural role. Fig. 2 shows the way in which the interactions presented as the first two entries serve to link adjacent molecules in a self-complementary fashion along the [001] direction, in the form of well defined chains, complemented by the π – π interactions between offset stacked dmbpy groups. The third entry in Tables 3 and 4 binds the DMF solvent molecules to the main molecule. The remaining three entries involve the less active (C–H)_{methyl} groups, and these interactions ultimately have the role of interlinking chains together in a rather weak fashion.

¹ In our experience with Cd complexes, we have detected that the bond-valence parameters presented by Brown (2006) for Cd–O and Cd–N ($R_{\text{Cd-O}} = 1.904$ and $R_{\text{Cd-N}} = 1.960$) usually lead to overestimated BVS values for the cation. This is not unexpected, since it is known that these parameters are not absolutely ‘universal’ but depend on, among other features, the coordination environment (Brown, 2008). We attempted to find better values for both bond-valence parameters and so, while keeping ‘b’ fixed at its standard value of 0.37, we performed a least-squares fit on *ca* 2000 CdO_nN_{6–n} coordination polyhedra in the CSD (Allen, 2002) of the valence sum equation $\Sigma(V_i)_{i:1>6} = V$ [with $V = 2$ the expected Cd valence and $V_i = \exp(R_x - R_i/b)$], where $R_x = R_{\text{Cd-O}}$ or $R_{\text{Cd-N}}$ are the parameters to be refined, and R_i are the actual Cd–O and Cd–N bond lengths. Upon convergence, this procedure led to slightly different values than those given by Brown (2006) (about 1% smaller, *viz.* $R_{\text{Cd-O}} = 1.886$ and $R_{\text{Cd-N}} = 1.946$) and with better performance; they resulted in a BVS for Cd1 in (I) of 2.17 versus a value of 2.26 calculated from Brown’s data.

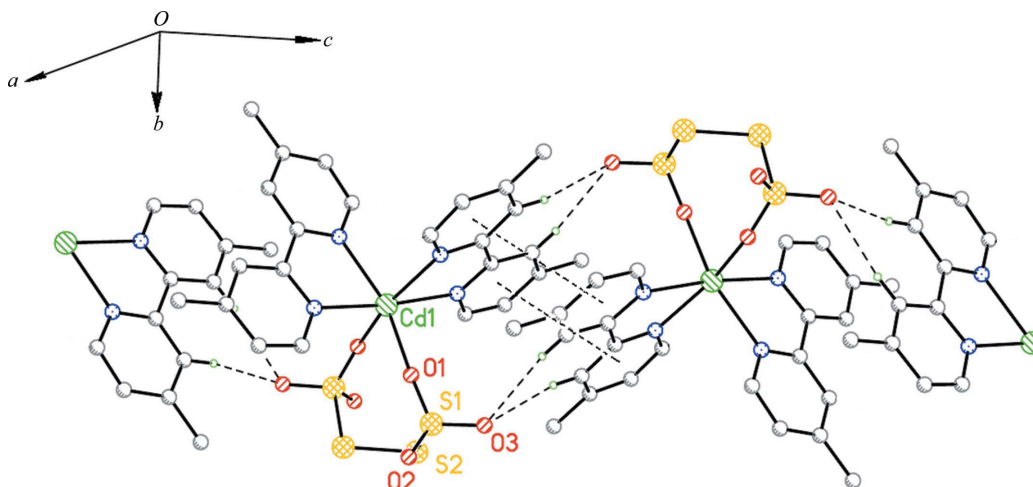


Figure 2

A simplified view of the [001] chain in (I). C–H...O hydrogen bonds and π – π interactions are shown as dashed lines.

This differentiated interaction scheme serves to provide, if not an explanation, at least a plausible argument for the behaviour of the cell metrics, *viz.* the increase in the *c* cell dimension when going from Zn to Cd (an expected fact), but a small decrease in the remaining two cell dimensions, more pronounced in the *a* dimension. Fig. 2 helps in understanding the increase along the [001] chains; this is the overall direction of the Cd–N bonds ($\sim 10\%$ longer than the corresponding Zn–N bonds), as well as of the bridging (C–H)_{aromatic}...O hydrogen bonds and π – π interactions, thus rendering the *c* cell dimension longer (and more rigid).

Along the remaining two directions, chains are instead held together by much more labile forces [mainly (C–H)_{methyl}...O contacts; Fig. 3]. These are, accordingly, ‘soft’ directions which

would not provide strong resistance to any eventual compression required by the close packing of the chains.

Experimental

In several previous attempts to obtain hybrid organic tetrathionate transition metal complexes using aqueous solutions, the anion decomposed systematically, yielding thiosulfate. In view of these failures, we thought of using a solvent in which the organic ligand is soluble but the other two components are only slightly soluble. In doing so, it was expected that the components would mix slowly to form the complex, while simultaneously displacing the solubility equilibrium. After some tests, we selected dimethylformamide (DMF) as an appropriate solvent. To a solution of 4,4'-dimethyl-2,2'-bipyridine in DMF (5 ml, 0.050 M), solid Cd or Zn diacetate dihydrate and potassium tetrathionate were added in a mass–volume ratio chosen to give a 0.050 M solution of each component. On standing, in both cases, a poorly crystallized precipitate appeared, which was digested over a period of time (one week in the Cd case and one month for Zn) to give crystals of the expected complexes in the form of well faceted colourless blocks suitable for X-ray diffraction analysis.

Compound (I)

Crystal data

[Cd(S₄O₆)(C₁₂H₁₂N₂)₂] \cdot 2C₃H₇NO
M_r = 851.30
 Monoclinic, C2/c
a = 20.7076 (7) Å
b = 10.7885 (3) Å
c = 17.5044 (5) Å
 β = 108.187 (3)°

V = 3715.2 (2) Å³
Z = 4
 Mo K α radiation
 μ = 0.87 mm⁻¹
T = 294 K
 0.15 \times 0.05 \times 0.04 mm

Data collection

Oxford Gemini S Ultra CCD area-detector diffractometer
 Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2009)
T_{min} = 0.94, *T_{max}* = 0.96

9819 measured reflections
 3844 independent reflections
 2693 reflections with *I* > 2 σ (*I*)
R_{int} = 0.025

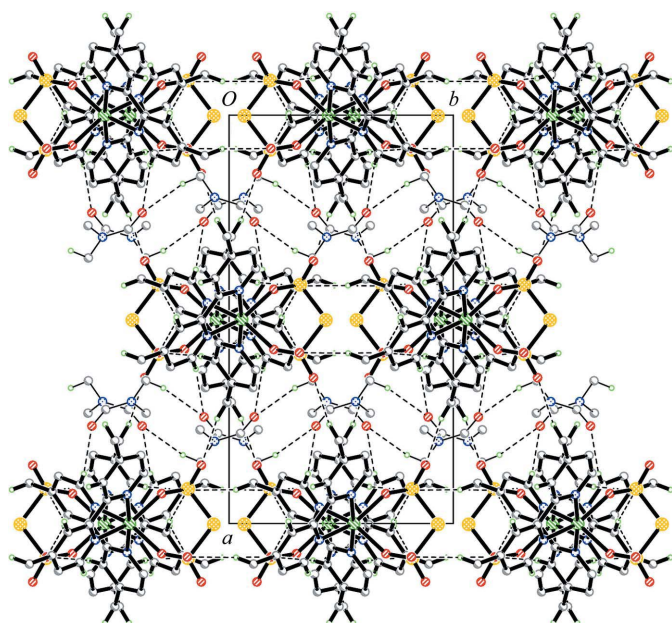


Figure 3

A packing view of (I), projected down [001], showing the loose manner in which the chains interact parallel to each other.

Table 1
Selected bond lengths (Å) for (I).

Cd1—O1	2.2767 (19)	Cd1—N2	2.3175 (19)
Cd1—N1	2.3156 (18)		

Table 2
Selected bond lengths (Å) for (II).

Zn1—O1	2.119 (2)	Zn1—N2	2.136 (3)
Zn1—N1	2.109 (3)		

Table 3
Geometry of hydrogen bonds and other noncovalent interactions (Å, °) for (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C4—H4...O3 ⁱ	0.93	2.50	3.418 (3)	170
C7—H7...O3 ⁱ	0.93	2.48	3.397 (3)	169
C10—H10...O4	0.93	2.51	3.320 (4)	146
C11—H11C...O2 ⁱⁱ	0.96	2.48	3.427 (4)	168
C12—H12A...O3 ⁱⁱⁱ	0.96	2.49	3.413 (3)	161
C13—H13C...O4 ^{iv}	0.96	2.57	3.517 (4)	167

Symmetry codes: (i) $x, -y, z - \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 1, y - 1, -z + \frac{1}{2}$; (iv) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	226 parameters
$wR(F^2) = 0.065$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{\max} = 0.34 \text{ e \AA}^{-3}$
3844 reflections	$\Delta\rho_{\min} = -0.33 \text{ e \AA}^{-3}$

Compound (II)

Crystal data

$[\text{Zn}(\text{S}_4\text{O}_6)(\text{C}_{12}\text{H}_{12}\text{N}_2)_2] \cdot 2\text{C}_3\text{H}_7\text{NO}$	$V = 3650.6 (4) \text{ \AA}^3$
$M_r = 804.27$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 20.8508 (12) \text{ \AA}$	$\mu = 0.96 \text{ mm}^{-1}$
$b = 10.8334 (8) \text{ \AA}$	$T = 294 \text{ K}$
$c = 16.9888 (10) \text{ \AA}$	$0.10 \times 0.05 \times 0.04 \text{ mm}$
$\beta = 107.956 (7)^\circ$	

Data collection

Oxford Gemini S Ultra CCD area-detector diffractometer	12111 measured reflections
Absorption correction: multi-scan (<i>CrysAlis PRO</i> ; Oxford Diffraction, 2009)	3945 independent reflections
$T_{\min} = 0.95, T_{\max} = 0.97$	2446 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.062$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$	226 parameters
$wR(F^2) = 0.104$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{\max} = 0.32 \text{ e \AA}^{-3}$
3945 reflections	$\Delta\rho_{\min} = -0.29 \text{ e \AA}^{-3}$

All H atoms were visible in difference maps, but were subsequently placed in geometrically idealized positions and allowed to ride on their parent atoms, with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic, and C—H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$

Table 4
Geometry of hydrogen bonds and other noncovalent interactions (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C4—H4...O3 ⁱ	0.93	2.49	3.411 (4)	170
C7—H7...O3 ⁱ	0.93	2.46	3.381 (4)	171
C10—H10...O4	0.93	2.47	3.250 (5)	142
C11—H11C...O2 ⁱⁱ	0.96	2.55	3.479 (5)	163
C12—H12A...O3 ⁱⁱⁱ	0.96	2.55	3.465 (5)	160
C13—H13C...O4 ^{iv}	0.96	2.59	3.525 (5)	166

Symmetry codes: (i) $x, -y, z - \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 1, y - 1, -z + \frac{1}{2}$; (iv) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

Table 5
 π — π contacts (Å, °) for (I) and (II).

Cg1 is the centroid of the N1/C1—C5 ring and Cg2 that of the N2/C6—C10 ring. IPD is the interplanar distance, CCD is the centre-to-centre distance and SA is the slippage angle. For details, see Janiak (2000).

Compound	Group 1/group 2	IPD (Å)	CCD (Å)	SA (°)
(I)	Cg1...Cg2 ^v	1.08 (12)	4.1042 (13)	28.32 (12)
(II)	Cg1...Cg2 ^v	1.67 (15)	4.1745 (18)	30.0 (4)

Symmetry code: (v) $-x + 1, -y, -z$.

for methyl H atoms. Methyl groups were permitted to rotate about the adjacent C—C or C—N bond. In (I), conventional weighting led to a rather low goodness-of-fit, for which a special scheme with enhanced weighting for high-angle reflections (provided in *SHELXL97*; Sheldrick, 2008) was applied.

For both compounds, data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

The authors acknowledge ANPCyT (project No. PME 2006-01113) for the purchase of the Oxford Gemini CCD diffractometer and the Spanish Research Council (CSIC) for the provision of a free-of-charge licence to the Cambridge Structural Database (Allen, 2002).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3139). Services for accessing these data are described at the back of the journal.

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supplementary materials

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Two isomorphous transition metal complexes displaying a coordinated tetra-thionate unit: bis(4,4'-dimethyl-2,2'-bipyridine- κ^2N,N')(tetrathionato- κ^2S,S')cadmium(II) dimethylformamide disolvate and the zinc(II) analogue

Miguel Angel Harvey, Sebastián Suarez, Fabio Doctorovich and Ricardo Baggio

Computing details

For both compounds, data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2009); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

(I) Bis(4,4'-dimethyl-2,2'-bipyridine- κ^2N,N')(tetrathionato- κ^2S,S')cadmium(II) dimethylformamide disolvate

Crystal data

[Cd(S₄O₆)(C₁₂H₁₂N₂)₂] \cdot 2C₃H₇NO
M_r = 851.30
 Monoclinic, *C2/c*
 Hall symbol: -C 2yc
a = 20.7076 (7) Å
b = 10.7885 (3) Å
c = 17.5044 (5) Å
 β = 108.187 (3)°
V = 3715.2 (2) Å³
Z = 4

F(000) = 1744
D_x = 1.522 Mg m⁻³
 Mo *K* α radiation, λ = 0.71073 Å
 Cell parameters from 2418 reflections
 θ = 3.7–28.1°
 μ = 0.87 mm⁻¹
T = 294 K
 Prism, colourless
 0.15 \times 0.05 \times 0.04 mm

Data collection

Oxford Gemini S Ultra CCD area-detector diffractometer
 ω scans, thick slices
 Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.94, *T_{max}* = 0.96
 9819 measured reflections

3844 independent reflections
 2693 reflections with *I* > 2 σ (*I*)
R_{int} = 0.025
 θ_{\max} = 26.5°, θ_{\min} = 3.6°
h = -25→24
k = -13→13
l = -13→21

Refinement

Refinement on *F*²
 Least-squares matrix: full
R[*F*² > 2 σ (*F*²)] = 0.029
wR(*F*²) = 0.065
S = 1.00
 3844 reflections
 226 parameters

0 restraints
 Primary atom site location: structure-invariant direct methods
 Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
 $w = [\exp(1.20(\sin\theta/\lambda)^2)]/[\sigma^2(F_o^2) + (0.0331P)^2]$
 where $P = 0.33333F_o^2 + 0.66667F_c^2$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.34 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cd1	0.5000	0.05562 (2)	0.2500	0.04902 (10)
S1	0.58500 (3)	0.31673 (6)	0.36429 (3)	0.04756 (15)
S2	0.50175 (4)	0.43161 (7)	0.30822 (5)	0.0791 (2)
O1	0.57359 (11)	0.19950 (18)	0.32421 (13)	0.0921 (7)
O2	0.64280 (10)	0.3761 (2)	0.35624 (13)	0.0983 (7)
O3	0.58172 (12)	0.3138 (2)	0.44390 (11)	0.0942 (7)
N1	0.57068 (10)	0.04451 (17)	0.17054 (11)	0.0483 (5)
N2	0.45980 (10)	-0.09723 (18)	0.15385 (11)	0.0500 (5)
C1	0.62399 (13)	0.1185 (2)	0.17821 (15)	0.0590 (7)
H1	0.6322	0.1819	0.2160	0.071*
C2	0.66702 (13)	0.1060 (3)	0.13347 (16)	0.0618 (7)
H2	0.7033	0.1603	0.1407	0.074*
C3	0.65629 (12)	0.0120 (3)	0.07735 (15)	0.0539 (6)
C4	0.60000 (12)	-0.0626 (2)	0.06785 (14)	0.0493 (6)
H4	0.5902	-0.1253	0.0295	0.059*
C5	0.55803 (11)	-0.04488 (19)	0.11482 (12)	0.0418 (5)
C6	0.49677 (11)	-0.12373 (19)	0.10555 (12)	0.0415 (5)
C7	0.47863 (12)	-0.2188 (2)	0.05011 (13)	0.0492 (6)
H7	0.5051	-0.2351	0.0170	0.059*
C8	0.42155 (14)	-0.2900 (2)	0.04323 (14)	0.0576 (6)
C9	0.38446 (14)	-0.2612 (3)	0.09368 (16)	0.0707 (8)
H9	0.3457	-0.3065	0.0913	0.085*
C10	0.40441 (14)	-0.1663 (3)	0.14700 (17)	0.0665 (7)
H10	0.3784	-0.1484	0.1804	0.080*
C11	0.70313 (16)	-0.0099 (3)	0.02856 (19)	0.0830 (9)
H11A	0.7162	0.0682	0.0116	0.124*
H11B	0.6803	-0.0588	-0.0178	0.124*
H11C	0.7429	-0.0531	0.0606	0.124*
C12	0.40119 (19)	-0.3912 (3)	-0.01794 (18)	0.0884 (10)
H12A	0.4172	-0.4693	0.0071	0.133*
H12B	0.4208	-0.3760	-0.0601	0.133*
H12C	0.3526	-0.3932	-0.0402	0.133*
N3	0.20135 (10)	0.06463 (19)	0.18402 (12)	0.0552 (5)
O4	0.26101 (12)	-0.1120 (2)	0.18838 (15)	0.0995 (7)
C13	0.15034 (16)	0.1281 (3)	0.2096 (2)	0.0961 (11)
H13A	0.1383	0.0784	0.2486	0.144*
H13B	0.1108	0.1418	0.1640	0.144*

H13C	0.1680	0.2063	0.2332	0.144*
C14	0.22956 (18)	0.1295 (3)	0.13132 (18)	0.0917 (10)
H14A	0.2649	0.0805	0.1217	0.138*
H14B	0.2481	0.2069	0.1554	0.138*
H14C	0.1947	0.1449	0.0813	0.138*
C15	0.22072 (15)	-0.0504 (3)	0.20863 (17)	0.0686 (7)
H15	0.2014	-0.0861	0.2447	0.082*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.05889 (18)	0.04432 (15)	0.04450 (15)	0.000	0.01706 (12)	0.000
S1	0.0500 (4)	0.0489 (3)	0.0423 (3)	-0.0059 (3)	0.0124 (3)	-0.0055 (3)
S2	0.0822 (5)	0.0793 (5)	0.0635 (5)	0.0290 (5)	0.0051 (4)	-0.0199 (4)
O1	0.0762 (14)	0.0635 (12)	0.1052 (16)	0.0086 (11)	-0.0170 (11)	-0.0356 (12)
O2	0.0538 (12)	0.1241 (18)	0.1094 (17)	-0.0224 (13)	0.0147 (12)	0.0315 (15)
O3	0.1243 (19)	0.1135 (17)	0.0521 (12)	0.0258 (15)	0.0380 (12)	0.0153 (11)
N1	0.0502 (12)	0.0452 (11)	0.0474 (11)	-0.0128 (10)	0.0120 (9)	-0.0033 (9)
N2	0.0513 (12)	0.0489 (11)	0.0521 (12)	-0.0121 (10)	0.0193 (10)	-0.0035 (9)
C1	0.0604 (17)	0.0532 (15)	0.0584 (16)	-0.0182 (14)	0.0114 (13)	-0.0055 (12)
C2	0.0456 (15)	0.0662 (16)	0.0684 (18)	-0.0197 (14)	0.0099 (13)	0.0136 (15)
C3	0.0420 (14)	0.0617 (15)	0.0554 (16)	0.0000 (13)	0.0114 (12)	0.0163 (13)
C4	0.0482 (14)	0.0525 (13)	0.0449 (13)	-0.0016 (13)	0.0114 (11)	0.0014 (11)
C5	0.0444 (13)	0.0385 (12)	0.0384 (12)	-0.0020 (11)	0.0071 (10)	0.0058 (10)
C6	0.0436 (13)	0.0380 (12)	0.0395 (12)	-0.0020 (11)	0.0082 (10)	0.0059 (10)
C7	0.0562 (15)	0.0435 (12)	0.0465 (14)	-0.0069 (12)	0.0142 (12)	-0.0022 (11)
C8	0.0693 (18)	0.0449 (13)	0.0484 (15)	-0.0136 (14)	0.0034 (13)	0.0029 (11)
C9	0.0620 (18)	0.0752 (19)	0.0708 (18)	-0.0324 (16)	0.0147 (15)	-0.0018 (16)
C10	0.0621 (17)	0.0730 (19)	0.0712 (18)	-0.0191 (16)	0.0305 (15)	-0.0025 (15)
C11	0.0598 (18)	0.111 (2)	0.087 (2)	-0.0010 (18)	0.0363 (17)	0.0148 (19)
C12	0.114 (3)	0.0622 (18)	0.077 (2)	-0.039 (2)	0.0127 (19)	-0.0135 (16)
N3	0.0535 (12)	0.0504 (12)	0.0608 (13)	-0.0064 (11)	0.0166 (10)	-0.0080 (10)
O4	0.0842 (16)	0.0774 (14)	0.138 (2)	0.0191 (13)	0.0359 (15)	-0.0176 (14)
C13	0.073 (2)	0.078 (2)	0.149 (3)	-0.0009 (19)	0.051 (2)	-0.022 (2)
C14	0.104 (3)	0.098 (2)	0.079 (2)	-0.026 (2)	0.036 (2)	0.0020 (19)
C15	0.0666 (19)	0.0639 (18)	0.0716 (19)	-0.0112 (17)	0.0160 (15)	-0.0053 (16)

Geometric parameters (\AA , $^\circ$)

Cd1—O1	2.2767 (19)	C7—C8	1.383 (3)
Cd1—O1 ⁱ	2.2767 (19)	C7—H7	0.9300
Cd1—N1 ⁱ	2.3156 (18)	C8—C9	1.375 (3)
Cd1—N1	2.3156 (18)	C8—C12	1.495 (3)
Cd1—N2	2.3175 (19)	C9—C10	1.360 (4)
Cd1—N2 ⁱ	2.3175 (19)	C9—H9	0.9300
S1—O2	1.403 (2)	C10—H10	0.9300
S1—O3	1.4165 (18)	C11—H11A	0.9600
S1—O1	1.4297 (19)	C11—H11B	0.9600
S1—S2	2.1011 (10)	C11—H11C	0.9600
S2—S2 ⁱ	2.0169 (15)	C12—H12A	0.9600

N1—C1	1.335 (3)	C12—H12B	0.9600
N1—C5	1.338 (3)	C12—H12C	0.9600
N2—C6	1.336 (3)	N3—C15	1.333 (3)
N2—C10	1.341 (3)	N3—C14	1.421 (3)
C1—C2	1.364 (4)	N3—C13	1.442 (3)
C1—H1	0.9300	O4—C15	1.204 (3)
C2—C3	1.381 (4)	C13—H13A	0.9600
C2—H2	0.9300	C13—H13B	0.9600
C3—C4	1.383 (3)	C13—H13C	0.9600
C3—C11	1.498 (4)	C14—H14A	0.9600
C4—C5	1.383 (3)	C14—H14B	0.9600
C4—H4	0.9300	C14—H14C	0.9600
C5—C6	1.494 (3)	C15—H15	0.9300
C6—C7	1.381 (3)		
O1—Cd1—O1 ⁱ	94.04 (10)	N2—C6—C5	116.37 (19)
O1—Cd1—N1 ⁱ	97.39 (8)	C7—C6—C5	122.3 (2)
O1 ⁱ —Cd1—N1 ⁱ	86.67 (8)	C6—C7—C8	120.8 (2)
O1—Cd1—N1	86.67 (8)	C6—C7—H7	119.6
O1 ⁱ —Cd1—N1	97.39 (8)	C8—C7—H7	119.6
N1 ⁱ —Cd1—N1	174.06 (9)	C9—C8—C7	116.9 (2)
O1—Cd1—N2	157.56 (7)	C9—C8—C12	122.4 (3)
O1 ⁱ —Cd1—N2	92.64 (8)	C7—C8—C12	120.7 (3)
N1 ⁱ —Cd1—N2	104.38 (7)	C10—C9—C8	120.0 (2)
N1—Cd1—N2	71.22 (6)	C10—C9—H9	120.0
O1—Cd1—N2 ⁱ	92.64 (8)	C8—C9—H9	120.0
O1 ⁱ —Cd1—N2 ⁱ	157.56 (7)	N2—C10—C9	123.2 (2)
N1 ⁱ —Cd1—N2 ⁱ	71.22 (6)	N2—C10—H10	118.4
N1—Cd1—N2 ⁱ	104.38 (7)	C9—C10—H10	118.4
N2—Cd1—N2 ⁱ	89.27 (10)	C3—C11—H11A	109.5
O2—S1—O3	114.41 (14)	C3—C11—H11B	109.5
O2—S1—O1	111.72 (15)	H11A—C11—H11B	109.5
O3—S1—O1	114.31 (14)	C3—C11—H11C	109.5
O2—S1—S2	106.56 (10)	H11A—C11—H11C	109.5
O3—S1—S2	100.87 (10)	H11B—C11—H11C	109.5
O1—S1—S2	107.87 (9)	C8—C12—H12A	109.5
S2 ⁱ —S2—S1	103.74 (5)	C8—C12—H12B	109.5
S1—O1—Cd1	149.51 (13)	H12A—C12—H12B	109.5
C1—N1—C5	118.2 (2)	C8—C12—H12C	109.5
C1—N1—Cd1	124.52 (16)	H12A—C12—H12C	109.5
C5—N1—Cd1	117.29 (14)	H12B—C12—H12C	109.5
C6—N2—C10	117.9 (2)	C15—N3—C14	121.7 (2)
C6—N2—Cd1	117.70 (14)	C15—N3—C13	121.2 (2)
C10—N2—Cd1	124.29 (16)	C14—N3—C13	117.2 (3)
N1—C1—C2	123.4 (2)	N3—C13—H13A	109.5
N1—C1—H1	118.3	N3—C13—H13B	109.5
C2—C1—H1	118.3	H13A—C13—H13B	109.5
C1—C2—C3	119.5 (2)	N3—C13—H13C	109.5
C1—C2—H2	120.3	H13A—C13—H13C	109.5

C3—C2—H2	120.3	H13B—C13—H13C	109.5
C2—C3—C4	117.1 (2)	N3—C14—H14A	109.5
C2—C3—C11	122.1 (2)	N3—C14—H14B	109.5
C4—C3—C11	120.8 (3)	H14A—C14—H14B	109.5
C3—C4—C5	120.7 (2)	N3—C14—H14C	109.5
C3—C4—H4	119.6	H14A—C14—H14C	109.5
C5—C4—H4	119.6	H14B—C14—H14C	109.5
N1—C5—C4	121.1 (2)	O4—C15—N3	125.9 (3)
N1—C5—C6	117.13 (19)	O4—C15—H15	117.1
C4—C5—C6	121.8 (2)	N3—C15—H15	117.1
N2—C6—C7	121.3 (2)		

Symmetry code: (i) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C4—H4 \cdots O3 ⁱⁱ	0.93	2.50	3.418 (3)	170
C7—H7 \cdots O3 ⁱⁱ	0.93	2.48	3.397 (3)	169
C10—H10 \cdots O4	0.93	2.51	3.320 (4)	146
C11—H11C \cdots O2 ⁱⁱⁱ	0.96	2.48	3.427 (4)	168
C12—H12A \cdots O3 ^{iv}	0.96	2.49	3.413 (3)	161
C13—H13C \cdots O4 ^v	0.96	2.57	3.517 (4)	167

Symmetry codes: (ii) $x, -y, z-1/2$; (iii) $-x+3/2, y-1/2, -z+1/2$; (iv) $-x+1, y-1, -z+1/2$; (v) $-x+1/2, y+1/2, -z+1/2$.

(II) Bis(4,4'-dimethyl-2,2'-bipyridine- κ^2N, N')(tetrathionato- κ^2S, S')cadmium(II) dimethylformamide disolvate

Crystal data

$[\text{Zn}(\text{S}_4\text{O}_6)(\text{C}_{12}\text{H}_{12}\text{N}_2)_2] \cdot 2\text{C}_3\text{H}_7\text{NO}$

$M_r = 804.27$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 20.8508$ (12) \AA

$b = 10.8334$ (8) \AA

$c = 16.9888$ (10) \AA

$\beta = 107.956$ (7) $^\circ$

$V = 3650.6$ (4) \AA^3

$Z = 4$

$F(000) = 1672$

$D_x = 1.463$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA

Cell parameters from 2102 reflections

$\theta = 3.5\text{--}28.8^\circ$

$\mu = 0.96$ mm^{-1}

$T = 294$ K

Prism, colourless

$0.10 \times 0.05 \times 0.04$ mm

Data collection

Oxford Gemini S Ultra CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans, thick slices

Absorption correction: multi-scan

(*CrysAlis PRO*; Oxford Diffraction, 2009)

$T_{\min} = 0.95, T_{\max} = 0.97$

12111 measured reflections

3945 independent reflections

2446 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.062$

$\theta_{\max} = 27.0^\circ, \theta_{\min} = 3.5^\circ$

$h = -26 \rightarrow 26$

$k = -13 \rightarrow 13$

$l = -21 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.052$

$wR(F^2) = 0.104$

$S = 1.03$

3945 reflections

226 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.005$

$\Delta\rho_{\max} = 0.32 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.5000	0.05985 (5)	0.2500	0.04149 (18)
S1	0.57909 (4)	0.31202 (8)	0.36779 (5)	0.0424 (2)
S2	0.50021 (5)	0.43416 (10)	0.30940 (6)	0.0700 (3)
O1	0.56286 (11)	0.1942 (2)	0.32708 (14)	0.0652 (7)
O2	0.63916 (11)	0.3628 (3)	0.35902 (15)	0.0764 (8)
O3	0.57462 (13)	0.3140 (3)	0.44977 (13)	0.0748 (8)
N1	0.56672 (12)	0.0504 (2)	0.17879 (15)	0.0407 (6)
N2	0.45588 (12)	-0.0803 (2)	0.16141 (15)	0.0414 (7)
C1	0.62052 (16)	0.1225 (3)	0.18716 (19)	0.0474 (9)
H1	0.6283	0.1872	0.2249	0.057*
C2	0.66462 (16)	0.1058 (3)	0.1429 (2)	0.0513 (9)
H2	0.7013	0.1583	0.1510	0.062*
C3	0.65451 (15)	0.0105 (4)	0.0862 (2)	0.0480 (9)
C4	0.59720 (16)	-0.0613 (3)	0.07514 (18)	0.0442 (8)
H4	0.5875	-0.1243	0.0360	0.053*
C5	0.55459 (14)	-0.0400 (3)	0.12157 (17)	0.0359 (7)
C6	0.49276 (15)	-0.1152 (3)	0.11258 (18)	0.0383 (8)
C7	0.47340 (16)	-0.2104 (3)	0.05736 (18)	0.0460 (8)
H7	0.4997	-0.2311	0.0239	0.055*
C8	0.41503 (18)	-0.2761 (3)	0.05085 (19)	0.0508 (9)
C9	0.37809 (18)	-0.2399 (4)	0.1009 (2)	0.0598 (10)
H9	0.3384	-0.2811	0.0983	0.072*
C10	0.39926 (16)	-0.1432 (4)	0.1547 (2)	0.0535 (10)
H10	0.3732	-0.1204	0.1879	0.064*
C11	0.70261 (18)	-0.0158 (4)	0.0385 (2)	0.0716 (12)
H11A	0.7169	0.0605	0.0205	0.107*
H11B	0.6806	-0.0657	-0.0089	0.107*
H11C	0.7412	-0.0591	0.0732	0.107*
C12	0.3930 (2)	-0.3805 (4)	-0.0092 (2)	0.0785 (13)
H12A	0.4011	-0.4575	0.0203	0.118*

H12B	0.4181	-0.3785	-0.0480	0.118*
H12C	0.3458	-0.3726	-0.0383	0.118*
N3	0.19834 (13)	0.0609 (3)	0.18132 (16)	0.0491 (7)
O4	0.25600 (13)	-0.1184 (3)	0.19203 (19)	0.0871 (9)
C13	0.1478 (2)	0.1295 (4)	0.2038 (3)	0.0907 (15)
H13A	0.1326	0.0827	0.2426	0.136*
H13B	0.1104	0.1454	0.1552	0.136*
H13C	0.1665	0.2064	0.2285	0.136*
C14	0.2296 (2)	0.1193 (4)	0.1266 (2)	0.0809 (13)
H14A	0.2639	0.0660	0.1187	0.121*
H14B	0.2496	0.1959	0.1504	0.121*
H14C	0.1963	0.1349	0.0743	0.121*
C15	0.21530 (19)	-0.0527 (4)	0.2094 (2)	0.0590 (10)
H15	0.1940	-0.0848	0.2456	0.071*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0414 (3)	0.0397 (3)	0.0429 (3)	0.000	0.0122 (2)	0.000
S1	0.0429 (5)	0.0435 (5)	0.0397 (5)	-0.0051 (4)	0.0112 (4)	-0.0032 (4)
S2	0.0766 (7)	0.0627 (7)	0.0578 (6)	0.0251 (6)	0.0018 (5)	-0.0164 (5)
O1	0.0612 (15)	0.0436 (16)	0.0741 (16)	0.0018 (13)	-0.0036 (13)	-0.0181 (13)
O2	0.0464 (14)	0.096 (2)	0.0844 (18)	-0.0230 (15)	0.0161 (13)	0.0091 (17)
O3	0.104 (2)	0.080 (2)	0.0458 (14)	0.0132 (17)	0.0322 (14)	0.0081 (14)
N1	0.0386 (14)	0.0382 (17)	0.0420 (15)	-0.0071 (13)	0.0078 (12)	-0.0018 (13)
N2	0.0375 (15)	0.0397 (17)	0.0452 (15)	-0.0081 (13)	0.0103 (12)	-0.0017 (13)
C1	0.0432 (19)	0.042 (2)	0.051 (2)	-0.0081 (17)	0.0059 (17)	-0.0003 (17)
C2	0.0362 (19)	0.057 (3)	0.056 (2)	-0.0076 (18)	0.0079 (17)	0.0100 (19)
C3	0.0362 (18)	0.059 (2)	0.047 (2)	0.0035 (18)	0.0099 (16)	0.0205 (19)
C4	0.0483 (19)	0.046 (2)	0.0373 (17)	0.0021 (18)	0.0124 (15)	0.0014 (16)
C5	0.0353 (17)	0.036 (2)	0.0333 (16)	-0.0002 (15)	0.0052 (14)	0.0066 (14)
C6	0.0384 (18)	0.039 (2)	0.0339 (17)	0.0006 (16)	0.0051 (15)	0.0031 (15)
C7	0.050 (2)	0.042 (2)	0.0431 (18)	-0.0034 (18)	0.0097 (16)	-0.0043 (17)
C8	0.063 (2)	0.038 (2)	0.0419 (19)	-0.0115 (19)	0.0027 (18)	-0.0024 (17)
C9	0.052 (2)	0.057 (3)	0.062 (2)	-0.027 (2)	0.006 (2)	-0.003 (2)
C10	0.043 (2)	0.061 (3)	0.057 (2)	-0.0110 (19)	0.0164 (17)	0.002 (2)
C11	0.057 (2)	0.093 (3)	0.074 (3)	0.007 (2)	0.034 (2)	0.017 (2)
C12	0.101 (3)	0.049 (3)	0.069 (3)	-0.026 (2)	0.000 (2)	-0.009 (2)
N3	0.0466 (16)	0.0467 (19)	0.0539 (17)	-0.0067 (16)	0.0151 (14)	-0.0073 (16)
O4	0.0615 (18)	0.067 (2)	0.130 (3)	0.0112 (16)	0.0251 (18)	-0.0105 (19)
C13	0.070 (3)	0.067 (3)	0.141 (4)	0.004 (3)	0.042 (3)	-0.025 (3)
C14	0.089 (3)	0.085 (3)	0.071 (3)	-0.019 (3)	0.028 (2)	0.010 (2)
C15	0.055 (2)	0.062 (3)	0.057 (2)	-0.016 (2)	0.0125 (19)	-0.003 (2)

Geometric parameters (\AA , $^\circ$)

Zn1—O1	2.119 (2)	C7—C8	1.384 (4)
Zn1—O1 ⁱ	2.119 (2)	C7—H7	0.9300
Zn1—N1	2.109 (3)	C8—C9	1.368 (5)
Zn1—N1 ⁱ	2.109 (3)	C8—C12	1.497 (5)

Zn1—N2	2.136 (3)	C9—C10	1.370 (5)
Zn1—N2 ⁱ	2.136 (3)	C9—H9	0.9300
S1—O2	1.417 (2)	C10—H10	0.9300
S1—O3	1.424 (2)	C11—H11A	0.9600
S1—O1	1.442 (2)	C11—H11B	0.9600
S1—S2	2.1056 (13)	C11—H11C	0.9600
S2—S2 ⁱ	2.016 (2)	C12—H12A	0.9600
N1—C1	1.338 (4)	C12—H12B	0.9600
N1—C5	1.348 (4)	C12—H12C	0.9600
N2—C10	1.337 (4)	N3—C15	1.328 (4)
N2—C6	1.348 (4)	N3—C13	1.435 (4)
C1—C2	1.367 (4)	N3—C14	1.436 (4)
C1—H1	0.9300	O4—C15	1.211 (4)
C2—C3	1.383 (5)	C13—H13A	0.9600
C2—H2	0.9300	C13—H13B	0.9600
C3—C4	1.389 (4)	C13—H13C	0.9600
C3—C11	1.499 (4)	C14—H14A	0.9600
C4—C5	1.377 (4)	C14—H14B	0.9600
C4—H4	0.9300	C14—H14C	0.9600
C5—C6	1.493 (4)	C15—H15	0.9300
C6—C7	1.368 (4)		
N1—Zn1—N1 ⁱ	174.45 (15)	N2—C6—C5	115.0 (3)
N1—Zn1—O1	89.77 (10)	C7—C6—C5	123.0 (3)
N1 ⁱ —Zn1—O1	94.04 (10)	C6—C7—C8	120.5 (3)
N1—Zn1—O1 ⁱ	94.04 (10)	C6—C7—H7	119.7
N1 ⁱ —Zn1—O1 ⁱ	89.77 (10)	C8—C7—H7	119.7
O1—Zn1—O1 ⁱ	93.27 (13)	C9—C8—C7	116.9 (3)
N1—Zn1—N2	77.20 (10)	C9—C8—C12	121.8 (3)
N1 ⁱ —Zn1—N2	98.79 (10)	C7—C8—C12	121.3 (3)
O1—Zn1—N2	166.73 (9)	C8—C9—C10	120.4 (3)
O1 ⁱ —Zn1—N2	90.15 (9)	C8—C9—H9	119.8
N1—Zn1—N2 ⁱ	98.79 (10)	C10—C9—H9	119.8
N1 ⁱ —Zn1—N2 ⁱ	77.20 (10)	N2—C10—C9	122.8 (3)
O1—Zn1—N2 ⁱ	90.15 (9)	N2—C10—H10	118.6
O1 ⁱ —Zn1—N2 ⁱ	166.73 (9)	C9—C10—H10	118.6
N2—Zn1—N2 ⁱ	89.42 (14)	C3—C11—H11A	109.5
O2—S1—O3	115.04 (16)	C3—C11—H11B	109.5
O2—S1—O1	112.20 (17)	H11A—C11—H11B	109.5
O3—S1—O1	113.95 (17)	C3—C11—H11C	109.5
O2—S1—S2	107.08 (13)	H11A—C11—H11C	109.5
O3—S1—S2	100.03 (12)	H11B—C11—H11C	109.5
O1—S1—S2	107.26 (10)	C8—C12—H12A	109.5
S2 ⁱ —S2—S1	103.49 (7)	C8—C12—H12B	109.5
S1—O1—Zn1	155.98 (15)	H12A—C12—H12B	109.5
C1—N1—C5	117.7 (3)	C8—C12—H12C	109.5
C1—N1—Zn1	126.2 (2)	H12A—C12—H12C	109.5
C5—N1—Zn1	116.0 (2)	H12B—C12—H12C	109.5
C10—N2—C6	117.4 (3)	C15—N3—C13	121.4 (4)

C10—N2—Zn1	126.9 (2)	C15—N3—C14	121.1 (3)
C6—N2—Zn1	115.47 (19)	C13—N3—C14	117.5 (4)
N1—C1—C2	123.2 (3)	N3—C13—H13A	109.5
N1—C1—H1	118.4	N3—C13—H13B	109.5
C2—C1—H1	118.4	H13A—C13—H13B	109.5
C1—C2—C3	119.9 (3)	N3—C13—H13C	109.5
C1—C2—H2	120.1	H13A—C13—H13C	109.5
C3—C2—H2	120.1	H13B—C13—H13C	109.5
C2—C3—C4	116.9 (3)	N3—C14—H14A	109.5
C2—C3—C11	122.4 (3)	N3—C14—H14B	109.5
C4—C3—C11	120.8 (3)	H14A—C14—H14B	109.5
C5—C4—C3	120.6 (3)	N3—C14—H14C	109.5
C5—C4—H4	119.7	H14A—C14—H14C	109.5
C3—C4—H4	119.7	H14B—C14—H14C	109.5
N1—C5—C4	121.6 (3)	O4—C15—N3	125.9 (4)
N1—C5—C6	115.8 (3)	O4—C15—H15	117.1
C4—C5—C6	122.6 (3)	N3—C15—H15	117.1
N2—C6—C7	122.0 (3)		

Symmetry code: (i) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C4—H4 \cdots O3 ⁱⁱ	0.93	2.49	3.411 (4)	170
C7—H7 \cdots O3 ⁱⁱ	0.93	2.46	3.381 (4)	171
C10—H10 \cdots O4	0.93	2.47	3.250 (5)	142
C11—H11C \cdots O2 ⁱⁱⁱ	0.96	2.55	3.479 (5)	163
C12—H12A \cdots O3 ^{iv}	0.96	2.55	3.465 (5)	160
C13—H13C \cdots O4 ^v	0.96	2.59	3.525 (5)	166

Symmetry codes: (ii) $x, -y, z-1/2$; (iii) $-x+3/2, y-1/2, -z+1/2$; (iv) $-x+1, y-1, -z+1/2$; (v) $-x+1/2, y+1/2, -z+1/2$.

π - π contacts (\AA , $^\circ$) for (I) and (II)

Compound	Group 1/group 2	IPD (\AA)	CCD (\AA)	SA ($^\circ$)
(I)	Cg1 \cdots Cg2 ^v	1.08 (12)	4.1042 (13)	28.32 (12)
(II)	Cg1 \cdots Cg2 ^v	1.67 (15)	4.1745 (18)	30.0 (4)

Symmetry code: (v) $-x+1, -y, -z$. Notes: Cg1 is the centroid of the N1/C1—C5 ring and Cg2 that of the N2/C6—C10 ring. IPD is the interplanar distance, CCD is the centre-to-centre distance and SA is the slippage angle. For details, see Janiak (2000).