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Three zinc(II) complexes presenting a ZnN_6 chromophore and with peroxodisulfate as the counter-ion

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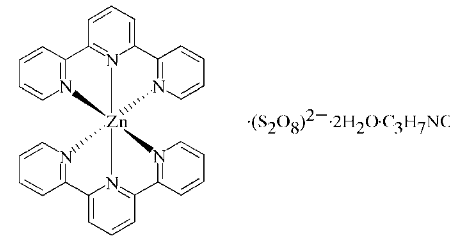
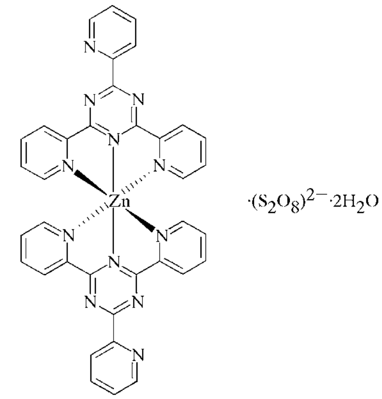
The crystal structures of three Zn complexes with the peroxodisulfate anion (pds^{2-}) acting as counter-ion are reported, namely bis(2,2′:6′,2″-terpyridine-κ^3N)zinc(II) hexaoxo-μ-peroxo-disulfate(VI) dihydrate *N*,*N*-dimethylformamide solvate, $[Zn(C_{15}H_{11}N_3)_2](S_2O_8)\cdot 2H_2O\cdot C_3H_7NO$ or $[Zn(tpy)_2](pds)\cdot 2H_2O\cdot DMF$, (I), bis[2,4,6-tris(2-pyridyl)-1,3,5-triazine-κ^2N^2,N^4]zinc(II) hexaoxo-μ-peroxo-disulfate(VI) dihydrate, $[Zn(C_{18}H_{12}N_6)_2](S_2O_8)\cdot 2H_2O$ or $[Zn(tpt)_2](pds)\cdot 2H_2O$, (II), and bis[2,6-bis(1*H*-benzimidazol-2-yl-κN^3)pyridine]zinc(II) hexaoxo-μ-peroxo-disulfate(VI) *N*,*N*-dimethylformamide trisolvate, $[Zn(C_{19}H_{13}N_5)_2](S_2O_8)\cdot 3C_3H_7NO$ or $[Zn(bbp)_2](pds)\cdot 3DMF$, (III), where tpy is 2,2′:6′,2″-terpyridine, tpt is 2,4,6-tris(2-pyridyl)-1,3,5-triazine, bbp is 2,6-bis(1*H*-benzimidazol-2-yl)pyridine and DMF is *N*,*N*-dimethylformamide. The three structures are monomeric and present the Zn cation in a distorted octahedral environment, defined by two chelating tricoordinated ligands at almost right angles to each other. These cationic entities interact with an anionic network composed of hydrogen-bonded pds^{2-} anions and solvate water and DMF molecules *via* Coulombic forces, and with each other through a number of π–π and C=C$\cdots\pi$ contacts connecting the aromatic rings. The pds^{2-} anions stabilize the structures in unprecedented counter-ion behaviour.

Comment

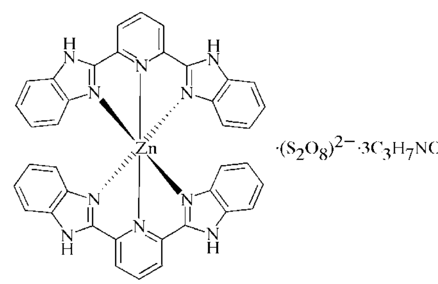
In the preceding articles of this series on crystal structures containing the peroxodisulfate anion, pds^{2-} (Harvey, Baggio, Garland, Burton & Baggio, 2001; Harvey, Baggio, Garland & Baggio, 2001), we have explored the complexing capabilities of the base towards some group 12 metals. Our results confirmed both the ability of the anion to coordinate Cd and Hg and its flexibility in adopting a variety of different coordination modes (polydentate, chelate, bridging, *etc.*). Continuing our investigations on group 12 cations, we have now



(I)



(II)



(III)

explored the system [Zn^{2+} + pds^{2-} + *L*], where *L* is a dinitrogenated (N2) or trinitrogenated (N3) organic ligand. Our results to date show the N3 type [*viz*. 2,2′:6′,2″-terpyridine (tpy), 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpt) or 2,6-bis(benzimidazol-2-yl)pyridine (bbp)] to be more efficient in coordinating to Zn than the N2 type [2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) or 2,9-dimethylphenanthroline (dmph)]. While no crystalline products containing pds^{2-} have been obtained to date starting from the latter ligands, preparations including tpy, tpt and bbp readily yielded powdered material and, with some effort, small crystals suitable for structural analysis. In all cases, the psd^{2-} group acts as a counter-ion, which constitutes a rather unusual behaviour of this anion in metal–organic compounds: the only ionic forms reported to date are the K^+ and $NH_4{}^+$ inorganic salts (Naumov *et al.*, 1997; Sivertsen & Sorum, 1969). Thus, the structures described herein, *viz*. $[Zn(tpy)_2](pds)\cdot 2H_2O\cdot DMF$, (I), $[Zn(tpt)_2](pds)\cdot 2H_2O$, (II), and $[Zn(bbp)_2](pds)\cdot 3DMF$, (III), are the first in which the pds^{2-} group acts as a counter-ion.

The three title compounds are ionic, presenting $[Zn(N3)_2]^{2+}$ cationic centres, with N3 being tpy in (I), tpt in (II) and bbp in

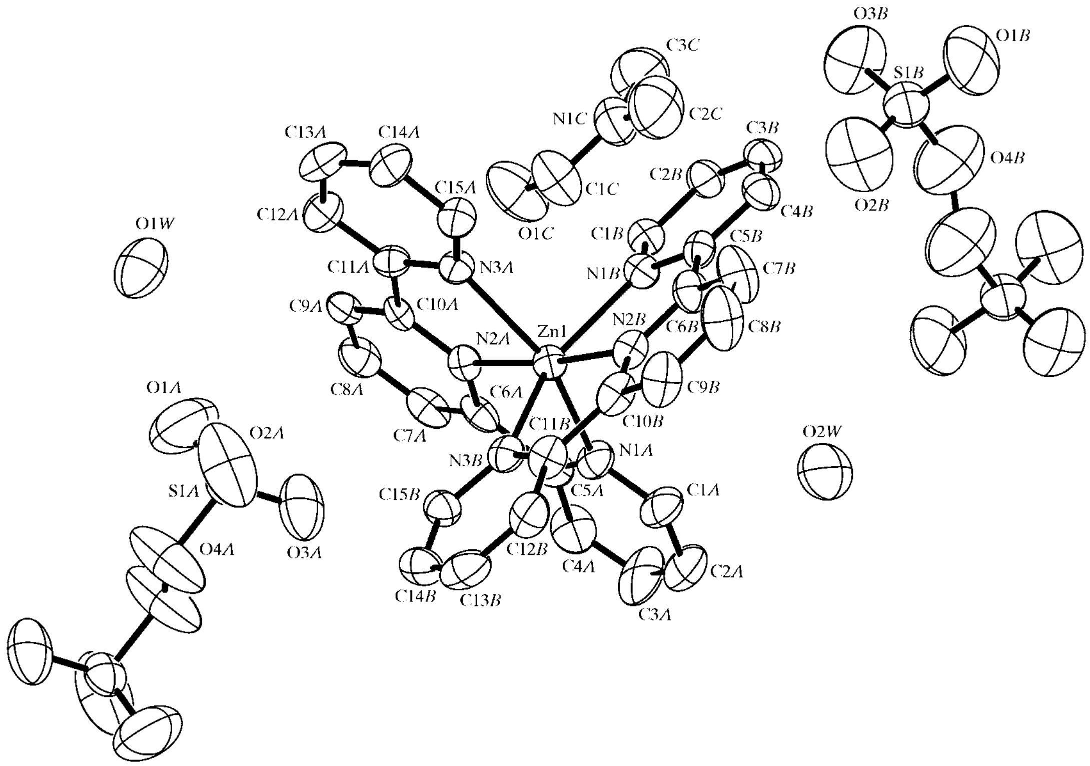


Figure 1
A molecular diagram for (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

(III), and one pds^{2-} anion balancing charges, plus some solvate molecules stabilizing the structures, *viz*. one DMF and two water molecules in (I), two water molecules in (II), and three DMF molecules in (III). Figs. 1, 2 and 3 show views of the three compounds. The analogies in coordination to the metal centre are apparent. In all cases, the ligands act in a double-tridentate mode, with the coordination planes (defined by the three bonded N atoms) being nearly perpendicular to each other, subtending dihedral angles of 91.4 (1)/91.8 (1)/ 91.6 (1)° [in this discussion, three numbers separated by a solidus (/) will mean the numerical values corresponding to homologous quantities in structures (I), (II) and (III), respectively]. The ligands bind to the cation in a slightly slanted way, the metal centre being offset from the two coordination planes (*A* and *B*) by 0.026 (1) and 0.108 (1)/ 0.024 (1) and 0.156 (1)/0.014 (1) and 0.083 (1) Å, respectively.

The intrinsic pseudosymmetry displayed by the ligands, in addition to their special coordination disposition, gives the ensemble in general (and the Zn coordination polyhedron in particular) a 'quasi'-S_4 character, with the pseudo-C_4 axis being along the N2*A*—Zn1—N2*B* direction (hereinafter the apical line), the remaining two then constituting the basal plane. The Zn—N coordination distances are in accord with this distortion, with Zn—$N_{central}$ [2.060 (7)/2.048 (4)/ 2.132 (8) Å] being distinctly different from the mean values of Zn—$N_{lateral}$ [2.186 (16)/2.20 (5)/2.197 (19) Å]. The effect is comparable with that found in similarly coordinated [Zn(N3)$_2$] cores in the Cambridge Structural Database [CSD, Version 5.25 of 2003; Allen, 2002; refcodes HUGWOV, KOFQIF, LOXDEH, PULCEE, PULCII, QARJEY and XIZNAV; mean Zn—$N_{central}$ = 2.076 (11) Å and mean Zn—$N_{lateral}$ = 2.187 (20) Å]. In addition, the chelating character of the N3 ligands forces some N—Zn—N angles to deviate

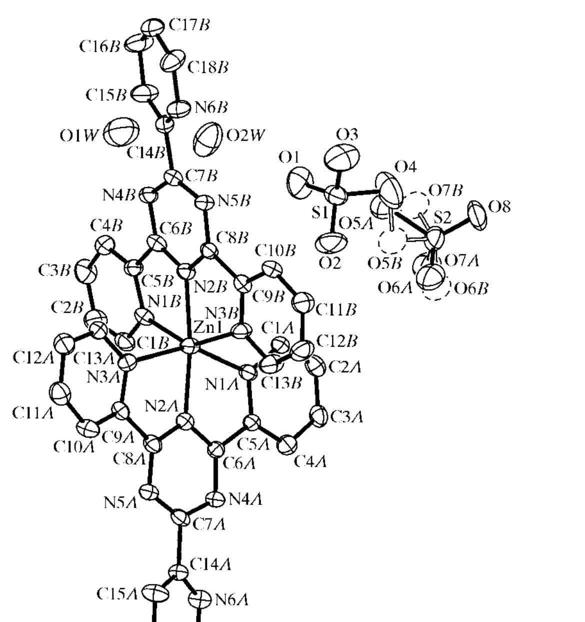


Figure 2
A molecular diagram for (II). Displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted for clarity.

significantly from idealized values (Tables 1, 3 and 5). Thus, the N2*A*—Zn1—N2*B* apical lines subtend angles of 173.8 (3)/165.3 (3)/173.6 (3)° instead of the ideal 180°, and the expected right angles present a broad span [74.3 (3)–110.1 (3)/73.4 (3)–117.9 (3)/74.5 (3)–109.2 (3)°].

The effect is also felt in the geometry of the ligand, leading to a variety of twisted conformations which, though recognizable as originating from a planar pattern, present rather large average deviations from their mean planes [0.078 (1) and 0.062 (1)/0.050 (1) and 0.057 (1)/0.126 (1) and 0.079 (1) Å]. The deformation is mainly achieved by the constituent planar rings losing their relative coplanar orientation, up to maximum angular deviations of 10.3 (2)/7.9 (2)/13.5 (2)°. In structure (II), the deviation from planarity is enhanced by the terminal pyridine moieties being significantly rotated from the core mean plane by 19.3 (1) and 16.1 (1)° for moieties *A* and *B*, respectively.

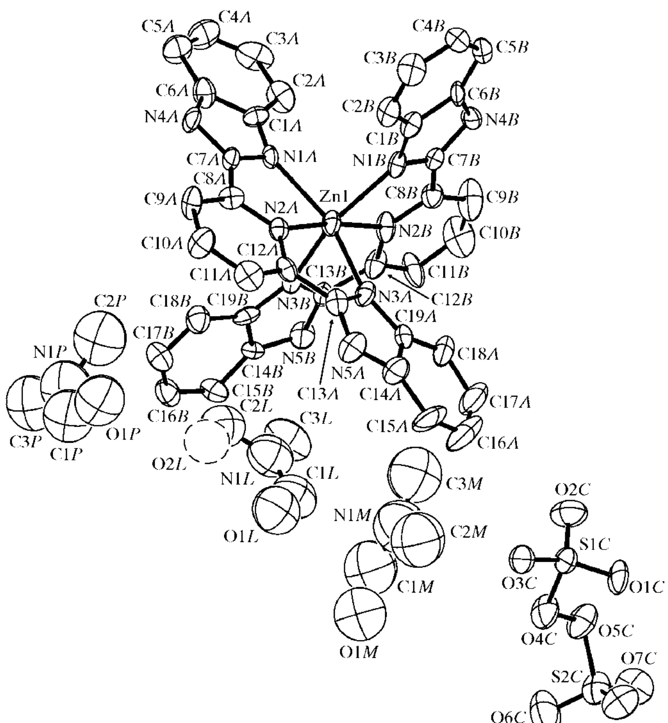


Figure 3
A molecular diagram for (III). Displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted for clarity.

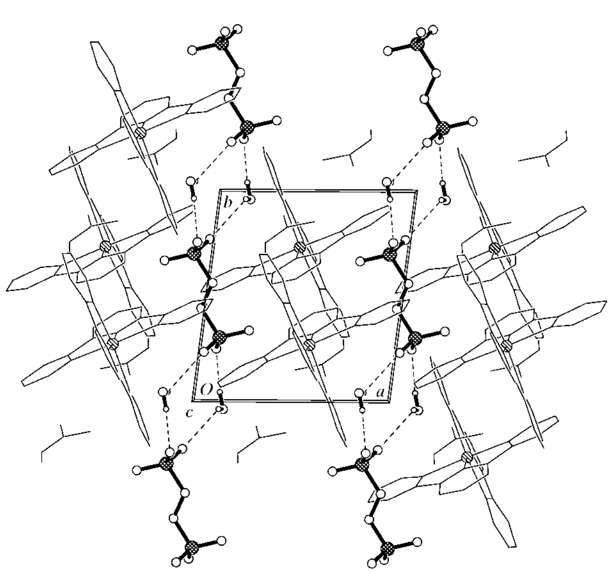


Figure 4
A packing view of (I), showing the negatively charged chains (heavy lines) running along the crystallographic *b* axis through the channels left by the cationic array (thin lines). Only H atoms involved in hydrogen bonding are included.

All three structures balance their cationic charge through one pds^{2-} counter-ion per asymmetric unit. In structure (I), this is achieved *via* two independent halves located on two different symmetry centres, and in structures (II) and (III) by a single unit lying on a general position. Unfortunately, the anion in (II) appeared severely disordered and had to be modelled split into two similarly populated moieties [occupancies 0.526 (6):0.474 (6)], and is therefore excluded from the following analysis. The remaining three units to be discussed [two in (I) and one in (III)] display bond distances and angles which approximately match those already reported in the literature. There is, however, a conspicuous exception to the observation noted in all previously described moieties, *viz*. that one of the three $O_{term}—S—O_{core}$ angles is some 10° smaller than the other two, which corresponds to an almost planar $O_{term}—S—O_{core}—O_{core}$ disposition for the atoms involved, expressed in a torsion angle nearly (or exactly) equal to 180°, as shown in the last column of Table 7 (Harvey, Baggio, Garland, Burton & Baggio, 2001; Harvey, Baggio, Garland & Baggio, 2001). The effect is seen in structure (III) (fourth column, third and fifth entries; Table 7). However, neither independent moiety in (I) follows this trend, either because there is no distinctly smaller $O_{term}—S—O_{core}$ angle, as in moiety *A*, or because where there is a difference in angles, the associated $O_{term}—S—O_{core}—O_{core}$ is not near 180°, as in moiety *B* (second column, third entry; Table 7). The reasons for this are not clear.

The packing of all three structures can be viewed as an ensemble of spheroidal [(I) and (III)] or prolate [(II)] isolated

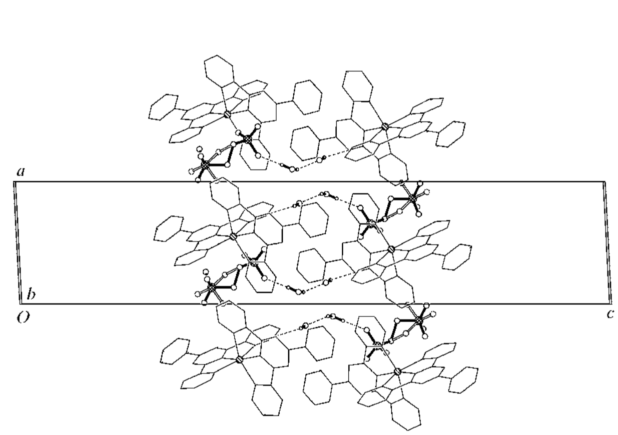


Figure 5
A packing view of (II), showing the [pds^{2-} + $2H_2O$] clusters (heavy lines) as pendant attachements of the cationic network (thin lines). Only part of the unit cell is shown for clarity and only H atoms involved in hydrogen bonding are included.

$[Zn(N3)_2]^{2+}$ groups forming a cationic network, with voids filled by an array of hydrogen-bonded pds^{2-} anions, solvate water molecules and/or some DMF solvate molecules. These interactions can be internal to an anionic linear array and non-interacting with the cations [as in structure (I), Fig. 4], can serve both as an internal connector and as a link from the anionic group through one side to the cationic centres [as in structure (II), Fig. 5], or can bridge two different cationic sites through pds^{2-} anions [structure (III), Fig. 6]. The most important hydrogen-bonding interactions are presented in Tables 2, 4 and 6.

The cationic monomers, in turn, interact with each other through a variety of medium-range contacts, linking aromatic rings in a 'face-to-face' or parallel-displaced arrangement (hereinafter π–π), as well as in an 'edge-to-face' ($C{=}C\cdots\pi$) conformation (for details, see Janiak, 2000). The general trend is very similar in all three structures (Fig. 7). Due to the planar ligands being almost at right angles to each other, symmetry operations, such as a unit-cell translation along the shortest axis [as in (I) and (II)] or an inversion centre [as in (III)], end up favouring the parallel (or perpendicular) approach of adjacent aromatic rings, to build up the two types of interactions described. Due to their similarity, we discuss only the case of structure (I), which is representative of all three. Full information for all three structures can be found from Fig. 7 and Table 8. Fig. 7 displays two neighbouring units of (I) displaced one unit-cell edge along *b*, and shows the two types of interactions linking the adjacent moieties into a 'dimeric' unit, *viz*. a parallel-displaced π–π interaction, linking pyridines N3*B*/C11*B*–C15*B* and N1*B*′/C1*B*′–C5*B*′, with a centre-to-centre distance of 3.67 (1) Å and a slippage angle (the angle subtended by the ring normal and the line joining ring centres) of ~22.1 (1)°, and a $C{=}C\cdots\pi$ contact involving pyridines N1*A*′/C1*A*′–C5*A*′ and N3*B*/C11*B*–C15*B*, with an interplanar angle of 97.0 (1)° and an edge-to-plane distance (bond centre to ring centre) of 4.00 (1) Å. These values, and the corresponding ones for (II) and (II), are normal for these types of contact (Janiak, 2000).

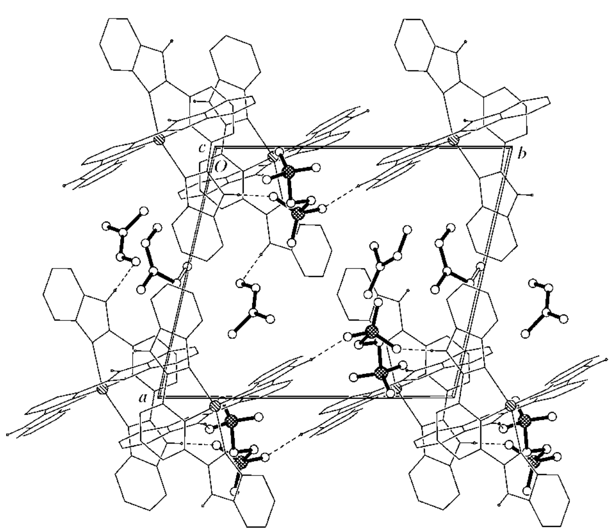


Figure 6
A packing view of (III), showing the pds^{2-} anions (heavy lines) as acceptors of $(N-H)_{cation}\cdots O_{pds}$ hydrogen bonds bridging neighbouring cations (thin lines). Only H atoms involved in hydrogen bonding are included.

Summarizing, we have attempted to produce some $[Zn^{2+}pds^{2-}]$ complexes using N2- and N3-type ligands. The only successful trials were those involving the N3 ligands, which were already known to be extremely versatile when coordinating to other transition metals, binding through either a single or a double tridentate bite provided by one or two ligands, respectively. In the former mode (triple bite of a single N3 ligand), coordination of the accompanying anion is possible, a situation which often leads to the formation of dimers or polymers. The latter case (two N3 ligands), instead, usually produces monomers, as in the complexes reported here, since such coordination leaves no room for any direct anion–cation interaction. Examples of these two different binding modes can be found for most of the transition metals for which these types of complexes have been reported. The single exception seems to be octahedral Zn. Although there are several examples of structures presenting one single N3 ligand bound to a pentacoordinated Zn (CSD refcodes BUJLUN, DOLVIJ, GADLUT, OFABOM, PUWTOQ, TPYZNC, UCECOU and WIBVOZ), none has been reported for hexacoordinated Zn. All the reported cases (CSD refcodes HUGWOV, KOFQIF, LOXDEH, PULCEE, PULCII and QARJEY and XIZNAV) have two such tridentate N3 groups bound to Zn at right angles to each other. It appears that the $[Zn(N3)_2]^{2+}$ chromophore is extremely stable and N3 ligands tend to adopt this particular configuration whenever coordinating to Zn in an octahedral configuration. Our synthetic trials with tpy, tpt and bbp (providing the first reported examples of metal–organic compounds where the pds^{2-} group acts as a counter-ion) appear to confirm this tendency, and at the same time seem to discourage the choice of N3 ligands when trying to coordinate a mild base to Zn. Further synthetic work with the ligands of the N2 group (bpy, phen, dmph), so far unsuccessful, is in progress.

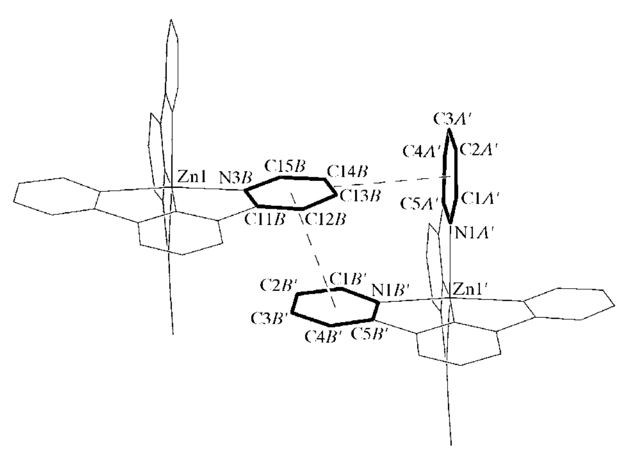


Figure 7
A schematic diagram showing the interactions between $[Zn(N3)_2]^{2+}$ groups in (I).

Experimental

The title compounds were prepared by diffusion of an aqueous solution of $[Zn(CH_3COO)_2]\cdot 2H_2O$ and $K_2(S_2O_8)$ into another solution of the corresponding organic ligand, *i.e.* tpy in DMF for (I), tpt in methanol for (II) and bbp in DMF for (III) (typical quantities: 5 ml of each solution, each component in a 0.025 *M* concentration). The time required for the development of crystals suitable for X-ray diffraction was 15–20 d. All starting materials were of reagent quality and were used without further purification. The formulation of the three compounds was supported by elemental analysis for CHN performed on a Carlo–Erba EA 1108 instrument (O, S and Zn were not analysed). Elemental analysis for (I) required: C 47.57, H 3.99, N 11.77, O 21.12, S 7.70, Zn 7.85%; found: C 47.4, H 4.0, N 11.9%. Elemental analysis for (II) required: C 47.09, H 3.07, N 18.31, O 17.42, S 6.98, Zn 7.12%; found: C 47.1, H 3.1, N 18.4%. Elemental analysis for (III) required: C 51.34, H 4.31, N 16.56, O 16.01, S 5.83, Zn 5.95%; found: C 51.2, H 4.2, N 16.7%.

Compound (I)

Crystal data

$[Zn(C_{15}H_{11}N_3)_2](S_2O_8)\cdot 2H_2O\cdot C_3H_7NO$
$M_r = 833.15$
Triclinic, $P\overline{1}$
$a = 8.7932$ (18) Å
$b = 9.4508$ (19) Å
$c = 22.629$ (5) Å
$\alpha = 89.95$ (3)°
$\beta = 82.97$ (3)°
$\gamma = 82.84$ (3)°
$V = 1851.7$ (7) Å^3
$Z = 2$
$D_x = 1.494$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 184 reflections
$\theta = 2.4$–22.3°
$\mu = 0.85$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.20 × 0.10 × 0.05 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan [*SADABS* (Sheldrick, 1996) in *SAINT* (Bruker, 2000)]
$T_{min} = 0.90$, $T_{max} = 0.96$
18 342 measured reflections
6389 independent reflections
2422 reflections with $I > 2\sigma(I)$
$R_{int} = 0.072$
$\theta_{max} = 25.0°$
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -25 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.155$
$S = 0.81$
6391 reflections
493 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0107P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.009$
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Zn1—N2*A*	2.066 (5)	Zn1—N3*B*	2.183 (5)
Zn1—N2*B*	2.068 (5)	Zn1—N1*B*	2.186 (5)
Zn1—N1*A*	2.178 (5)	Zn1—N3*A*	2.191 (5)
N2*A*—Zn1—N2*B*	173.7 (2)	N1*A*—Zn1—N1*B*	94.0 (2)
N2*A*—Zn1—N1*A*	76.1 (2)	N3*B*—Zn1—N1*B*	150.3 (2)
N2*B*—Zn1—N1*A*	109.9 (2)	N2*A*—Zn1—N3*A*	74.4 (2)
N2*A*—Zn1—N3*B*	106.9 (2)	N2*B*—Zn1—N3*A*	99.7 (2)
N2*B*—Zn1—N3*B*	75.3 (3)	N1*A*—Zn1—N3*A*	150.4 (2)
N1*A*—Zn1—N3*B*	92.3 (2)	N3*B*—Zn1—N3*A*	95.22 (19)
N2*A*—Zn1—N1*B*	102.8 (2)	N1*B*—Zn1—N3*A*	93.45 (19)
N2*B*—Zn1—N1*B*	75.3 (2)		

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1*A*—H1*AA*···O2*W*	0.93	2.48	3.326 (11)	152
C1*B*—H1*BA*···O2*A*^{i}	0.93	2.41	3.182 (9)	140
C3*B*—H3*BA*···O1*C*^{i}	0.93	2.40	3.272 (10)	157
C9*B*—H9*BA*···O2*B*^{ii}	0.93	2.29	3.144 (10)	153
O1*W*—H1*WA*···O1*A*	0.82 (7)	2.01 (7)	2.720 (10)	145 (10)
O1*W*—H1*WB*···O2*A*^{iii}	0.82 (3)	2.25 (6)	2.986 (10)	149 (11)
O2*W*—H2*WA*···O1*B*^{iv}	0.82 (2)	2.44 (10)	2.816 (11)	109 (9)
O2*W*—H2*WB*···O3*B*^{v}	0.82 (5)	2.27 (7)	2.866 (10)	130 (8)

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

Compound (II)

Crystal data

$[Zn(C_{18}H_{12}N_6)_2](S_2O_8)\cdot 2H_2O$
$M_r = 918.19$
Monoclinic, $P2_1/n$
$a = 8.9490$ (18) Å
$b = 9.782$ (2) Å
$c = 43.031$ (9) Å
$\beta = 92.95$ (3)°
$V = 3761.9$ (13) Å^3
$Z = 4$
$D_x = 1.621$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 212 reflections
$\theta = 2.1$–24.4°
$\mu = 0.84$ mm^{-1}
$T = 293$ (2) K
Needle, brown
0.40 × 0.05 × 0.02 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan [*SADABS* (Sheldrick, 1996) in *SAINT* (Bruker, 2000)]
$T_{min} = 0.95$, $T_{max} = 0.98$
21 243 measured reflections
6601 independent reflections
2740 reflections with $I > 2\sigma(I)$
$R_{int} = 0.072$
$\theta_{max} = 25.0°$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 11$
$l = -49 \rightarrow 50$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.120$
$S = 0.83$
6597 reflections
553 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.011$
$\Delta\rho_{max} = 0.86$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

Zn1—N2*A*	2.049 (4)	Zn1—N1*B*	2.159 (5)
Zn1—N2*B*	2.050 (4)	Zn1—N3B	2.232 (5)
Zn1—N1*A*	2.153 (5)	Zn1—N3*A*	2.264 (5)
N2*A*—Zn1—N2*B*	165.3 (2)	N1*A*—Zn1—N3*B*	93.22 (19)
N2*A*—Zn1—N1*A*	75.5 (2)	N1*B*—Zn1—N3*B*	147.8 (2)
N2*B*—Zn1—N1*A*	117.8 (2)	N2*A*—Zn1—N3*A*	73.8 (2)
N2*A*—Zn1—N1*B*	111.3 (2)	N2*B*—Zn1—N3*A*	92.68 (19)
N2*B*—Zn1—N1*B*	74.9 (2)	N1*A*—Zn1—N3*A*	149.25 (19)
N1*A*—Zn1—N1*B*	96.11 (18)	N1*B*—Zn1—N3*A*	95.91 (19)
N2*A*—Zn1—N3*B*	100.8 (2)	N3*B*—Zn1—N3*A*	91.49 (19)
N2*B*—Zn1—N3*B*	73.5 (2)		

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C1A—H1AA···O2^{i}	0.93	2.45	3.354 (8)	163
C2A—H2AA···O6A^{i}	0.93	2.37	3.101 (10)	135
C1B—H1BA···O8^{ii}	0.93	2.40	3.326 (9)	174
O1W—H1WA···N5B^{iii}	0.83 (4)	2.44 (3)	3.217 (9)	157 (5)
O2W—H2WA···O1W	0.81 (3)	1.97 (3)	2.625 (9)	137 (3)
O2W—H2WB···O1	0.82 (5)	2.05 (7)	2.787 (8)	151 (5)

Symmetry codes: (i) $1+x, y, z$; (ii) $1+x, y-1, z$; (iii) $1-x, 2-y, -z$.

Compound (III)

Crystal data

$[Zn(C_{19}H_{13}N_5)_2](S_2O_8)\cdot 3C_3H_7NO$
M_r = 1099.45
Triclinic, $P\overline{1}$
a = 12.301 (3) Å
b = 13.984 (3) Å
c = 16.183 (3) Å
α = 102.83 (3)°
β = 105.49 (3)°
γ = 98.69 (3)°
V = 2549.2 (12) Å^3
Z = 2
D_x = 1.430 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 234 reflections
θ = 2.5–24.0°
μ = 0.64 mm^{-1}
T = 293 (2) K
Prism, colourless
0.50 × 0.25 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan [*SADABS* (Sheldrick, 1996) in *SAINT* (Bruker, 2000)]
T_{min} = 0.83, T_{max} = 0.91
31 134 measured reflections
8987 independent reflections
3809 reflections with $I > 2\sigma(I)$
R_{int} = 0.083
θ_{max} = 25.0°
$h = -14 \rightarrow 13$
$k = -16 \rightarrow 16$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.198
S = 0.98
8993 reflections
677 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.74 e Å^{-3}

Table 5
Selected geometric parameters (Å, °) for (III).

Zn1—N2A	2.127 (5)	Zn1—N1A	2.193 (5)
Zn1—N2B	2.134 (5)	Zn1—N3B	2.199 (5)
Zn1—N1B	2.170 (5)	Zn1—N3A	2.219 (6)
N2A—Zn1—N2B	173.6 (2)	N1B—Zn1—N3B	149.67 (18)
N2A—Zn1—N1B	108.04 (17)	N1A—Zn1—N3B	94.68 (18)
N2B—Zn1—N1B	75.26 (19)	N2A—Zn1—N3A	74.86 (19)
N2A—Zn1—N1A	76.52 (19)	N2B—Zn1—N3A	99.4 (2)
N2B—Zn1—N1A	109.1 (2)	N1B—Zn1—N3A	97.14 (19)
N1B—Zn1—N1A	92.18 (18)	N1A—Zn1—N3A	151.37 (19)
N2A—Zn1—N3B	102.29 (18)	N3B—Zn1—N3A	90.81 (19)
N2B—Zn1—N3B	74.6 (2)		

Table 6
Hydrogen-bonding geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
N4A—H4NA···O1C^{i}	0.86	1.96	2.817 (6)	176
N5A—H5NA···O1P^{ii}	0.86	1.86	2.706 (12)	170
N4B—H4NB···O3C^{iii}	0.86	1.99	2.794 (7)	154
N5B—H5NB···O7C^{iv}	0.86	1.88	2.703 (7)	161
C10A—H10A···O1L^{ii}	0.93	2.17	3.063 (15)	160
C16A—H16A···O3C	0.93	2.50	3.414 (12)	168
C10B—H10B···O6C^{iii}	0.93	2.51	3.213 (10)	133
C11B—H11B···O6C^{iv}	0.93	2.52	3.430 (10)	166
C1P—H1PA···O2C^{v}	0.93	2.35	3.213 (15)	154

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

Table 7
Selected bond and torsion angles (°) for the pds^{2-} anion in structures (I) and (III).

Bond–torsion angle pair	(I), $x = A$	(I), $x = B$	(III), $x = C$	Previous work†
O1x—S1x—O4x	101.8 (5)	104.7 (5)		
O1x—S1x—O4x—O4x^{i}	68.5 (8)	101.9 (10)		
O2x—S1x—O4x	102.2 (4)‡	110.6 (4)		
O2x—S1x—O4x—O4x^{i}	−172.3 (8)‡	−24.0 (11)		
O3x—S1x—O4x	108.1 (4)	94.3 (4)‡		
O3x—S1x—O4x—O4x^{i}	−47.2 (8)	139.6 (10)‡		
O1x—S1x—O4x			104.9 (3)	98.3 (3)‡
O1x—S1x—O4x—O5x			−61.6 (6)	172.9 (4)‡
O2x—S1x—O4x			105.8 (4)	106.8 (3)
O2x—S1x—O4x—O5x			58.8 (7)	53.2 (5)
O3x—S1x—O4x			100.0 (3)‡	105.7 (2)
O3x—S1x—O4x—O5x			179.5 (5)‡	−68.3 (4)
O6x—S2x—O5x			104.8 (4)	97.2 (3)‡
O6x—S2x—O5x—O4x			64.0 (7)	176.2 (4)‡
O7x—S2x—O5x			99.1 (3)‡	103.9 (3)
O7x—S2x—O5x—O4x			−178.2 (6)‡	56.0 (5)
O8x—S2x—O5x			104.8 (3)	106.3 (3)
O8x—S2x—O5x—O4x			−59.5 (6)	−64.4 (5)

† Harvey, Baggio, Garland, Burton & Baggio (2001) ‡ Bond–torsion angle pairs most nearly fulfilling the correlating conditions (see text). Symmetry code: (i) $2-x, 2-y, -z$.

For all three title compounds, the crystals diffracted very poorly, with insignificant data beyond 2θ = 50°. In all cases, they provided extremely low N_{obs}/N_{total} ratios (0.38, 0.42 and 0.43, respectively). H atoms attached to C or N atoms and unambiguously defined by the stereochemistry were placed in their calculated positions (C—H = 0.93 Å and N—H = 0.86 Å) and allowed to ride. The terminal methyl groups in the DMF molecules (C—H = 0.96 Å) were also allowed to rotate. The H atoms of the water molecules were located in structure (I) and three out of four were located in structure (II) (the remaining H atom was probably highly delocalized, due to it not being involved in hydrogen bonding). They were refined with restrained O—H distances of 0.82 Å, and (when applicable) with an H···H minimum of 1.36 Å. The pds^{2-} anion in (II), as well as a DMF molecule in (III), appeared disordered and were refined with restrained bond distances. For this reason, the anion in (II) was not considered when dis-

Table 8
Intercationic contacts (Å, °) for (I), (II) and (III).

Compound	Group 1/Group 2	Contact type	IPD (Å)	CCD (Å)	SA (°)	ECD (Å)	IPA (°)
(I)	N3*B*,C11*B*–C15*B*/N1*B*′,C1*B*′–C5*B*	π–π	3.48 (1)	3.67 (1)	22.1 (1)		
(I)	C13*B*–C14*B*/N1*A*′,C1*A*′–C5*A*′	C=C···π				4.00 (1)	97.0 (1)
(II)	N1*B*,C1*B*–C5*B*/N3*B*′,C9*B*′–C13*B*′	π–π	3.53 (1)	3.99 (1)	22.6 (1)		
(II)	C2*B*–C3*B*/N3*A*′,C9*A*′–C15*A*′	C=C···π				3.90 (1)	100.9 (1)
(III)	N3*B*,N5*B*,C13*B*–C19*B*/N3*B*′,N5*B*′,C13*B*′–C19*B*′	π–π	3.37 (1)	3.65 (1)	22.6 (1)		
(III)	C15*B*–C16*B*/C1*A*′–C6*A*′	C=C···π				4.25 (1)	94.6 (1)

Notes: see Figs. 1–3 and Fig. 7 for details of the atom labelling. IPD is the interplanar distance, CCD the centre-to-centre distance, SA the slippage angle, ECD the edge-to-centre distance and IPA the interplanar angle.

cussing the pds^{2-} geometry. Full use of the CCDC package was made for searching in the CSD (Allen, 2002).

For all three compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1063). Services for accessing these data are described at the back of the journal.

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