

"A strong intramolecular C—H···O bond leading to a bizarre molecular conformation."

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Abstract

Three complexes, formulated as Cd(pds)(DMPhen)₂, Zn(pds(TMPhen))₂ and Cd(pds(TMPhen))₂ are presented, where (pds): S₂O₈, peroxydisulfato, (DMPhen): C₁₄H₁₂N₂, 2,9-Dimethyl-1,10-phenanthroline; (TMPhen): C₁₆H₁₆N₂, 3,4,7,8-tetramethyl-1,10-phenanthroline. All three complexes present the same topological coordination, with three chelating ligands in a MN₄O₂ polyhedron (M=Zn, Cd). The main difference resides in that first two complexes are bisected by a twofold axis, providing thus a symmetrical environment to the cation, while in the third one this symmetry is disrupted into a clearly unsymmetrical disposition by way of an unusually strong C—H···O intramolecular bond. The situation is compared with similar interactions in the literature.

1. Introduction

In the last fifteen years we have made several contributions to the structural chemistry of group XII divalent cations, in particular Cd and Zn, complexed to the peroxydisulfate anion S₂O₈ (pds) and several bidentate, nitrogenated aromatic bases (nab). In all these cases, the basic general formula appeared to be *M*(pds)(nab)₂, plus the eventual inclusion of some water molecules, either coordinated or as a solvate (We summarize in Fig 1 details of these complexes, including the ones to be described in the present work). Even if too few structures to make any confident statistical analysis, the results suggested some kind of a trend between the size and/or methylated state of the nitrogenated base and the way the pds anion performed in coordination. Thus, for the smallest one, (nab) = 2,2'-bipyridine (Bpy), the structures obtained (I and II) showed two coordinated pds units in a bridging —O—S—O— mode. For the intermediate (nab) = 1,10-phenanthroline (Phen), one of these pds appears replaced by a (smaller) coordinated water molecule, while the bound pds acts as a pendant monocoordinated ligand (III and IV). Finally, at the beginning of this work we had at hand only one single example of a bulkier (nab) species, represented by (nab) = 2,9-Dimethyl-1,10-phenanthroline, (DMPhen) (V), where the single coordinated pds folds into itself to bind through both ends, acting in a chelating fashion. In order to go a bit further in this analysis we synthesized two new complexes of this sort, with *M* = Zn (VI) and *M* = Cd (VII), with a common, still larger (nab) ligand, 3,4,7,8-tetramethyl-1,10-phenanthroline (TMPhen). We shall see that they present the same topology as compound V, but with subtle, interesting differences regarding intramolecular interactions which we shall discuss in detail.

Since comparison with the DMPhen structure (V) will be an important part of the discussion, and taking into account that the available data in the correct space group *C2/c* (as disclosed in Marsh, 2004) come from an averaging process (without further refinement) of previous results in *Cc* by our team (Harvey *et al.*, 2001a), we indulge in including herein, for completeness, a fresh refinement in *C2/c* of the original data of this latter structure, in addition to the synthesis and crystal structure of the two new complexes, VI and VII. Even if in this discussion we shall restrict to the pds anion, it is

pertinent to state that the tetrathionate anion (S_4O_6) behaves in a rather similar way, and that the tetrathionate Zn and Cd complexes with (nab) = DMPhen = 4,4'-dimethyl, 1,10-bipyridine (Harvey *et al.*, 2013) are isostructural to their pds analogue V.

2. Experimental

2.1. Synthesis and crystallization

Compounds VI and VII were synthesized in a similar fashion: a solution (4 ml) containing 0.050 mmol (13.5 mg) of potassium peroxodisulfate and 0.100 mmol (23.6 mg) of tetramethyl phenanthroline (in a 3:1 methanol:water mixture) were added to 0.050 mmol of the corresponding metal acetate (ZnAc: 11.0 mg; CdAc: 13.3 mg). An initial precipitate of extremely small needles was readily digested, but in a few days a crop of single crystals suitable for X-ray diffraction were obtained, in the form of colorless blocks. For the synthesis of V see Harvey *et al.*, 2001a.

2.2. Refinement

Data for VI and VII were collected with an OXFORD GEMINI CCD diffractometer. Those for V (the same set used in the original publication, Harvey *et al.*, 2001a), were at the time gathered with a 4 circle diffractometer Siemens R3m. All the hydrogen atoms were found in a difference map, but further idealized and allowed to ride on their parent atoms with $(C-H)_{\text{arom}} = 0.93$, $(C-H)_{\text{methyl}} = 0.98\text{\AA}$, and $U_{\text{iso}}(H) = 1.2/1.5 \times U_{\text{equiv}}(\text{Host})$, respectively. For structure V a soft restraint in displacement factors was applied (RIGU in SHELXL-2014)

3. Results and discussion

Data collection details and refinement results for V, VI and VII are summarized in Table 1. Selected bond distances and angles are presented in Table 2.

The Zn complex VI crystallizes in Pbc_a, and the elemental unit is bisected by a twofold symmetry axis, with what only half of the molecule is independent ($z'=1/2$); even if in a different space group, these properties are shared by structure V. The Cd counterpart (VII), in turn, crystallizes in P-1 with a full molecule in the asymmetric unit.

All three compounds present a topologically similar molecular configuration (Figure 2) consisting in a central cation to which three (bidentate) chelating ligands bind, viz., two N,N'-aromatic bases and one O,O'-pds unit.

In particular, the "close" character of the pds anion tends to confirm the observed trend that methylated (bulkier) bases favour the chelating behaviour of pds.

Coordination distances in all three compounds are basically featureless, and agree with expected values for each cation-ligand pair. However, an interesting difference arises in the asymmetric way in which the ligands bind in VII, contrasting dramatically with the two-fold arrangement in V and VI, and we shall devote some time to analyze this behaviour.

The chelating character of the ligands involved induce highly distorted coordination polyhedra. Proof of this is presented in Table 1, which shows the departure of "trans" angles in V, VI and VII from their expected values of 180° for a regular octahedron. This makes the polyhedra difficult to classify, and impairs the description of coordination in terms of any regular model. In this regard all three compounds are suitable for the analysis via the Vectorial Bond Valence Model (VBVM) suggested by Harvey *et al.*, 2006, an approach tending to a simpler description of multidentate binding, in which the action of each ligand is integrated into a single interaction vector, or VBV (Vectorial Bond Valence), derived from the individual bond valences of the coordinating atoms. In particular, for this kind of three-ligand coordination geometry the VBVM predicts a nil resultant of the vectorial sum of the three VBV vectors, and, as a consequence, their disposition in a planar array.

The first condition is satisfactorily complied with a very short resultant for the Bond Valence Vectors (0.08, 0.03 and 0.08 valence units for V, VI and VII, respectively). The second requirement (planar array of vectors), applies *sensu stricto* in V and VI, due to the intrinsic two fold symmetry around the cation, and it falls well within experimental error in VII, where the calculated angles between Bond Valence vectors add up to $359.5 (3)^\circ$ and the plane defined by their extremes leave the Cd cation only $0.09 (2) \text{ \AA}$ aside.

As an unwitting bonus of this description, these planes appear as a natural reference frame for describing ligand orientations in the polyhedra, evidencing in V and VI their adherence to twofold symmetry and in VII significant departures from a symmetric arrangement. This can be visualized in Fig.3, where a schematic representation (with an exaggerated perspective) is made of the ligand bites (open lining) as well as the VBV representing their joint effect as a ligand, in full lining. At the left, the explanation of a group of angles helping to describe the orientation of the coordinations planes: angles labeled α give account of the angular separation in the plane between vectors, while those labeled ω measure the out-of-plane rotation of the coordination planes around the corresponding VBV vectors.

It is apparent, either by visual inspection of Fig.3 or through the analysis of the ω values (Table 6) that the coordination polyhedron in VII is abnormally distorted. Since this could be the result of packing strain (intermolecular interactions) or just due to genuine intramolecular forces, we shall first analyze (and compare) the three packing arrangements for V, VI and VII. The most relevant, non-covalent interactions involved are presented in Table 3 (H-bonds), Table 4 (π - π contacts) and Table 5 ($X-Y \cdots \pi$ contacts). The first column includes a code, which labels each interaction for easy reference; the last column, the role the interaction plays in packing. For the time being we shall leave aside intramolecular H-bonds (#1b, #2b and #1c), to be discussed later.

Figure 4 presents packing views of all three structures: it is apparent that in spite of crystallizing in different space groups, with different symmetry environments, the *leitmotives* are strictly the same, viz., $\pi \cdots \pi$ bound chains running along $[10\bar{1}]$ in V and $[001]$ in VI and VII, the link being the stacking interaction appearing in Table 4, which in all cases connect inversion related moieties. The remaining intermolecular interactions are weak and serve either to strengthen the link within the chains (marked as "intrachain" in the tables) or to weakly connect parallel chains with each other ("interchain") to end up defining weakly bound 3D structures. This description is valid for all three structures, and (short of a larger number of "intrachain" contacts) there is nothing special about packing interactions in VII as to ascribe them the responsibility for the coordination "anomaly".

It is thus time to analyze the internal (intramolecular) interactions, which we have postponed so far. The symmetric cases V and VI present different behaviours regarding these contacts. Methyl groups in 2,9 inhibit structure V to enter in any significant $(C-H)_{\text{arom}} \cdots O_{\text{pds}}$ intramolecular contact, as suggested in Fig 2 and disclosed in Table 3, where only weak, intermolecular ones are to be found. Structure VI, in turn, having sites 2 and 9 free, is amenable of a closer approach of $(C-H)_{\text{arom}}$ donors and O_{pds} acceptors, and in fact a pair of weak, bifurcated bonds set up (#1b and #2b, Fig 2 and Table 3).

But it is in structure VII where things deviate significantly from normal, with a strong $C-H \cdots O$ bond internally linking one of the TMPhen groups and the pds anion.

In order to evaluate how strong the interaction is, as compared with similar interactions in the literature, we made a search in the CSD of $(C-H)_{\text{arom}} \cdots O$ intramolecular bonds, with almost no restrictions (viz., $2 \text{ \AA} < H \cdots O < 2.6 \text{ \AA}$; $120^\circ < C-H \cdots O < 180^\circ$) The results (from ca 30000 entries analyzed) are quoted in Fig. 5, where the distance (a) and angle (b) histograms, as well as the combined scatterplot (c) are presented. The two H-bonds in VI, marked in cyan appear to be absolutely average, as are their structural consequences. The one in VII, instead (marked in red) appears endowed with a rather exceptional character, in particular its nearly "straight" $C-H \cdots O$ disposition.

Having disclosed that the interaction was statistically unusual (at least in geometrical terms), an immediate question to be made was how frequent this kind of disrupting behaviour was, among similar interactions. Some simplifying hypothesis had to be made on defining "similar interactions": the ones herein chosen were:

- (a) C—H···O intramolecular contacts, with H at least 10 atoms away from O.
- (b) $2.3 \text{ \AA} < \text{H}\cdots\text{O} < 2.5 \text{ \AA}$, $150^\circ < \text{C—H}\cdots\text{O} < 180^\circ$
- (c) The structure should be a Transition Metal complex.

This search provided around 750 hits. The analysis of the results (through individual visual inspection of most of the structures) disclosed that even if many interactions of the sort could be found in these complexes, the vast majority occurred between monocoordinated ligands or pendant groups, all of them with a free rotation at some point in the chain, which made the C—H···O contact almost irrelevant in terms of configurational energy. And this made clear that it was the chelating character of the ligands involved in VII, with the subsequent deformation of the coordination polyhedron, which made the case outstanding.

Summarizing:

The question if C—H···O contacts should be considered genuine interactions (able to determine conformation) or just a passive consequence of the latter has been a controversial issue since the early '60s, perhaps not yet fully resolved in spite of a number of good contributions devoted to the subject, somehow summarized in the classical *The Weak Hydrogen Bond*, by Desiraju & Steiner (1999). Recent results are in line with its real existence, both in the solid state (e.g. Jones *et al.*, 2012) as in solution (e.g., Donati *et al.*, 2002), but even so the ambiguity herein presented is still to be answered:

Either it is the (packing assisted) asymmetry with which ligand TMPhen binds Cd1 the reason allowing for an unusual closeness between C1—H1 and O7, giving room to a strong H-bond, or (the other way round) it is this H-bond the cause, and the asymmetric coordination its concomitant consequence.

We have presented solid arguments which sustain the latter hypothesis, that it is precisely the presence of this H-bond which disrupts the expected symmetrical geometry in the Cd(pds)(TMPhen)₂ unit, constituting thus a rare case of a non-conventional C—H···O bond being responsible of a surprising molecular configuration.

Table 1

Experimental details

	(V)	(VI)	(VII)
Crystal data			
Chemical formula	C ₂₈ H ₂₄ CdN ₄ O ₈ S ₂	C ₃₂ H ₃₂ N ₄ O ₈ S ₂ Zn	C ₃₂ H ₃₂ CdN ₄ O ₈ S ₂
<i>M</i> _r	721.03	730.10	777.13
Crystal system, space group	Monoclinic, <i>C2/c</i>	Orthorhombic, <i>Pbcn</i>	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	296	294	294
<i>a</i> , <i>b</i> , <i>c</i> (Å)	22.233 (12), 9.566 (5), 16.017 (8)	15.6244 (2), 10.8803 (2), 17.9446 (3)	8.601 (3), 11.063 (4), 16.932 (5)
α , β , γ (°)	90, 123.78 (3), 90	90, 90, 90	98.788 (5), 97.713 (5), 97.943 (5)
<i>V</i> (Å ³)	2831 (3)	3050.55 (9)	1557.0 (9)
<i>Z</i>	4	4	2
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.98	1.00	0.90
Crystal size (mm)	0.80 × 0.30 × 0.15	0.35 × 0.20 × 0.16	0.28 × 0.16 × 0.14

Data collection

Diffractometer	Siemens R3m diffractometer	Oxford Diffraction Gemini CCD S Ultra diffractometer	Oxford Diffraction Gemini CCD S Ultra diffractometer
Absorption correction	ψ scan P3/P4-PC version V4.27, Siemens (1991)	Multi-scan <i>CrysAlis PRO</i> , Oxford Diffraction (2009)	Multi-scan <i>CrysAlis PRO</i> , Oxford Diffraction (2009)
T_{\min} , T_{\max}	0.70, 0.88	0.76, 0.84	0.76, 0.84
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2562, 2495, 2300	63344, 3988, 3341	41025, 7888, 6692
R_{int}	0.040	0.049	0.057
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.595	0.688	0.696
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.027, 0.073, 1.11	0.033, 0.092, 1.04	0.033, 0.071, 1.07
No. of reflections	2495	3988	7888
No. of parameters	197	217	432
No. of restraints	195	0	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e \AA^{-3})	0.47, -0.41	0.47, -0.53	0.54, -0.57

Computer programs: P3/P4-PC version V4.27, Siemens (1991), *CrysAlis PRO* (Oxford Diffraction, 2009), *CrysAlis PRO*, *SHELXS97* (Sheldrick, 2008), *SHELXL2014/6* (Sheldrick, 2015), *SHELXTL* (Sheldrick, 2008), *SHELXL2014/6*, *PLATON* (Spek, 2009).

Table 2

Selected geometric parameters (\AA , $^\circ$) for V, VI and VII.

V			
Cd1—N2	2.307 (2)	N1—Cd1—N1 ⁱ	171.15 (10)
Cd1—O1	2.314 (2)	O1—Cd1—N2 ⁱ	161.06 (8)
Cd1—N1	2.409 (3)	O1 ⁱ —Cd1—N2	161.06 (8)
VI			
Zn1—N1	2.0950 (14)	N1—Zn1—N1 ⁱ	168.3 (2)
Zn1—O1	2.1476 (13)	N2—Zn1—O1 ⁱ	167.8 (2)
Zn1—N2	2.1853 (14)	N2 ⁱ —Zn1—O1	167.8 (2)
VII			
Cd1—N1	2.3075 (19)	O8—Cd1—N2	158.5 (2)
Cd1—N2	2.3278 (19)	N1—Cd1—N21	152.0 (2)
Cd1—O8	2.3232 (18)	N22—Cd1—O1	142.4 (2)
Cd1—N22	2.3304 (19)		
Cd1—N21	2.327 (2)		
Cd1—O1	2.3371 (19)		

Symmetry code for V and VI: (i) -x, y, -z+1/2.

Table 3

Hydrogen-bond geometry (Å, °) for V, VI and VII.

Structure	Label	D—H···A	D—H	H···A	D···A	D—H···A	Character
V	#1a	C3-H3···O3 ⁱⁱ	0.93	2.54	3.228 (5)	131	Interchain
	#2a	C14-H14B···O2 ⁱⁱⁱ	0.96	2.45	3.397 (5)	167	Interchain
	#3a	C14-H14C···O2 ^{iv}	0.96	2.54	3.331 (5)	140	Interchain
VI	#1b	C1—H1···O1 ⁱ	0.93	2.53	3.117 (2)	121	Intramolecular
	#2b	C1—H1···O2 ⁱ	0.93	2.45	3.286 (2)	150	Intramolecular
	#3b	C15—H15B···O3 ⁱⁱ	0.96	2.51	3.451 (2)	166	Interchain
	#4b	C13—H13B···O2 ⁱⁱⁱ	0.96	2.59	3.324 (2)	133	Interchain
	#5b	C16—H16B···O2 ^{iv}	0.96	2.59	3.543 (3)	172	Interchain
	#6b	C13—H13A···Cg3 ^v	0.96	2.73	3.9857	127	Interchain
VII	#1c	C1—H1···O7	0.93	2.37	3.296 (3)	171	Intramolecular
	#2c	C26—H26···O2 ⁱ	0.93	2.29	3.204 (3)	165	Intrachain
	#3c	C15—H15B···Cg1 ^{iv}	0.96	2.89	3.578 (4)	129	Intrachain
	#4c	C34—H34C···Cg4 ⁱ	0.96	2.88	3.599 (3)	133	Intrachain
	#5c	C36—H36B···O6 ⁱⁱ	0.96	2.47	3.165 (4)	130	Interchain
	#6c	C13—H13A···Cg1 ⁱⁱⁱ	0.96	2.93	3.607 (4)	128	Interchain
	#7c	C35—H35C···Cg6 ^v	0.96	2.69	3.604 (4)	158	Interchain

General Ring Codes (all structures): Cg1:N1,C1,C2,C3,C4,C12; Cg2: N2,C10,C9,C8,C7,C11; Cg3 = C4,C5,C6,C7,C11,C12:

Cg4:N21,C21,C22,C23,C24,C32; Cg5:N22,C30,C29,C28,C27,C31; Cg6:C24,C25,C26,C27,C31,C32 Symmetry codes for V: (ii) 1/2-x,-1/2-y,1-z; (iii) -x,-y,-z; (iv) x,1+y,z Symmetry codes for VI: (i) -x, y, -z+1/2; (ii) x, y-1, z; (iii) x+1/2, y-1/2, -z+1/2; (iv) -x-1/2, y-1/2, z; (v) -x+1/2, y+1/2, z. Symmetry codes for VII: (i) -x+1, -y+1, -z+2; (ii) x+1, y, z; (iii) -x+1, -y, -z+1; (iv) -x+1, -y+1, -z+1; (v) -x+2, -y+1, -z+2.

Table 4

π - π contacts (Å, °) for V, VI and VII.

Structure	Label	Cg···Cg	ccd	da	sa	ipd	Character
V	#4a	Cg1···Cg3 ^v	3.823 (3)	0.95 (14)	15.0(1.6)	3.69 (3)	Intrachain
VI	#7b	Cg2···Cg3 ^{vi}	3.8101 (10)	2.34 (8)	25.5 (7)	3.44 (2)	Intrachain
VII	#8c	Cg2···Cg3 ^v	3.737 (3)	0.9 (2)	21.3 (7)	3.48 (2)	Intrachain
	#9c	Cg3···Cg3 ^v	3.717 (3)	0	21.5	3.4577 (9)	Intrachain

#10c	Cg4...Cg6 ^{vi}	3.700 (2)	0.6 (2)	21.8 (3)	3.43 (2)	Intrachain
#11c	Cg6...Cg6 ^{vi}	3.669 (2)	0	20.9	3.4269 (9)	Intrachain

ccd: center-to-center distance; da: dihedral angle between planes, sa: slippage angle (average angle subtended by the intercentroid vector to the plane normal), ipd: interplanar distance (average distance from one plane to the neighbouring centroid); For details, see Janiak (2000). Symmetry codes for V: (v) 1/2-x, 1/2-y, 1-z Symmetry codes for VI: (vi) = -x, -y, -z Symmetry codes for VII: (v) = 1-x, 1-y, 1-z; (vi) = 1-x, 1-y, 2-z;

Table 5

X-Y... π contacts (\AA , $^\circ$) for V and VII.

Structure	Label	X-Y...Cg	Y...Cg	Y...Cg _{perp}	X-Y...Cg	Character
V	#5a	S1-O3...Cg1	3.568 (4)	3.475 (15)	105.0 (2)	Intramolecular
VII	#12c	S1-O3...Cg2 ^{vii}	3.102 (3)	3.013	112.9 (2)	Interchain

Symmetry codes for VII: (vii) -1+x, y, z

Table 6

Distortion angles as defined in Fig 3 ($^\circ$).

Angle	V	VI	VIII
α_1	111.1	116.7	119.0
α_2	111.1	116.7	111.0
α_3	137.9	126.6	129.4
ω_1	49.0	67.5	71.1
ω_2	55.9	55.8	27.0
ω_3	55.9	55.8	84.7

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References

- Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond*, Oxford University Press.
- Díaz de Vivar, M. E., Harvey, M. A., Garland, M. T., Baggio, S. & Baggio, R. (2005). *Acta Cryst.* **C61**, m240–m244.
- Donati, A., Ristori, S., Bonechi, C., Panza, L., Martini, G. & Rossi, C. (2002). *J. Am. Chem. Soc.*, **124**, 8778–8779
- Harvey, M. A., Baggio, S. & Baggio, R. (2006). *Acta Cryst.* **B62**, 1038–1042.
- Harvey, M. A., Baggio, S., Garland, M. T. & Baggio, R. (2001*b*). *Aust. J. Chem.* **54**, 711–716.
- Harvey, M. A., Baggio, S., Garland, M. T., Burton, G. & Baggio, R. (2001*a*). *Aust. J. Chem.* **54**, 307–311.
- Harvey, M. A., Díaz de Vivar, M. E., Baggio, R. & Baggio, S. (2011). *J. Chem. Crystallogr.* **41**, 1717–1721.
- Harvey, M. A., Suarez, S., Doctorovich, F. & Baggio, R. (2013). *Acta Cryst.* **C69**, 745–749.
- Janiak, C. (2000). *J. Chem. Soc., Dalton Trans.*, pp. 3885–3898.
- Jones, C. R., Baruah, P. K., Thompson, A. L., Scheiner, S. & Smith, M. D. (2012). *J. Am. Chem. Soc.* **134**, 12064–12071.

Marsh, R. E. (2004). *Acta Cryst.* B60, 252-253.

Oxford Diffraction (2009). *CrysAlis PRO*, version 171.33.48. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

Sheldrick, G. M. (2008). *Acta Cryst.* A64, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C71, 5–8.

Siemens (1991). *P3/P4-PC Diffractometer Program*. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Spek, A. L. (2009). *Acta Cryst.* D65, 148–155.

Figure 1

The different coordination modes in the $M(\text{pds})(\text{nab})_2$ family. **I:** $\{[\text{Cd}(\text{pds})(\text{Bpy})_2]\}_n$; P-1 (Harvey *et al.*, 2001*b*); **II:** $\{[\text{Hg}(\text{pds})(\text{Bpy})_2]\}_n$; $P2_1/n$ (Díaz de Vivar *et al.*, 2005), **III:** $\text{Cd}(\text{pds})(\text{Phen})_2(\text{H}_2\text{O})$, P-1, (Harvey *et al.*, 2001*a*); **IV:** $\text{Zn}(\text{pds})(\text{Phen})_2(\text{H}_2\text{O})$, P-1, (Harvey *et al.*, 2011); **V:** $\text{Cd}(\text{pds})(\text{DMPhen})_2$, C2/c (Harvey *et al.*, 2001*a*; Marsh, 2004 and This work); **VI:** $\text{Zn}(\text{pds})(\text{TMPhen})_2$, P-1, This work; **VII:** $\text{Cd}(\text{pds})(\text{TMPhen})_2$, *Pbcn*, This work. Ligand code: Bpy = 2,2'-bipyridine; Phen = 1,10-phenanthroline, DMPhen = 2,9-Dimethyl-1,10-phenanthroline, TMPhen = 3,4,7,8-tetramethyl-1,10-phenanthroline.

Figure 2

Ellipsoid plots of V, VI and VII, drawn at a 50% probability level.

Figure 3

Schematic representation of the ligands distortion. In open bonds, the chelating ligands, (drawn as connected to each other, for clarity); in full line, the VB vectors, representing the integrated action of each ligand. Angle codes explained in the text.

Figure 4

The π bonded 1D leitmotives in all three structures. Stacking interactions labeled as in Table 4.

Figure 5

Statistical analysis of intramolecular $(\text{C-H})_{\text{arom}} \cdots \text{O}$ bonds as found in the literature. In cyan, those found in VI; in red, the one in VII.

supporting information

"A strong intramolecular C–H···O bond leading to a bizarre molecular conformation."

Miguel Angel Harvey,* Sebastián Suarez and Ricardo Baggio

Computing details

Data collection: P3/P4-PC version V4.27, Siemens (1991) for (V); *CrysAlis PRO* (Oxford Diffraction, 2009) for (VI), (VII). Cell refinement: P3/P4-PC version V4.27, Siemens (1991) for (V); *CrysAlis PRO* for (VI), (VII). Data reduction: P3/P4-PC version V4.27, Siemens (1991) for (V); *CrysAlis PRO* for (VI), (VII). For all compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014/6* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL2014/6*, *PLATON* (Spek, 2009).

(V)*Crystal data*

$C_{28}H_{24}CdN_4O_8S_2$
 $M_r = 721.03$
 Monoclinic, *C2/c*
 $a = 22.233$ (12) Å
 $b = 9.566$ (5) Å
 $c = 16.017$ (8) Å
 $\beta = 123.78$ (3)°
 $V = 2831$ (3) Å³
 $Z = 4$

$F(000) = 1456$
 $D_x = 1.691$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 40 reflections
 $\theta = 7.5$ – 15°
 $\mu = 0.98$ mm⁻¹
 $T = 296$ K
 Block, colourless
 0.80 × 0.30 × 0.15 mm

Data collection

Siemens R3m
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 P3/P4-PC version V4.27, Siemens (1991)
 $T_{\min} = 0.70$, $T_{\max} = 0.88$
 2562 measured reflections

2495 independent reflections
 2300 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$
 $\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 2.2^\circ$
 $h = 0 \rightarrow 26$
 $k = 0 \rightarrow 11$
 $l = -19 \rightarrow 15$
 2 standard reflections every 98 reflections
 intensity decay: 2%

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.073$
 $S = 1.11$
 2495 reflections
 197 parameters
 195 restraints

Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 2.2422P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.47$ e Å⁻³
 $\Delta\rho_{\min} = -0.41$ e Å⁻³

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	0.0000	0.08973 (3)	0.2500	0.02566 (11)
S1	0.07113 (5)	-0.23114 (8)	0.22102 (7)	0.0491 (2)
O1	0.04563 (12)	-0.0900 (2)	0.20412 (17)	0.0433 (5)
O2	0.04309 (19)	-0.3067 (3)	0.1303 (2)	0.0819 (9)
O3	0.14664 (16)	-0.2448 (4)	0.2948 (2)	0.0944 (10)
O4	0.04040 (15)	-0.3065 (3)	0.2828 (2)	0.0699 (8)
N1	0.11739 (11)	0.0703 (2)	0.40497 (16)	0.0289 (4)
N2	0.08013 (11)	0.2280 (2)	0.23846 (16)	0.0278 (4)
C1	0.13651 (16)	0.0027 (3)	0.4888 (2)	0.0378 (6)
C2	0.20758 (18)	-0.0459 (4)	0.5553 (2)	0.0518 (8)
H2	0.2192	-0.0960	0.6122	0.062*
C3	0.25910 (17)	-0.0202 (4)	0.5371 (2)	0.0504 (7)
H3	0.3057	-0.0549	0.5801	0.060*
C4	0.24159 (15)	0.0594 (3)	0.4528 (2)	0.0376 (6)
C5	0.29429 (16)	0.0998 (3)	0.4334 (3)	0.0451 (7)
H5	0.3417	0.0686	0.4758	0.054*
C6	0.27702 (15)	0.1821 (3)	0.3550 (2)	0.0460 (7)
H6	0.3125	0.2076	0.3443	0.055*
C7	0.20481 (14)	0.2306 (3)	0.2885 (2)	0.0360 (6)
C8	0.18446 (17)	0.3241 (3)	0.2091 (3)	0.0473 (7)
H8	0.2188	0.3552	0.1974	0.057*
C9	0.11524 (18)	0.3689 (3)	0.1499 (3)	0.0479 (7)
H9	0.1025	0.4334	0.0991	0.057*
C10	0.06267 (15)	0.3185 (3)	0.1647 (2)	0.0344 (6)
C11	0.15031 (13)	0.1874 (3)	0.30242 (19)	0.0267 (5)
C12	0.16911 (14)	0.1021 (3)	0.3876 (2)	0.0282 (5)
C13	0.08122 (18)	-0.0186 (4)	0.5129 (2)	0.0529 (8)
H13A	0.0432	0.0490	0.4773	0.079*
H13B	0.1035	-0.0075	0.5838	0.079*
H13C	0.0614	-0.1110	0.4931	0.079*
C14	-0.01427 (16)	0.3639 (3)	0.0986 (2)	0.0431 (7)
H14A	-0.0436	0.3085	0.1126	0.065*
H14B	-0.0306	0.3519	0.0295	0.065*
H14C	-0.0181	0.4607	0.1109	0.065*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.02103 (15)	0.02505 (15)	0.03202 (16)	0.000	0.01544 (12)	0.000
S1	0.0680 (5)	0.0367 (4)	0.0609 (5)	0.0191 (4)	0.0471 (4)	0.0096 (3)
O1	0.0568 (13)	0.0337 (10)	0.0519 (12)	0.0094 (8)	0.0380 (11)	0.0020 (8)
O2	0.139 (3)	0.0502 (14)	0.0877 (16)	-0.0057 (16)	0.0822 (17)	-0.0174 (13)
O3	0.0681 (14)	0.120 (3)	0.0945 (19)	0.0418 (15)	0.0448 (13)	0.0377 (18)
O4	0.0990 (19)	0.0534 (14)	0.0872 (19)	0.0259 (13)	0.0703 (17)	0.0269 (13)
N1	0.0253 (9)	0.0300 (11)	0.0295 (9)	0.0008 (8)	0.0141 (8)	0.0000 (8)
N2	0.0260 (9)	0.0255 (10)	0.0333 (10)	-0.0022 (7)	0.0174 (8)	-0.0011 (8)
C1	0.0420 (13)	0.0373 (14)	0.0302 (11)	-0.0003 (10)	0.0176 (10)	0.0023 (10)
C2	0.0444 (13)	0.0607 (19)	0.0385 (15)	0.0076 (12)	0.0158 (11)	0.0121 (14)

C3	0.0363 (14)	0.0574 (18)	0.0426 (14)	0.0092 (13)	0.0127 (12)	0.0083 (13)
C4	0.0254 (11)	0.0390 (14)	0.0390 (12)	0.0040 (9)	0.0121 (9)	-0.0051 (10)
C5	0.0246 (12)	0.0519 (17)	0.0529 (15)	0.0008 (11)	0.0180 (12)	-0.0072 (12)
C6	0.0285 (12)	0.0529 (16)	0.0584 (15)	-0.0030 (11)	0.0252 (11)	-0.0071 (12)
C7	0.0308 (11)	0.0348 (13)	0.0496 (13)	-0.0071 (9)	0.0270 (10)	-0.0071 (11)
C8	0.0467 (14)	0.0466 (16)	0.0616 (16)	-0.0057 (12)	0.0382 (13)	0.0037 (13)
C9	0.0499 (13)	0.0442 (16)	0.0602 (18)	-0.0026 (11)	0.0372 (13)	0.0136 (14)
C10	0.0387 (12)	0.0275 (12)	0.0384 (12)	-0.0024 (9)	0.0224 (10)	0.0036 (10)
C11	0.0241 (10)	0.0243 (11)	0.0324 (11)	-0.0032 (8)	0.0161 (8)	-0.0065 (9)
C12	0.0252 (10)	0.0259 (11)	0.0321 (11)	-0.0014 (8)	0.0150 (9)	-0.0056 (9)
C13	0.0528 (17)	0.069 (2)	0.0405 (17)	-0.0018 (16)	0.0284 (15)	0.0095 (16)
C14	0.0409 (14)	0.0390 (15)	0.0449 (16)	0.0026 (11)	0.0211 (12)	0.0121 (13)

Geometric parameters (Å, °) for (V)

Cd1—N2	2.307 (2)	C1—C2	1.405 (4)
Cd1—N2 ⁱ	2.308 (2)	C1—C13	1.494 (4)
Cd1—O1 ⁱ	2.314 (2)	C2—C3	1.352 (5)
Cd1—O1	2.314 (2)	C3—C4	1.404 (4)
Cd1—N1	2.409 (3)	C4—C12	1.408 (4)
Cd1—N1 ⁱ	2.409 (3)	C4—C5	1.422 (4)
S1—O2	1.419 (3)	C5—C6	1.344 (5)
S1—O3	1.423 (3)	C6—C7	1.423 (4)
S1—O1	1.431 (2)	C7—C8	1.407 (4)
S1—O4	1.648 (3)	C7—C11	1.411 (4)
O4—O4 ⁱ	1.494 (6)	C8—C9	1.352 (5)
N1—C1	1.329 (3)	C9—C10	1.402 (4)
N1—C12	1.359 (4)	C10—C14	1.491 (4)
N2—C10	1.336 (3)	C11—C12	1.438 (4)
N2—C11	1.363 (3)		
N2—Cd1—N2 ⁱ	110.03 (11)	C10—N2—Cd1	125.77 (17)
N2—Cd1—O1 ⁱ	161.06 (8)	C11—N2—Cd1	112.87 (16)
N2 ⁱ —Cd1—O1 ⁱ	84.62 (8)	N1—C1—C2	121.3 (3)
N2—Cd1—O1	84.62 (8)	N1—C1—C13	118.7 (3)
N2 ⁱ —Cd1—O1	161.06 (8)	C2—C1—C13	119.9 (3)
O1 ⁱ —Cd1—O1	84.03 (11)	C3—C2—C1	120.4 (3)
N2—Cd1—N1	71.60 (8)	C2—C3—C4	119.4 (3)
N2 ⁱ —Cd1—N1	113.83 (8)	C3—C4—C12	117.5 (3)
O1 ⁱ —Cd1—N1	91.75 (8)	C3—C4—C5	122.4 (3)
O1—Cd1—N1	81.65 (8)	C12—C4—C5	120.1 (3)
N2—Cd1—N1 ⁱ	113.83 (8)	C6—C5—C4	121.4 (3)
N2 ⁱ —Cd1—N1 ⁱ	71.61 (8)	C5—C6—C7	120.5 (3)
O1 ⁱ —Cd1—N1 ⁱ	81.65 (8)	C8—C7—C11	117.1 (3)
O1—Cd1—N1 ⁱ	91.75 (8)	C8—C7—C6	123.1 (3)
N1—Cd1—N1 ⁱ	171.15 (10)	C11—C7—C6	119.7 (3)
O2—S1—O3	116.6 (2)	C9—C8—C7	120.3 (3)
O2—S1—O1	112.62 (17)	C8—C9—C10	120.2 (3)
O3—S1—O1	113.85 (19)	N2—C10—C9	120.9 (3)
O2—S1—O4	107.39 (17)	N2—C10—C14	118.2 (2)
O3—S1—O4	98.78 (18)	C9—C10—C14	121.0 (3)

O1—S1—O4	105.86 (13)	N2—C11—C7	121.5 (2)
S1—O1—Cd1	146.99 (14)	N2—C11—C12	118.8 (2)
O4 ⁱ —O4—S1	108.4 (2)	C7—C11—C12	119.6 (2)
C1—N1—C12	118.9 (2)	N1—C12—C4	122.2 (3)
C1—N1—Cd1	129.28 (18)	N1—C12—C11	119.2 (2)
C12—N1—Cd1	109.09 (17)	C4—C12—C11	118.5 (2)
C10—N2—C11	119.8 (2)		
O2—S1—O1—Cd1	135.8 (3)	C11—N2—C10—C14	-178.0 (2)
O3—S1—O1—Cd1	-88.7 (3)	Cd1—N2—C10—C14	17.2 (4)
O4—S1—O1—Cd1	18.7 (3)	C8—C9—C10—N2	1.4 (5)
O2—S1—O4—O4 ⁱ	-57.55 (19)	C8—C9—C10—C14	-178.5 (3)
O3—S1—O4—O4 ⁱ	-179.04 (19)	C10—N2—C11—C7	-4.8 (4)
O1—S1—O4—O4 ⁱ	62.98 (17)	Cd1—N2—C11—C7	161.95 (19)
C12—N1—C1—C2	-5.1 (4)	C10—N2—C11—C12	173.3 (2)
Cd1—N1—C1—C2	154.1 (2)	Cd1—N2—C11—C12	-19.9 (3)
C12—N1—C1—C13	173.6 (3)	C8—C7—C11—N2	3.7 (4)
Cd1—N1—C1—C13	-27.3 (4)	C6—C7—C11—N2	-177.9 (3)
N1—C1—C2—C3	2.4 (5)	C8—C7—C11—C12	-174.4 (2)
C13—C1—C2—C3	-176.2 (3)	C6—C7—C11—C12	4.0 (4)
C1—C2—C3—C4	2.0 (5)	C1—N1—C12—C4	3.4 (4)
C2—C3—C4—C12	-3.5 (5)	Cd1—N1—C12—C4	-159.6 (2)
C2—C3—C4—C5	174.9 (3)	C1—N1—C12—C11	-173.7 (2)
C3—C4—C5—C6	-176.5 (3)	Cd1—N1—C12—C11	23.2 (3)
C12—C4—C5—C6	1.9 (5)	C3—C4—C12—N1	0.9 (4)
C4—C5—C6—C7	-0.4 (5)	C5—C4—C12—N1	-177.6 (3)
C5—C6—C7—C8	175.8 (3)	C3—C4—C12—C11	178.0 (3)
C5—C6—C7—C11	-2.5 (5)	C5—C4—C12—C11	-0.4 (4)
C11—C7—C8—C9	-0.1 (5)	N2—C11—C12—N1	-3.4 (3)
C6—C7—C8—C9	-178.4 (3)	C7—C11—C12—N1	174.7 (2)
C7—C8—C9—C10	-2.4 (5)	N2—C11—C12—C4	179.4 (2)
C11—N2—C10—C9	2.2 (4)	C7—C11—C12—C4	-2.5 (4)
Cd1—N2—C10—C9	-162.7 (2)		

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

(VI)

Crystal data

$C_{32}H_{32}N_4O_8S_2Zn$

$M_r = 730.10$

Orthorhombic, $Pbcn$

$a = 15.6244$ (2) Å

$b = 10.8803$ (2) Å

$c = 17.9446$ (3) Å

$V = 3050.55$ (9) Å³

$Z = 4$

$F(000) = 1512$

$D_x = 1.590$ Mg m⁻³

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

$\mu = 1.00$ mm⁻¹

$T = 294$ K

Blocks, colorless

$0.35 \times 0.20 \times 0.16$ mm

Data collection

Oxford Diffraction Gemini CCD S Ultra
diffractometer

ω scans, thick slices

Absorption correction: multi-scan

CrysAlis PRO, Oxford Diffraction (2009)

$T_{\min} = 0.76$, $T_{\max} = 0.84$

63344 measured reflections

3988 independent reflections
 3341 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$
 $\theta_{\text{max}} = 29.3^\circ$, $\theta_{\text{min}} = 3.8^\circ$

$h = -21 \rightarrow 21$
 $k = -14 \rightarrow 14$
 $l = -23 \rightarrow 23$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.092$
 $S = 1.04$
 3988 reflections
 217 parameters
 0 restraints

Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0436P)^2 + 2.8456P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.47 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.53 \text{ e } \text{\AA}^{-3}$

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.0000	0.15234 (2)	0.2500	0.01734 (9)
S1	-0.07734 (3)	0.42233 (4)	0.17271 (2)	0.02274 (11)
O1	-0.05400 (9)	0.29339 (12)	0.18073 (7)	0.0249 (3)
O2	-0.15306 (9)	0.45546 (14)	0.21252 (9)	0.0374 (4)
O3	-0.06987 (11)	0.46565 (14)	0.09785 (8)	0.0389 (4)
O4	0.00284 (9)	0.50125 (14)	0.20933 (8)	0.0313 (3)
N1	0.11590 (9)	0.13279 (13)	0.19251 (8)	0.0190 (3)
N2	-0.03181 (10)	0.01731 (13)	0.16421 (8)	0.0191 (3)
C1	0.18924 (11)	0.18781 (16)	0.20877 (10)	0.0217 (3)
H1	0.1887	0.2477	0.2458	0.026*
C2	0.26765 (11)	0.16206 (16)	0.17409 (10)	0.0211 (4)
C3	0.26914 (11)	0.07603 (16)	0.11707 (10)	0.0223 (4)
C4	0.19057 (11)	0.01752 (16)	0.09742 (10)	0.0210 (3)
C5	0.18323 (13)	-0.07255 (17)	0.03903 (10)	0.0262 (4)
H5	0.2314	-0.0919	0.0109	0.031*
C6	0.10858 (13)	-0.12971 (17)	0.02393 (10)	0.0253 (4)
H6	0.1067	-0.1873	-0.0143	0.030*
C7	0.03198 (12)	-0.10420 (16)	0.06522 (10)	0.0208 (3)
C8	-0.04694 (13)	-0.16591 (16)	0.05399 (10)	0.0226 (4)
C9	-0.11588 (12)	-0.13397 (17)	0.09853 (10)	0.0242 (4)
C10	-0.10495 (12)	-0.04113 (16)	0.15199 (10)	0.0227 (4)
H10	-0.1521	-0.0192	0.1807	0.027*
C11	0.03636 (11)	-0.01425 (15)	0.12169 (9)	0.0186 (3)
C12	0.11614 (11)	0.04729 (15)	0.13729 (9)	0.0182 (3)
C13	0.34554 (12)	0.22736 (18)	0.20309 (11)	0.0265 (4)
H13A	0.3835	0.2454	0.1624	0.040*
H13B	0.3744	0.1758	0.2385	0.040*
H13C	0.3286	0.3026	0.2268	0.040*
C14	0.35083 (13)	0.0417 (2)	0.07834 (12)	0.0320 (4)

supporting information

H14A	0.3946	0.1000	0.0909	0.048*
H14B	0.3419	0.0420	0.0254	0.048*
H14C	0.3683	-0.0389	0.0940	0.048*
C15	-0.05618 (14)	-0.26544 (18)	-0.00342 (11)	0.0301 (4)
H15A	-0.1114	-0.2593	-0.0266	0.045*
H15B	-0.0507	-0.3443	0.0202	0.045*
H15C	-0.0123	-0.2564	-0.0405	0.045*
C16	-0.20162 (13)	-0.1962 (2)	0.09203 (12)	0.0350 (5)
H16A	-0.2241	-0.1837	0.0428	0.052*
H16B	-0.2403	-0.1620	0.1280	0.052*
H16C	-0.1951	-0.2827	0.1011	0.052*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.01923 (15)	0.01694 (15)	0.01584 (15)	0.000	0.00453 (10)	0.000
S1	0.0253 (2)	0.0201 (2)	0.0228 (2)	-0.00006 (16)	-0.00201 (17)	0.00241 (16)
O1	0.0321 (7)	0.0201 (6)	0.0225 (6)	0.0026 (5)	0.0000 (5)	0.0021 (5)
O2	0.0297 (8)	0.0318 (8)	0.0506 (10)	0.0035 (6)	0.0052 (7)	-0.0070 (7)
O3	0.0524 (10)	0.0348 (8)	0.0294 (8)	-0.0018 (7)	-0.0063 (7)	0.0121 (6)
O4	0.0350 (7)	0.0312 (7)	0.0276 (8)	-0.0083 (6)	-0.0022 (6)	0.0049 (6)
N1	0.0217 (7)	0.0183 (7)	0.0170 (7)	0.0003 (6)	0.0040 (6)	0.0000 (5)
N2	0.0221 (7)	0.0172 (7)	0.0179 (7)	0.0002 (6)	0.0029 (6)	0.0003 (5)
C1	0.0242 (9)	0.0183 (8)	0.0226 (9)	-0.0003 (7)	0.0050 (7)	-0.0015 (6)
C2	0.0211 (9)	0.0194 (8)	0.0228 (8)	0.0002 (6)	0.0039 (7)	0.0037 (6)
C3	0.0234 (9)	0.0207 (8)	0.0226 (8)	0.0042 (7)	0.0052 (7)	0.0037 (7)
C4	0.0238 (8)	0.0191 (8)	0.0200 (8)	0.0037 (7)	0.0050 (7)	0.0011 (6)
C5	0.0309 (10)	0.0252 (9)	0.0226 (9)	0.0058 (8)	0.0084 (7)	-0.0039 (7)
C6	0.0336 (10)	0.0221 (9)	0.0203 (9)	0.0046 (7)	0.0050 (7)	-0.0044 (7)
C7	0.0284 (9)	0.0169 (8)	0.0170 (8)	0.0028 (7)	0.0011 (7)	0.0014 (6)
C8	0.0322 (10)	0.0171 (8)	0.0185 (8)	0.0002 (7)	-0.0020 (7)	0.0006 (6)
C9	0.0287 (9)	0.0226 (9)	0.0212 (9)	-0.0028 (7)	-0.0014 (7)	0.0000 (7)
C10	0.0234 (8)	0.0227 (8)	0.0220 (8)	-0.0007 (7)	0.0030 (7)	0.0013 (7)
C11	0.0233 (8)	0.0163 (8)	0.0161 (8)	0.0021 (6)	0.0017 (6)	0.0015 (6)
C12	0.0236 (8)	0.0154 (7)	0.0156 (7)	0.0022 (6)	0.0031 (6)	0.0026 (6)
C13	0.0233 (9)	0.0252 (9)	0.0310 (10)	-0.0019 (7)	0.0045 (7)	0.0011 (7)
C14	0.0245 (9)	0.0356 (11)	0.0357 (11)	0.0023 (8)	0.0088 (8)	-0.0079 (9)
C15	0.0402 (11)	0.0245 (9)	0.0257 (9)	-0.0019 (8)	-0.0026 (8)	-0.0061 (7)
C16	0.0317 (10)	0.0402 (12)	0.0330 (11)	-0.0102 (9)	0.0006 (9)	-0.0098 (9)

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

Zn1—N1	2.0950 (14)	C5—H5	0.9300
Zn1—N1 ⁱ	2.0951 (14)	C6—C7	1.435 (3)
Zn1—O1 ⁱ	2.1476 (13)	C6—H6	0.9300
Zn1—O1	2.1476 (13)	C7—C11	1.410 (2)
Zn1—N2 ⁱ	2.1853 (14)	C7—C8	1.418 (3)
Zn1—N2	2.1853 (14)	C8—C9	1.385 (3)
S1—O2	1.4281 (15)	C8—C15	1.502 (2)
S1—O3	1.4285 (15)	C9—C10	1.404 (3)
S1—O1	1.4567 (13)	C9—C16	1.506 (3)

supporting information

S1—O4	1.6548 (15)	C10—H10	0.9300
O4—O4 ⁱ	1.462 (3)	C11—C12	1.442 (2)
N1—C1	1.325 (2)	C13—H13A	0.9600
N1—C12	1.359 (2)	C13—H13B	0.9600
N2—C10	1.326 (2)	C13—H13C	0.9600
N2—C11	1.354 (2)	C14—H14A	0.9600
C1—C2	1.402 (2)	C14—H14B	0.9600
C1—H1	0.9300	C14—H14C	0.9600
C2—C3	1.387 (3)	C15—H15A	0.9600
C2—C13	1.502 (3)	C15—H15B	0.9600
C3—C4	1.427 (3)	C15—H15C	0.9600
C3—C14	1.500 (2)	C16—H16A	0.9600
C4—C12	1.403 (2)	C16—H16B	0.9600
C4—C5	1.439 (2)	C16—H16C	0.9600
C5—C6	1.349 (3)		
N1—Zn1—N1 ⁱ	168.35 (8)	C5—C6—H6	119.1
N1—Zn1—O1 ⁱ	91.03 (5)	C7—C6—H6	119.1
N1 ⁱ —Zn1—O1 ⁱ	97.30 (5)	C11—C7—C8	118.20 (16)
N1—Zn1—O1	97.30 (5)	C11—C7—C6	117.70 (17)
N1 ⁱ —Zn1—O1	91.03 (5)	C8—C7—C6	124.08 (16)
N1 ⁱ —Zn1—N2 ⁱ	77.38 (6)	C9—C8—C7	118.38 (16)
O1—Zn1—O1 ⁱ	88.78 (7)	C9—C8—C15	120.13 (17)
N1—Zn1—N2 ⁱ	94.71 (6)	C7—C8—C15	121.49 (17)
O1 ⁱ —Zn1—N2 ⁱ	89.04 (5)	C8—C9—C10	118.70 (17)
O1—Zn1—N2 ⁱ	167.83 (5)	C8—C9—C16	122.29 (17)
N1—Zn1—N2	77.37 (6)	C10—C9—C16	119.01 (17)
N1 ⁱ —Zn1—N2	94.71 (6)	N2—C10—C9	124.26 (17)
O1 ⁱ —Zn1—N2	167.83 (5)	N2—C10—H10	117.9
O1—Zn1—N2	89.04 (5)	C9—C10—H10	117.9
N2 ⁱ —Zn1—N2	95.52 (8)	N2—C11—C7	122.86 (16)
O2—S1—O3	117.05 (10)	N2—C11—C12	116.90 (15)
O2—S1—O1	113.65 (9)	C7—C11—C12	120.23 (16)
O3—S1—O1	112.97 (9)	N1—C12—C4	122.13 (16)
O2—S1—O4	107.31 (9)	N1—C12—C11	117.19 (15)
O3—S1—O4	98.06 (9)	C4—C12—C11	120.67 (15)
O1—S1—O4	105.72 (8)	C2—C13—H13A	109.5
S1—O1—Zn1	147.54 (8)	C2—C13—H13B	109.5
O4 ⁱ —O4—S1	110.51 (12)	H13A—C13—H13B	109.5
C1—N1—C12	117.87 (15)	C2—C13—H13C	109.5
C1—N1—Zn1	126.37 (12)	H13A—C13—H13C	109.5
C12—N1—Zn1	115.52 (11)	H13B—C13—H13C	109.5
C10—N2—C11	117.58 (15)	C3—C14—H14A	109.5
C10—N2—Zn1	129.41 (12)	C3—C14—H14B	109.5
C11—N2—Zn1	112.86 (11)	H14A—C14—H14B	109.5
N1—C1—C2	124.57 (16)	C3—C14—H14C	109.5
N1—C1—H1	117.7	H14A—C14—H14C	109.5
C2—C1—H1	117.7	H14B—C14—H14C	109.5
C3—C2—C1	118.48 (17)	C8—C15—H15A	109.5
C3—C2—C13	124.13 (16)	C8—C15—H15B	109.5
C1—C2—C13	117.36 (16)	H15A—C15—H15B	109.5

C2—C3—C4	117.96 (16)	C8—C15—H15C	109.5
C2—C3—C14	121.60 (17)	H15A—C15—H15C	109.5
C4—C3—C14	120.41 (16)	H15B—C15—H15C	109.5
C12—C4—C3	118.95 (16)	C9—C16—H16A	109.5
C12—C4—C5	117.53 (16)	C9—C16—H16B	109.5
C3—C4—C5	123.52 (16)	H16A—C16—H16B	109.5
C6—C5—C4	121.94 (17)	C9—C16—H16C	109.5
C6—C5—H5	119.0	H16A—C16—H16C	109.5
C4—C5—H5	119.0	H16B—C16—H16C	109.5
C5—C6—C7	121.88 (17)		
O2—S1—O1—Zn1	-75.62 (18)	C15—C8—C9—C10	179.58 (17)
O3—S1—O1—Zn1	147.93 (15)	C7—C8—C9—C16	-178.56 (18)
O4—S1—O1—Zn1	41.81 (18)	C15—C8—C9—C16	0.2 (3)
O2—S1—O4—O4 ⁱ	43.02 (11)	C11—N2—C10—C9	0.6 (3)
O3—S1—O4—O4 ⁱ	164.71 (10)	Zn1—N2—C10—C9	-174.53 (13)
O1—S1—O4—O4 ⁱ	-78.59 (10)	C8—C9—C10—N2	-1.5 (3)
C12—N1—C1—C2	-1.5 (3)	C16—C9—C10—N2	177.88 (18)
Zn1—N1—C1—C2	172.58 (13)	C10—N2—C11—C7	0.9 (2)
N1—C1—C2—C3	2.1 (3)	Zn1—N2—C11—C7	176.86 (13)
N1—C1—C2—C13	-176.01 (17)	C10—N2—C11—C12	-178.04 (15)
C1—C2—C3—C4	-0.6 (3)	Zn1—N2—C11—C12	-2.09 (18)
C13—C2—C3—C4	177.41 (16)	C8—C7—C11—N2	-1.5 (3)
C1—C2—C3—C14	-178.75 (17)	C6—C7—C11—N2	-179.96 (16)
C13—C2—C3—C14	-0.7 (3)	C8—C7—C11—C12	177.39 (15)
C2—C3—C4—C12	-1.3 (2)	C6—C7—C11—C12	-1.0 (2)
C14—C3—C4—C12	176.83 (17)	C1—N1—C12—C4	-0.7 (2)
C2—C3—C4—C5	179.53 (17)	Zn1—N1—C12—C4	-175.37 (13)
C14—C3—C4—C5	-2.3 (3)	C1—N1—C12—C11	178.29 (15)
C12—C4—C5—C6	-1.9 (3)	Zn1—N1—C12—C11	3.58 (19)
C3—C4—C5—C6	177.26 (18)	C3—C4—C12—N1	2.1 (3)
C4—C5—C6—C7	0.0 (3)	C5—C4—C12—N1	-178.75 (16)
C5—C6—C7—C11	1.5 (3)	C3—C4—C12—C11	-176.87 (15)
C5—C6—C7—C8	-176.81 (18)	C5—C4—C12—C11	2.3 (2)
C11—C7—C8—C9	0.6 (2)	N2—C11—C12—N1	-0.9 (2)
C6—C7—C8—C9	178.92 (17)	C7—C11—C12—N1	-179.87 (15)
C11—C7—C8—C15	-178.16 (16)	N2—C11—C12—C4	178.08 (15)
C6—C7—C8—C15	0.2 (3)	C7—C11—C12—C4	-0.9 (2)
C7—C8—C9—C10	0.8 (3)		

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

(VII)

Crystal data

C₃₂H₃₂CdN₄O₈S₂
M_r = 777.13
 Triclinic, *P* $\bar{1}$
a = 8.601 (3) Å
b = 11.063 (4) Å
c = 16.932 (5) Å
 α = 98.788 (5)°

β = 97.713 (5)°
 γ = 97.943 (5)°
V = 1557.0 (9) Å³
Z = 2
F(000) = 792
D_x = 1.658 Mg m⁻³
 Mo *K* α radiation, λ = 0.71069 Å

$\mu = 0.90 \text{ mm}^{-1}$
 $T = 294 \text{ K}$

Blocks, colorless
 $0.28 \times 0.16 \times 0.14 \text{ mm}$

Data collection

Oxford Diffraction Gemini CCD S Ultra diffractometer
 ω scans, thick slices
 Absorption correction: multi-scan
CrysAlis PRO, Oxford Diffraction (2009)
 $T_{\text{min}} = 0.76$, $T_{\text{max}} = 0.84$
 41025 measured reflections

7888 independent reflections
 6692 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.057$
 $\theta_{\text{max}} = 29.6^\circ$, $\theta_{\text{min}} = 3.7^\circ$
 $h = -11 \rightarrow 11$
 $k = -15 \rightarrow 14$
 $l = -22 \rightarrow 23$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.071$
 $S = 1.07$
 7888 reflections
 432 parameters
 0 restraints

Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0258P)^2 + 0.357P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.54 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.57 \text{ e } \text{\AA}^{-3}$

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cd1	0.47097 (2)	0.33533 (2)	0.72920 (2)	0.01922 (6)
S1	0.05625 (7)	0.35870 (6)	0.71408 (3)	0.02590 (13)
S2	0.20697 (7)	0.06721 (6)	0.75623 (4)	0.02696 (13)
O1	0.21331 (18)	0.37290 (16)	0.69045 (10)	0.0286 (4)
O2	0.0350 (2)	0.45715 (18)	0.77528 (10)	0.0423 (5)
O3	-0.06850 (19)	0.31860 (17)	0.64709 (10)	0.0334 (4)
O4	0.0523 (2)	0.24624 (17)	0.76875 (10)	0.0345 (4)
O5	0.06436 (19)	0.13190 (16)	0.71331 (10)	0.0338 (4)
O6	0.1605 (2)	0.03554 (17)	0.82923 (10)	0.0362 (4)
O7	0.2034 (2)	-0.03378 (16)	0.69173 (11)	0.0402 (4)
O8	0.34975 (18)	0.15938 (15)	0.77001 (11)	0.0322 (4)
N1	0.4486 (2)	0.23623 (17)	0.59702 (11)	0.0217 (4)
N2	0.6357 (2)	0.45495 (17)	0.66216 (11)	0.0202 (4)
C1	0.3553 (3)	0.1293 (2)	0.56479 (14)	0.0260 (5)
H1	0.3023	0.0868	0.5992	0.031*
C2	0.3309 (3)	0.0759 (2)	0.48279 (15)	0.0287 (5)
C3	0.4100 (3)	0.1376 (2)	0.43121 (14)	0.0292 (5)
C4	0.5109 (3)	0.2525 (2)	0.46361 (13)	0.0261 (5)
C5	0.5991 (3)	0.3243 (3)	0.41633 (14)	0.0319 (6)
H5	0.5911	0.2950	0.3612	0.038*
C6	0.6933 (3)	0.4328 (3)	0.44856 (15)	0.0316 (6)
H6	0.7466	0.4770	0.4150	0.038*
C7	0.7140 (3)	0.4823 (2)	0.53374 (14)	0.0244 (5)

supporting information

C8	0.8184 (3)	0.5928 (2)	0.57091 (15)	0.0280 (5)
C9	0.8314 (3)	0.6286 (2)	0.65367 (16)	0.0297 (6)
C10	0.7359 (3)	0.5573 (2)	0.69553 (14)	0.0255 (5)
H10	0.7432	0.5837	0.7509	0.031*
C11	0.6269 (2)	0.4147 (2)	0.58217 (13)	0.0201 (5)
C12	0.5256 (2)	0.2986 (2)	0.54680 (13)	0.0205 (5)
C13	0.2189 (3)	-0.0455 (3)	0.45618 (17)	0.0414 (7)
H13A	0.2722	-0.1055	0.4282	0.062*
H13B	0.1276	-0.0336	0.4207	0.062*
H13C	0.1856	-0.0747	0.5028	0.062*
C14	0.3930 (4)	0.0845 (3)	0.34201 (16)	0.0467 (7)
H14A	0.3078	0.0153	0.3282	0.070*
H14B	0.4903	0.0575	0.3307	0.070*
H14C	0.3700	0.1470	0.3106	0.070*
C15	0.9139 (3)	0.6671 (3)	0.52125 (17)	0.0409 (7)
H15A	0.9716	0.7417	0.5551	0.061*
H15B	0.8436	0.6879	0.4782	0.061*
H15C	0.9874	0.6190	0.4988	0.061*
C16	0.9451 (3)	0.7398 (3)	0.70052 (18)	0.0469 (8)
H16A	0.9266	0.8118	0.6777	0.070*
H16B	1.0523	0.7264	0.6978	0.070*
H16C	0.9289	0.7522	0.7560	0.070*
N21	0.4943 (2)	0.51270 (17)	0.82643 (10)	0.0198 (4)
N22	0.6494 (2)	0.31779 (18)	0.84169 (11)	0.0219 (4)
C21	0.4298 (3)	0.6120 (2)	0.81585 (14)	0.0242 (5)
H21	0.3598	0.6073	0.7682	0.029*
C22	0.4590 (3)	0.7236 (2)	0.87092 (14)	0.0253 (5)
C23	0.5539 (3)	0.7279 (2)	0.94438 (14)	0.0252 (5)
C24	0.6237 (2)	0.6230 (2)	0.95815 (13)	0.0230 (5)
C25	0.7238 (3)	0.6180 (2)	1.03197 (14)	0.0283 (5)
H25	0.7414	0.6853	1.0742	0.034*
C26	0.7930 (3)	0.5181 (2)	1.04171 (14)	0.0290 (6)
H26	0.8567	0.5182	1.0907	0.035*
C27	0.7714 (3)	0.4113 (2)	0.97874 (14)	0.0254 (5)
C28	0.8425 (3)	0.3054 (3)	0.98739 (15)	0.0289 (6)
C29	0.8136 (3)	0.2077 (2)	0.92287 (16)	0.0302 (6)
C30	0.7184 (3)	0.2201 (2)	0.85173 (15)	0.0282 (5)
H30	0.7025	0.1550	0.8082	0.034*
C31	0.6738 (2)	0.4133 (2)	0.90545 (13)	0.0204 (5)
C32	0.5953 (2)	0.5188 (2)	0.89612 (12)	0.0192 (5)
C33	0.3872 (3)	0.8322 (2)	0.84782 (17)	0.0366 (6)
H33A	0.3236	0.8597	0.8873	0.055*
H33B	0.3216	0.8077	0.7957	0.055*
H33C	0.4704	0.8985	0.8457	0.055*
C34	0.5838 (3)	0.8423 (2)	1.00842 (16)	0.0383 (6)
H34A	0.5273	0.9039	0.9894	0.058*
H34B	0.6956	0.8740	1.0200	0.058*
H34C	0.5476	0.8220	1.0567	0.058*
C35	0.9459 (3)	0.3000 (3)	1.06551 (16)	0.0418 (7)
H35A	0.9709	0.2179	1.0644	0.063*
H35B	0.8903	0.3204	1.1100	0.063*

H35C	1.0423	0.3582	1.0719	0.063*
C36	0.8790 (3)	0.0884 (3)	0.92540 (19)	0.0466 (7)
H36A	0.8525	0.0550	0.9719	0.070*
H36B	0.9925	0.1045	0.9288	0.070*
H36C	0.8337	0.0299	0.8772	0.070*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.02200 (9)	0.01855 (9)	0.01524 (9)	0.00058 (6)	0.00083 (6)	0.00144 (6)
S1	0.0251 (3)	0.0305 (3)	0.0203 (3)	0.0087 (2)	-0.0032 (2)	0.0011 (2)
S2	0.0275 (3)	0.0217 (3)	0.0298 (3)	-0.0027 (2)	0.0021 (2)	0.0066 (3)
O1	0.0237 (8)	0.0303 (10)	0.0302 (9)	0.0031 (7)	-0.0029 (7)	0.0073 (7)
O2	0.0526 (12)	0.0470 (12)	0.0256 (10)	0.0267 (10)	-0.0045 (8)	-0.0061 (8)
O3	0.0268 (9)	0.0404 (11)	0.0285 (9)	0.0075 (8)	-0.0071 (7)	0.0006 (8)
O4	0.0375 (10)	0.0416 (12)	0.0276 (9)	0.0128 (8)	0.0068 (8)	0.0085 (8)
O5	0.0339 (9)	0.0285 (10)	0.0333 (10)	-0.0021 (8)	-0.0063 (8)	0.0036 (8)
O6	0.0416 (10)	0.0378 (11)	0.0325 (10)	0.0050 (8)	0.0091 (8)	0.0145 (8)
O7	0.0562 (12)	0.0229 (10)	0.0384 (11)	-0.0037 (8)	0.0110 (9)	0.0014 (8)
O8	0.0249 (8)	0.0239 (9)	0.0449 (11)	-0.0048 (7)	-0.0021 (8)	0.0118 (8)
N1	0.0247 (10)	0.0216 (10)	0.0182 (9)	0.0033 (8)	0.0032 (8)	0.0023 (8)
N2	0.0184 (9)	0.0222 (10)	0.0197 (9)	0.0035 (7)	0.0004 (7)	0.0051 (8)
C1	0.0308 (13)	0.0234 (13)	0.0219 (12)	0.0020 (10)	0.0030 (10)	0.0009 (10)
C2	0.0312 (13)	0.0239 (13)	0.0273 (13)	0.0086 (10)	-0.0034 (10)	-0.0033 (10)
C3	0.0337 (13)	0.0335 (15)	0.0197 (12)	0.0161 (11)	-0.0003 (10)	-0.0031 (10)
C4	0.0292 (12)	0.0339 (14)	0.0179 (11)	0.0151 (10)	0.0032 (9)	0.0046 (10)
C5	0.0388 (14)	0.0442 (17)	0.0176 (12)	0.0176 (12)	0.0087 (10)	0.0073 (11)
C6	0.0338 (14)	0.0438 (17)	0.0261 (13)	0.0148 (12)	0.0120 (11)	0.0192 (12)
C7	0.0197 (11)	0.0321 (14)	0.0264 (12)	0.0101 (10)	0.0055 (9)	0.0138 (10)
C8	0.0181 (11)	0.0359 (15)	0.0363 (14)	0.0088 (10)	0.0053 (10)	0.0208 (12)
C9	0.0207 (12)	0.0295 (14)	0.0380 (15)	-0.0008 (10)	-0.0004 (10)	0.0117 (11)
C10	0.0192 (11)	0.0324 (14)	0.0223 (12)	-0.0003 (10)	-0.0022 (9)	0.0055 (10)
C11	0.0179 (10)	0.0264 (13)	0.0192 (11)	0.0092 (9)	0.0029 (9)	0.0089 (9)
C12	0.0196 (11)	0.0244 (12)	0.0188 (11)	0.0090 (9)	0.0018 (9)	0.0038 (9)
C13	0.0487 (17)	0.0294 (15)	0.0359 (15)	-0.0007 (12)	-0.0062 (13)	-0.0086 (12)
C14	0.0608 (19)	0.052 (2)	0.0227 (14)	0.0156 (15)	0.0005 (13)	-0.0085 (13)
C15	0.0316 (14)	0.0490 (18)	0.0494 (17)	0.0053 (12)	0.0117 (13)	0.0283 (15)
C16	0.0359 (15)	0.0462 (19)	0.0509 (18)	-0.0166 (13)	-0.0026 (13)	0.0140 (15)
N21	0.0197 (9)	0.0229 (10)	0.0166 (9)	0.0025 (8)	0.0021 (7)	0.0040 (8)
N22	0.0216 (9)	0.0223 (10)	0.0221 (10)	0.0027 (8)	0.0038 (8)	0.0055 (8)
C21	0.0245 (12)	0.0265 (13)	0.0215 (12)	0.0044 (10)	0.0033 (9)	0.0039 (10)
C22	0.0254 (12)	0.0225 (13)	0.0276 (13)	-0.0005 (9)	0.0077 (10)	0.0043 (10)
C23	0.0263 (12)	0.0230 (13)	0.0240 (12)	-0.0041 (9)	0.0092 (10)	-0.0005 (10)
C24	0.0200 (11)	0.0293 (13)	0.0167 (11)	-0.0045 (9)	0.0045 (9)	0.0011 (9)
C25	0.0272 (12)	0.0361 (15)	0.0166 (11)	-0.0052 (11)	0.0020 (9)	-0.0004 (10)
C26	0.0238 (12)	0.0446 (16)	0.0151 (11)	-0.0036 (11)	-0.0018 (9)	0.0070 (11)
C27	0.0180 (11)	0.0386 (15)	0.0205 (12)	0.0006 (10)	0.0043 (9)	0.0102 (10)
C28	0.0171 (11)	0.0443 (16)	0.0290 (13)	0.0045 (10)	0.0065 (10)	0.0163 (12)
C29	0.0224 (12)	0.0385 (16)	0.0369 (14)	0.0115 (11)	0.0101 (11)	0.0185 (12)
C30	0.0266 (12)	0.0297 (14)	0.0301 (13)	0.0070 (10)	0.0067 (10)	0.0063 (11)
C31	0.0160 (10)	0.0253 (12)	0.0188 (11)	-0.0020 (9)	0.0039 (8)	0.0042 (9)

supporting information

C32	0.0159 (10)	0.0246 (12)	0.0160 (11)	-0.0019 (9)	0.0039 (8)	0.0037 (9)
C33	0.0435 (15)	0.0251 (14)	0.0403 (16)	0.0055 (12)	0.0034 (12)	0.0056 (12)
C34	0.0467 (16)	0.0282 (15)	0.0338 (15)	-0.0008 (12)	0.0056 (12)	-0.0073 (11)
C35	0.0306 (14)	0.065 (2)	0.0366 (15)	0.0123 (13)	0.0039 (12)	0.0256 (15)
C36	0.0467 (17)	0.0494 (19)	0.0535 (19)	0.0232 (14)	0.0117 (14)	0.0223 (15)

Geometric parameters (Å, °) for (VII)

Cd1—N1	2.3075 (19)	C14—H14C	0.9600
Cd1—O8	2.3232 (18)	C15—H15A	0.9600
Cd1—N21	2.327 (2)	C15—H15B	0.9600
Cd1—N2	2.3278 (19)	C15—H15C	0.9600
Cd1—N22	2.3304 (19)	C16—H16A	0.9600
Cd1—O1	2.3371 (19)	C16—H16B	0.9600
S1—O3	1.4222 (17)	C16—H16C	0.9600
S1—O2	1.4333 (19)	N21—C21	1.322 (3)
S1—O1	1.4544 (18)	N21—C32	1.355 (3)
S1—O4	1.6597 (19)	N22—C30	1.325 (3)
S2—O6	1.4272 (18)	N22—C31	1.362 (3)
S2—O7	1.4320 (19)	C21—C22	1.399 (3)
S2—O8	1.4514 (17)	C21—H21	0.9300
S2—O5	1.6454 (18)	C22—C23	1.384 (3)
O4—O5	1.480 (2)	C22—C33	1.504 (3)
N1—C1	1.328 (3)	C23—C24	1.414 (3)
N1—C12	1.357 (3)	C23—C34	1.503 (3)
N2—C10	1.322 (3)	C24—C32	1.405 (3)
N2—C11	1.348 (3)	C24—C25	1.432 (3)
C1—C2	1.399 (3)	C25—C26	1.347 (4)
C1—H1	0.9300	C25—H25	0.9300
C2—C3	1.380 (3)	C26—C27	1.438 (3)
C2—C13	1.509 (4)	C26—H26	0.9300
C3—C4	1.423 (4)	C27—C31	1.407 (3)
C3—C14	1.515 (3)	C27—C28	1.412 (3)
C4—C12	1.406 (3)	C28—C29	1.384 (4)
C4—C5	1.428 (3)	C28—C35	1.506 (3)
C5—C6	1.344 (4)	C29—C30	1.399 (3)
C5—H5	0.9300	C29—C36	1.509 (4)
C6—C7	1.440 (3)	C30—H30	0.9300
C6—H6	0.9300	C31—C32	1.445 (3)
C7—C11	1.411 (3)	C33—H33A	0.9600
C7—C8	1.417 (4)	C33—H33B	0.9600
C8—C9	1.382 (4)	C33—H33C	0.9600
C8—C15	1.505 (3)	C34—H34A	0.9600
C9—C10	1.395 (3)	C34—H34B	0.9600
C9—C16	1.503 (4)	C34—H34C	0.9600
C10—H10	0.9300	C35—H35A	0.9600
C11—C12	1.443 (3)	C35—H35B	0.9600
C13—H13A	0.9600	C35—H35C	0.9600
C13—H13B	0.9600	C36—H36A	0.9600
C13—H13C	0.9600	C36—H36B	0.9600
C14—H14A	0.9600	C36—H36C	0.9600

C14—H14B	0.9600		
N1—Cd1—O8	92.85 (7)	C3—C14—H14C	109.5
N1—Cd1—N21	152.02 (7)	H14A—C14—H14C	109.5
O8—Cd1—N21	112.40 (7)	H14B—C14—H14C	109.5
N1—Cd1—N2	71.27 (7)	C8—C15—H15A	109.5
O8—Cd1—N2	158.54 (6)	C8—C15—H15B	109.5
N21—Cd1—N2	86.65 (7)	H15A—C15—H15B	109.5
N1—Cd1—N22	128.61 (7)	C8—C15—H15C	109.5
O8—Cd1—N22	77.30 (6)	H15A—C15—H15C	109.5
N21—Cd1—N22	71.29 (7)	H15B—C15—H15C	109.5
N2—Cd1—N22	101.00 (7)	C9—C16—H16A	109.5
N1—Cd1—O1	85.06 (6)	C9—C16—H16B	109.5
O8—Cd1—O1	85.92 (6)	H16A—C16—H16B	109.5
N21—Cd1—O1	84.94 (6)	C9—C16—H16C	109.5
N2—Cd1—O1	106.32 (7)	H16A—C16—H16C	109.5
N22—Cd1—O1	142.43 (6)	H16B—C16—H16C	109.5
O3—S1—O2	117.21 (11)	C21—N21—C32	117.7 (2)
O3—S1—O1	113.08 (11)	C21—N21—Cd1	125.21 (15)
O2—S1—O1	113.93 (12)	C32—N21—Cd1	116.69 (14)
O3—S1—O4	106.56 (11)	C30—N22—C31	117.3 (2)
O2—S1—O4	98.35 (11)	C30—N22—Cd1	126.18 (16)
O1—S1—O4	105.54 (9)	C31—N22—Cd1	116.25 (14)
O6—S2—O7	116.46 (11)	N21—C21—C22	125.0 (2)
O6—S2—O8	113.18 (11)	N21—C21—H21	117.5
O7—S2—O8	114.04 (11)	C22—C21—H21	117.5
O6—S2—O5	107.04 (10)	C23—C22—C21	117.6 (2)
O7—S2—O5	98.35 (11)	C23—C22—C33	123.4 (2)
O8—S2—O5	105.77 (10)	C21—C22—C33	119.0 (2)
S1—O1—Cd1	141.34 (10)	C22—C23—C24	118.9 (2)
O5—O4—S1	106.47 (12)	C22—C23—C34	120.8 (2)
O4—O5—S2	108.11 (12)	C24—C23—C34	120.4 (2)
S2—O8—Cd1	144.53 (10)	C32—C24—C23	118.6 (2)
C1—N1—C12	117.72 (19)	C32—C24—C25	118.2 (2)
C1—N1—Cd1	125.25 (15)	C23—C24—C25	123.2 (2)
C12—N1—Cd1	116.71 (15)	C26—C25—C24	121.5 (2)
C10—N2—C11	117.90 (19)	C26—C25—H25	119.2
C10—N2—Cd1	125.90 (15)	C24—C25—H25	119.2
C11—N2—Cd1	116.20 (15)	C25—C26—C27	122.0 (2)
N1—C1—C2	124.8 (2)	C25—C26—H26	119.0
N1—C1—H1	117.6	C27—C26—H26	119.0
C2—C1—H1	117.6	C31—C27—C28	119.0 (2)
C3—C2—C1	118.1 (2)	C31—C27—C26	117.9 (2)
C3—C2—C13	124.0 (2)	C28—C27—C26	123.2 (2)
C1—C2—C13	117.8 (2)	C29—C28—C27	118.4 (2)
C2—C3—C4	118.7 (2)	C29—C28—C35	121.5 (2)
C2—C3—C14	121.3 (2)	C27—C28—C35	120.2 (2)
C4—C3—C14	120.0 (2)	C28—C29—C30	118.3 (2)
C12—C4—C3	118.6 (2)	C28—C29—C36	123.4 (2)
C12—C4—C5	117.7 (2)	C30—C29—C36	118.3 (3)
C3—C4—C5	123.7 (2)	N22—C30—C29	124.9 (2)

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C6—C5—C4	122.4 (2)	N22—C30—H30	117.5
C6—C5—H5	118.8	C29—C30—H30	117.5
C4—C5—H5	118.8	N22—C31—C27	122.1 (2)
C5—C6—C7	121.7 (2)	N22—C31—C32	117.88 (19)
C5—C6—H6	119.1	C27—C31—C32	120.0 (2)
C7—C6—H6	119.1	N21—C32—C24	122.0 (2)
C11—C7—C8	119.0 (2)	N21—C32—C31	117.77 (19)
C11—C7—C6	117.5 (2)	C24—C32—C31	120.3 (2)
C8—C7—C6	123.6 (2)	C22—C33—H33A	109.5
C9—C8—C7	118.0 (2)	C22—C33—H33B	109.5
C9—C8—C15	121.5 (2)	H33A—C33—H33B	109.5
C7—C8—C15	120.5 (2)	C22—C33—H33C	109.5
C8—C9—C10	118.4 (2)	H33A—C33—H33C	109.5
C8—C9—C16	122.9 (2)	H33B—C33—H33C	109.5
C10—C9—C16	118.7 (2)	C23—C34—H34A	109.5
N2—C10—C9	124.8 (2)	C23—C34—H34B	109.5
N2—C10—H10	117.6	H34A—C34—H34B	109.5
C9—C10—H10	117.6	C23—C34—H34C	109.5
N2—C11—C7	121.8 (2)	H34A—C34—H34C	109.5
N2—C11—C12	117.89 (19)	H34B—C34—H34C	109.5
C7—C11—C12	120.3 (2)	C28—C35—H35A	109.5
N1—C12—C4	122.1 (2)	C28—C35—H35B	109.5
N1—C12—C11	117.48 (19)	H35A—C35—H35B	109.5
C4—C12—C11	120.4 (2)	C28—C35—H35C	109.5
C2—C13—H13A	109.5	H35A—C35—H35C	109.5
C2—C13—H13B	109.5	H35B—C35—H35C	109.5
H13A—C13—H13B	109.5	C29—C36—H36A	109.5
C2—C13—H13C	109.5	C29—C36—H36B	109.5
H13A—C13—H13C	109.5	H36A—C36—H36B	109.5
H13B—C13—H13C	109.5	C29—C36—H36C	109.5
C3—C14—H14A	109.5	H36A—C36—H36C	109.5
C3—C14—H14B	109.5	H36B—C36—H36C	109.5
H14A—C14—H14B	109.5		
O3—S1—O1—Cd1	-139.00 (15)	C3—C4—C12—C11	179.9 (2)
O2—S1—O1—Cd1	83.87 (18)	C5—C4—C12—C11	0.0 (3)
O4—S1—O1—Cd1	-22.89 (19)	N2—C11—C12—N1	-1.5 (3)
O3—S1—O4—O5	55.31 (14)	C7—C11—C12—N1	178.08 (19)
O2—S1—O4—O5	177.03 (13)	N2—C11—C12—C4	179.56 (19)
O1—S1—O4—O5	-65.17 (14)	C7—C11—C12—C4	-0.9 (3)
S1—O4—O5—S2	129.36 (11)	C32—N21—C21—C22	0.6 (3)
O6—S2—O5—O4	62.22 (15)	Cd1—N21—C21—C22	-172.20 (16)
O7—S2—O5—O4	-176.72 (13)	N21—C21—C22—C23	-4.6 (3)
O8—S2—O5—O4	-58.73 (15)	N21—C21—C22—C33	175.2 (2)
O6—S2—O8—Cd1	-139.60 (18)	C21—C22—C23—C24	3.7 (3)
O7—S2—O8—Cd1	84.2 (2)	C33—C22—C23—C24	-176.1 (2)
O5—S2—O8—Cd1	-22.7 (2)	C21—C22—C23—C34	-176.8 (2)
C12—N1—C1—C2	0.2 (3)	C33—C22—C23—C34	3.4 (3)
Cd1—N1—C1—C2	173.51 (17)	C22—C23—C24—C32	0.8 (3)
N1—C1—C2—C3	0.6 (4)	C34—C23—C24—C32	-178.8 (2)
N1—C1—C2—C13	-179.2 (2)	C22—C23—C24—C25	180.0 (2)

C1—C2—C3—C4	-0.6 (3)	C34—C23—C24—C25	0.4 (3)
C13—C2—C3—C4	179.2 (2)	C32—C24—C25—C26	1.7 (3)
C1—C2—C3—C14	178.5 (2)	C23—C24—C25—C26	-177.4 (2)
C13—C2—C3—C14	-1.8 (4)	C24—C25—C26—C27	0.4 (3)
C2—C3—C4—C12	-0.2 (3)	C25—C26—C27—C31	-0.3 (3)
C14—C3—C4—C12	-179.3 (2)	C25—C26—C27—C28	-179.9 (2)
C2—C3—C4—C5	179.7 (2)	C31—C27—C28—C29	0.3 (3)
C14—C3—C4—C5	0.6 (4)	C26—C27—C28—C29	179.9 (2)
C12—C4—C5—C6	-0.2 (3)	C31—C27—C28—C35	-179.2 (2)
C3—C4—C5—C6	179.8 (2)	C26—C27—C28—C35	0.4 (3)
C4—C5—C6—C7	1.4 (4)	C27—C28—C29—C30	1.5 (3)
C5—C6—C7—C11	-2.2 (3)	C35—C28—C29—C30	-179.0 (2)
C5—C6—C7—C8	176.6 (2)	C27—C28—C29—C36	-178.4 (2)
C11—C7—C8—C9	0.7 (3)	C35—C28—C29—C36	1.2 (4)
C6—C7—C8—C9	-178.0 (2)	C31—N22—C30—C29	0.4 (3)
C11—C7—C8—C15	179.7 (2)	Cd1—N22—C30—C29	-173.78 (17)
C6—C7—C8—C15	1.0 (3)	C28—C29—C30—N22	-1.9 (4)
C7—C8—C9—C10	-2.9 (3)	C36—C29—C30—N22	177.9 (2)
C15—C8—C9—C10	178.1 (2)	C30—N22—C31—C27	1.6 (3)
C7—C8—C9—C16	176.4 (2)	Cd1—N22—C31—C27	176.34 (15)
C15—C8—C9—C16	-2.6 (4)	C30—N22—C31—C32	-178.18 (19)
C11—N2—C10—C9	1.4 (3)	Cd1—N22—C31—C32	-3.5 (2)
Cd1—N2—C10—C9	-178.82 (17)	C28—C27—C31—N22	-2.0 (3)
C8—C9—C10—N2	1.9 (4)	C26—C27—C31—N22	178.40 (19)
C16—C9—C10—N2	-177.3 (2)	C28—C27—C31—C32	177.83 (19)
C10—N2—C11—C7	-3.7 (3)	C26—C27—C31—C32	-1.8 (3)
Cd1—N2—C11—C7	176.52 (15)	C21—N21—C32—C24	4.3 (3)
C10—N2—C11—C12	175.92 (19)	Cd1—N21—C32—C24	177.72 (15)
Cd1—N2—C11—C12	-3.9 (2)	C21—N21—C32—C31	-176.02 (18)
C8—C7—C11—N2	2.7 (3)	Cd1—N21—C32—C31	-2.6 (2)
C6—C7—C11—N2	-178.5 (2)	C23—C24—C32—N21	-5.0 (3)
C8—C7—C11—C12	-176.92 (19)	C25—C24—C32—N21	175.79 (19)
C6—C7—C11—C12	1.9 (3)	C23—C24—C32—C31	175.35 (19)
C1—N1—C12—C4	-1.0 (3)	C25—C24—C32—C31	-3.9 (3)
Cd1—N1—C12—C4	-174.88 (16)	N22—C31—C32—N21	4.1 (3)
C1—N1—C12—C11	-179.93 (19)	C27—C31—C32—N21	-175.70 (18)
Cd1—N1—C12—C11	6.2 (2)	N22—C31—C32—C24	-176.24 (18)
C3—C4—C12—N1	1.0 (3)	C27—C31—C32—C24	4.0 (3)
C5—C4—C12—N1	-178.9 (2)		

Selected geometric parameters (Å, °) for V, VI and VII.

V			
Cd1—N2	2.307 (2)	N1—Cd1—N1 ⁱ	171.15 (10)
Cd1—O1	2.314 (2)	O1—Cd1—N2 ⁱ	161.06 (8)
Cd1—N1	2.409 (3)	O1 ⁱ —Cd1—N2	161.06 (8)
VI			
Zn1—N1	2.0950 (14)	N1—Zn1—N1 ⁱ	168.3 (2)
Zn1—O1	2.1476 (13)	N2—Zn1—O1 ⁱ	167.8 (2)
Zn1—N2	2.1853 (14)	N2 ⁱ —Zn1—O1	167.8 (2)

VII			
Cd1—N1	2.3075 (19)	O8—Cd1—N2	158.5 (2)
Cd1—N2	2.3278 (19)	N1—Cd1—N21	152.0 (2)
Cd1—O8	2.3232 (18)	N22—Cd1—O1	142.4 (2)
Cd1—N22	2.3304 (19)		
Cd1—N21	2.327 (2)		
Cd1—O1	2.3371 (19)		

Symmetry code for V and VI: (i) -x, y, -z+1/2.

Hydrogen-bond geometry (Å, °) for V, VI and VII.

Structure	Label	D—H...A	D—H	H...A	D...A	D—H...A	Character
V	#1a	C3-H3...O3 ⁱⁱ	0.93	2.54	3.228 (5)	131	Interchain
	#2a	C14-H14B...O2 ⁱⁱⁱ	0.96	2.45	3.397 (5)	167	Interchain
	#3a	C14-H14C...O2 ^{iv}	0.96	2.54	3.331 (5)	140	Interchain
VI	#1b	C1—H1...O1 ⁱ	0.93	2.53	3.117 (2)	121	Intramolecular
	#2b	C1—H1...O2 ⁱ	0.93	2.45	3.286 (2)	150	Intramolecular
	#3b	C15—H15B...O3 ⁱⁱ	0.96	2.51	3.451 (2)	166	Interchain
	#4b	C13—H13B...O2 ⁱⁱⁱ	0.96	2.59	3.324 (2)	133	Interchain
	#5b	C16—H16B...O2 ^{iv}	0.96	2.59	3.543 (3)	172	Interchain
	#6b	C13—H13A...Cg3 ^v	0.96	2.73	3.9857	127	Interchain
VII	#1c	C1—H1...O7	0.93	2.37	3.296 (3)	171	Intramolecular
	#2c	C26—H26...O2 ⁱ	0.93	2.29	3.204 (3)	165	Intrachain
	#3c	C15—H15B...Cg1 ^{iv}	0.96	2.89	3.578 (4)	129	Intrachain
	#4c	C34—H34C...Cg4 ⁱ	0.96	2.88	3.599 (3)	133	Intrachain
	#5c	C36—H36B...O6 ⁱⁱ	0.96	2.47	3.165 (4)	130	Interchain
	#6c	C13—H13A...Cg1 ⁱⁱⁱ	0.96	2.93	3.607 (4)	128	Interchain
	#7c	C35—H35C...Cg6 ^v	0.96	2.69	3.604 (4)	158	Interchain

General Ring Codes (all structures): Cg1:N1,C1,C2,C3,C4,C12;Cg2: N2,C10,C9,C8,C7,C11; Cg3 = C4,C5,C6,C7,C11,C12:

Cg4:N21,C21,C22,C23,C24,C32; Cg5:N22,C30,C29,C28,C27,C31; Cg6:C24,C25,C26,C27,C31,C32 Symmetry codes for V: (ii) 1/2-x, -1/2-y, 1-z; (iii) -x, -y, -z; (iv) x, 1+y, z Symmetry codes for VI: (i) -x, y, -z+1/2; (ii) x, y-1, z; (iii) x+1/2, y-1/2, -z+1/2; (iv) -x-1/2, y-1/2, z; (v) -x+1/2, y+1/2, z. Symmetry codes for VII: (i) -x+1, -y+1, -z+2; (ii) x+1, y, z; (iii) -x+1, -y, -z+1; (iv) -x+1, -y+1, -z+1; (v) -x+2, -y+1, -z+2.

π - π contacts (\AA , $^\circ$) for V, VI and VII.

Structure	Label	Cg \cdots Cg	ccd	da	sa	ipd	Character
V	#4a	Cg1 \cdots Cg3 ^v	3.823 (3)	0.95 (14)	15.0(1.6)	3.69 (3)	Intrachain
VI	#7b	Cg2 \cdots Cg3 ^{vi}	3.8101 (10)	2.34 (8)	25.5 (7)	3.44 (2)	Intrachain
VII	#8c	Cg2 \cdots Cg3 ^v	3.737 (3)	0.9 (2)	21.3 (7)	3.48 (2)	Intrachain
	#9c	Cg3 \cdots Cg3 ^v	3.717 (3)	0	21.5	3.4577 (9)	Intrachain
	#10c	Cg4 \cdots Cg6 ^{vi}	3.700 (2)	0.6 (2)	21.8 (3)	3.43 (2)	Intrachain
	#11c	Cg6 \cdots Cg6 ^{vi}	3.669 (2)	0	20.9	3.4269 (9)	Intrachain

ccd: center-to-center distance; da: dihedral angle between planes, sa: slippage angle (average angle subtended by the intercentroid vector to the plane normal), ipd: interplanar distance (average distance from one plane to the neighbouring centroid); For details, see Janiak (2000). Symmetry codes for V: (v) 1/2-x, 1/2-y, 1-z Symmetry codes for VI: (vi) = -x, -y, -z Symmetry codes for VII: (v) = 1-x, 1-y, 1-z; (vi) = 1-x, 1-y, 2-z;

X - Y $\cdots\pi$ contacts (\AA , $^\circ$) for V and VII.

Structure	Label	X-Y \cdots Cg	Y \cdots Cg	Y \cdots Cg _{perp}	X-Y \cdots Cg	Character
V	#5a	S1-O3 \cdots Cg1	3.568 (4)	3.475 (15)	105.0 (2)	Intramolecular
VII	#12c	S1-O3 \cdots Cg2 ^{vii}	3.102 (3)	3.013	112.9 (2)	Interchain

Symmetry codes for VII: (vii) -1+x, y, z

Distortion angles as defined in Fig 3 ($^\circ$).

Angle	V	VI	VIII
α_1	111.1	116.7	119.0
α_2	111.1	116.7	111.0
α_3	137.9	126.6	129.4
ω_1	49.0	67.5	71.1
ω_2	55.9	55.8	27.0
ω_3	55.9	55.8	84.7