

Bis[(acetato- κ^2 O,O')]bis(4,4'-dimethyl-2,2'-bipyridyl- κ^2 N,N')zinc(II)] trithionate pentahydrate

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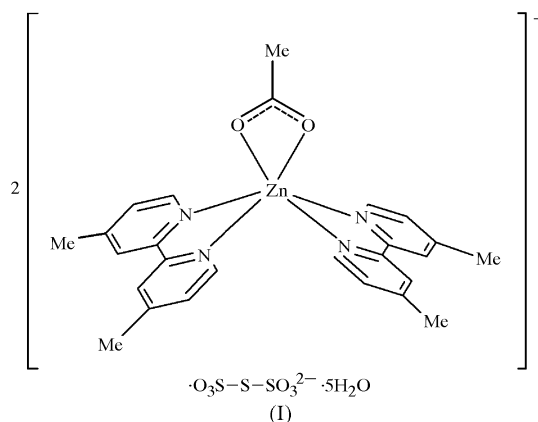
The title ionic zinc–acetate complex, $[\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)(\text{C}_{12}\text{H}_{12}\text{N}_2)_2]_2(\text{S}_3\text{O}_6) \cdot 5\text{H}_2\text{O}$, contains a ZnN_4O_2 nucleus provided by the three bidentate ligands acting in a chelating mode. The trithionate unit, in turn, acts as an isolated charge-balancing counter-ion. The structure has a three-dimensional assembly achieved through three different interaction types, *viz.* Coulomb, hydrogen bonding and π – π . The trithionate group and one of the solvent water molecules are disordered around inversion centers.

Comment

Many synthetic routes are available for the preparation of polythionate anions ($\text{O}_3\text{S}_n\text{O}_3^{2-}$, $2 \leq n$), even though mechanistic details are frequently obscured because of the numerous simultaneous and competing redox, catenation and/or disproportionation reactions that may occur. We have recently commented (Díaz de Vivar *et al.*, 2004, 2005) on the feasibility of producing novel thiosulfate complexes of group XII metals, complexes that are difficult to obtain by conventional methods, through the decomposition of less common sulfur oxoanions, such as dithionite and/or pyrosulfite. One of the reported ways to obtain trithionate ($\text{O}_3\text{S}_3\text{O}_3^{2-}$) is the reaction between aqueous thiosulfate and sulfur dioxide (Remy, 1956), but structures containing the anion are rare, as a survey of the current structural databases reveals. In the November 2004 update of the Cambridge Structural Database (CSD; Allen, 2002), out of a total of 132 structures containing polythionates of diverse chain lengths ($2 \leq n \leq 6$), the most common species by far were dithionates ($n = 2$), with 112 entries; only one trithionate, *viz.* *cis*-amminebromobis(ethylenediamine)cobalt(III) trithionate, hereafter (II) (Chun *et al.*, 2000), was found. Similarly sparse was the outcome of a search

of the 2004 release of the ICSD (2001), with only one fully reported structure, dipotassium trithionate, hereafter (III) (Christidis & Rentzeperis, 1985). We present here only the third reported structure containing a trithionate anion, *viz.* $[\text{Zn}(\text{acet})(\text{dmbpy})_2]_2(\text{S}_3\text{O}_6) \cdot 5\text{H}_2\text{O}$ (dmbpy is 4,4'-dimethyl-2,2'-bipyridyl and acet is acetate), (I), which was prepared serendipitously.

Fig. 1 shows an ellipsoid diagram of (I). The structure is ionic, and consists of monomeric $[\text{Zn}(\text{acet})(\text{dmbpy})_2]^+$ cations balanced by $\text{S}_3\text{O}_6^{2-}$ anions in a 2:1 ratio, together with two and a half independent solvent water molecules.



The six-coordinate Zn cation binds to three chelating ligands and, as a result of the angular restraints in force, the ZnN_4O_2 polyhedron appears highly distorted. However, the mean values of the Zn–N and Zn–O distances [2.110 (14) and 2.22 (3) Å, respectively] depart only slightly from the corresponding means in similar coordination spheres with no geometric restraints [2.14 (8) and 2.19 (15) Å, respectively, for 264 cases found in the CSD].

In spite of its being disordered about an inversion center, the trithionate ion could be adequately refined. When compared with the only other two reported structures containing this (counter-)anion, no significant differences could be detected, as the following values given in a (I)/(II)/(III) sequence confirm: $\langle \text{S}–\text{O} \rangle$ 1.43 (3)/1.443 (5)/1.45 (2) Å; $\langle \text{S}–\text{S} \rangle$ 2.10 (4)/2.102 (14)/2.08 (2) Å; S–S–S 107.1 (1)/107.1 (1)/106.4 (1)°. It is noteworthy that the anion shows the same characteristic feature frequently observed in many peroxodisulfates (Harvey, Baggio, Garland, Burton & Baggio, 2001; Harvey, Baggio, Garland & Baggio, 2001). The S–S–S–O groups that are more nearly planar (with torsion angles of 155–180°) are those that present a terminal S–S–O angle some 10° smaller than the other two S–S–O angles involving the remaining terminal O atoms (Table 1).

A feature in the structure is the three-dimensional assembly achieved through three different interaction types, *viz.* Coulomb, hydrogen bonding and π – π . Fig. 2 shows a projection on to the (111) plane, where two distinct types of one-dimensional array are apparent, *viz.* a cationic chain formed by the juxtaposition of π -bonded $[\text{Zn}(\text{acet})(\text{dmbpy})_2]^+$ monomers, and an anionic chain determined by the hydrogen-bonded solvent water molecules and trithionate anions. The former chain is built up around the inversion centers at $(0, \frac{1}{2}, \frac{1}{2})$

and $(\frac{1}{2}, \frac{1}{2}, 0)$, which through the duplication of moieties *dmbpy(A)* and *dmbpy(B)*, respectively, leads to two symmetry-related pairs of aromatic rings at a graphitic distance from each other (about 3.5 Å; see Table 3). For clarity, these chains have been represented in Fig. 2 with consecutive monomers drawn in contrasting line widths. The anionic arrays evolve between these cationic chains as wavy tightly woven strips, where the water molecules cluster around one another and act as connectors between trithionate anions. Details of the hydrogen-bonding scheme are presented in Table 2.

The interaction between the two different types of chains is achieved through the omnipresent Coloumb forces, as well as *via* a hydrogen bond connecting atom O3W, on the anionic side, with an acetate O atom on the cationic side. The final ensemble, depicted in Fig. 2, is a two-dimensional array some

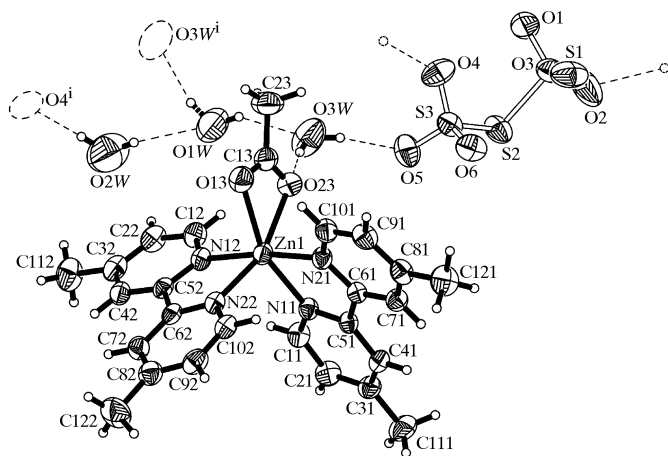


Figure 1
An XP diagram (Sheldrick, 1994) of (I), shown with 50% probability displacement ellipsoids. For clarity, only one of the two disordered moieties of the trithionate group is shown.

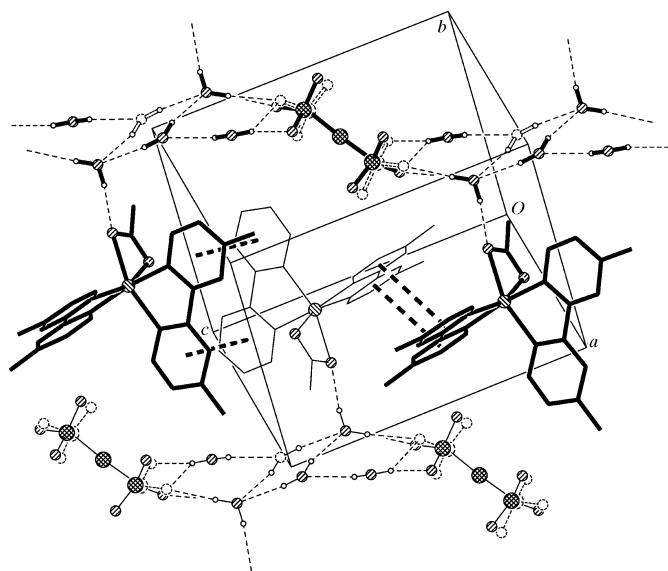


Figure 2
A projection of the structure on the (111) plane. See *Comment* and Table 3 for details.

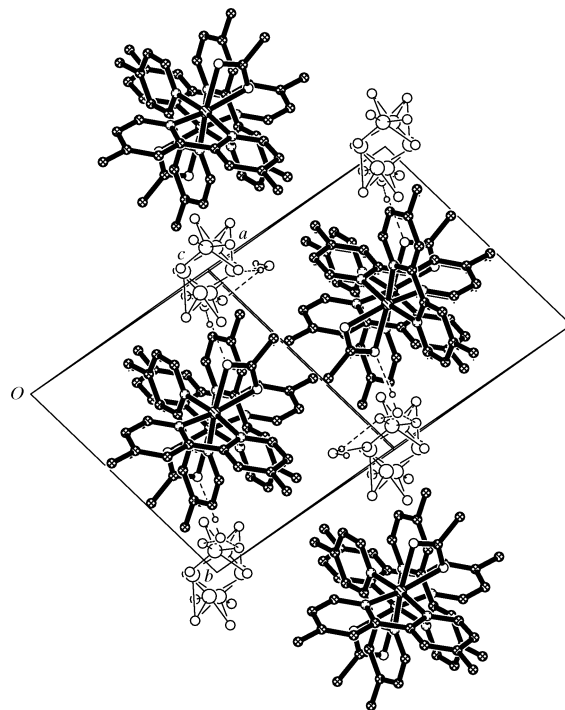


Figure 3
A projection of the structure down $[101]$, the chain direction, at 90° from the view in Fig. 2. Note the alternation of cationic (bold lines) and anionic (light lines) chains.

7 Å in width (the diameter of the rather ‘globular’ cationic unit). These planes stack along $[111]$, but with a lateral shift of one ‘interchain spacing’ perpendicular to the direction of the chain (Fig. 3), thus confronting positively charged columns in one sheet with negative ones in the neighboring sheet, and providing for stabilization of the three-dimensional structure.

Experimental

The title compound was obtained by dissolving the aromatic amine in ethanol (96%) and allowing this solution to diffuse slowly into an aqueous solution of $[\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2] \cdot 2\text{H}_2\text{O}$ and $\text{K}_2\text{S}_2\text{O}_5$ (molar ratio 1:1:2). After two months, crystals of a size suitable for X-ray analysis had developed.

Crystal data

$[\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)(\text{C}_{12}\text{H}_{12}\text{N}_2)_2]_2 \cdot (\text{S}_3\text{O}_6) \cdot 5\text{H}_2\text{O}$
 $M_r = 1268.04$
 Triclinic, $P\bar{1}$
 $a = 9.7456$ (11) Å
 $b = 11.2370$ (12) Å
 $c = 14.5676$ (16) Å
 $\alpha = 73.043$ (2)°
 $\beta = 70.943$ (2)°
 $\gamma = 85.260$ (2)°
 $V = 1442.2$ (3) Å³

$Z = 1$
 $D_x = 1.460$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 1232 reflections
 $\theta = 4.0\text{--}23.5^\circ$
 $\mu = 1.01$ mm⁻¹
 $T = 295$ (2) K
 Plate, colorless
 $0.25 \times 0.12 \times 0.08$ mm

Data collection

Bruker CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2001)
 $T_{\min} = 0.84$, $T_{\max} = 0.92$
 10 738 measured reflections

6282 independent reflections
 4707 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$
 $\theta_{\text{max}} = 28.1^\circ$
 $h = -12 \rightarrow 12$
 $k = -14 \rightarrow 14$
 $l = -18 \rightarrow 19$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.144$
 $S = 1.03$
6282 reflections
412 parameters
H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0784P)^2 + 0.0235P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.008$
 $\Delta\rho_{\max} = 0.62 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.34 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Zn1—N11	2.091 (2)	S1—O1	1.407 (11)
Zn1—N22	2.104 (2)	S1—O2	1.463 (9)
Zn1—N21	2.119 (2)	S1—S2	2.138 (9)
Zn1—N12	2.127 (2)	S2—S3	2.056 (7)
Zn1—O13	2.193 (2)	S3—O6	1.409 (9)
Zn1—O23	2.243 (2)	S3—O4	1.445 (9)
S1—O3	1.397 (10)	S3—O5	1.470 (10)
O3—S1—S2	105.8 (6)	O6—S3—S2	108.9 (5)
O1—S1—S2	107.9 (6)	O4—S3—S2	108.2 (5)
O2—S1—S2	98.1 (4)	O5—S3—S2	99.5 (4)
S1—S2—S3—O5	157.0 (3)	O2—S1—S2—S3	168.2 (5)

Table 2

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1W1 \cdots O3W ⁱ	0.85 (4)	1.94 (5)	2.759 (8)	160 (6)
O1W—H1W2 \cdots O3W	0.85 (4)	2.03 (5)	2.881 (9)	174 (9)
O2W—H2W1 \cdots O4 ⁱ	0.86 (5)	1.91 (4)	2.759 (8)	167 (8)
O2W—H2W2 \cdots O1W	0.86 (4)	2.24 (4)	3.077 (10)	163 (7)
O3W—H3W1 \cdots O23	0.85 (5)	2.02 (4)	2.858 (5)	169 (5)
O3W—H3W2 \cdots O5	0.86 (4)	2.09 (5)	2.894 (7)	157 (6)

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

Table 3

π - π contacts in (I).

cpd: (average) centroid-to-plane distance; ccd: centroid-to-centroid distance; sa: slippage angle, *i.e.* (average) angle between the intercentroid vector and the, not strictly parallel, plane normals. For details, see Janiak (2000).

Group 1	Group 2	cpd (\AA)	ccd (\AA)	sa ($^\circ$)
N11/C11/C21/ C31/C41/C51	N21 ⁱⁱ /C61 ⁱⁱ /C71 ⁱⁱ / C81 ⁱⁱ /C91 ⁱⁱ /C101 ⁱⁱ	3.417 (17)	3.542 (2)	15.2 (10)
N12/C12/C22/ C32/C42/C52	N22 ⁱⁱⁱ /C62 ⁱⁱⁱ /C72 ⁱⁱⁱ / C82 ⁱⁱⁱ /C92 ⁱⁱⁱ /C102 ⁱⁱⁱ	3.45 (2)	3.569 (2)	14.9 (15)

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

H atoms attached to C atoms were placed at calculated positions (aromatic C—H = 0.93 \AA and methyl C—H = 0.96 \AA) and allowed to ride. Methyl groups were allowed to rotate around the C—C axis. H atoms of water molecules were located from difference Fourier syntheses and refined with restrained O—H distances [0.85 (2) \AA]. All H atoms were assigned $U_{\text{iso}}(\text{H})$ values of $xU_{\text{eq}}(\text{host})$, with $x = 1.2$ for aromatic and water H atoms, and $x = 1.5$ for methyl H atoms. The trithionate group and one of the solvent water molecules (O1W) are disordered around inversion centers, each with an occupancy of 0.5.

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2000); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL97*.

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