

## A polymeric zinc thiosulfate complex containing anionic and cationic chains based on tetrahedral and octahedral zinc sites

M. Enriqueta Díaz de Vivar,<sup>a\*</sup> Sergio Baggio,<sup>a</sup>  
María Teresa Garland<sup>b</sup> and Ricardo Baggio<sup>c</sup>

<sup>a</sup>Universidad Nacional de la Patagonia, Sede Puerto Madryn, 9120 Puerto Madryn, Chubut, Argentina, and CenPat, CONICET, 9120 Puerto Madryn, Chubut, Argentina,

<sup>b</sup>Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile and CIMAT, Casilla 487-3, Santiago de Chile, Chile, and <sup>c</sup>Departamento de Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina

Correspondence e-mail: undiaz@cenpat.edu.ar

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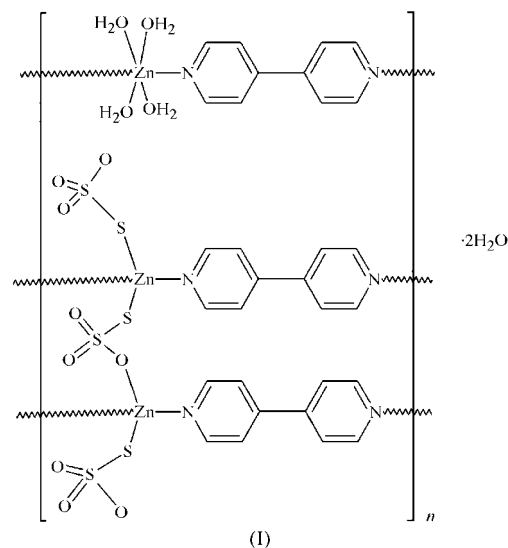
*catena*-Poly[[[tetraaquazinc(II)]- $\mu$ -4,4'-bipyridine- $\kappa^2N:N'$ ][[ $\mu$ -thiosulfato- $\kappa^2O:S$ -bis[(thiosulfato- $\kappa S$ )zinc(II)]]-di- $\mu$ -4,4'-pyridine- $\kappa^4N:N'$  dihydrate], {[Zn(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)(H<sub>2</sub>O)<sub>4</sub>][Zn<sub>2</sub>(S<sub>2</sub>O<sub>3</sub>)<sub>3</sub>-(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>]-2H<sub>2</sub>O]<sub>n</sub>}, is a polymeric zinc complex built up from thiosulfate-containing anionic chains, where the Zn atom is tetrahedrally coordinated, and aqua-containing cationic chains incorporating octahedrally coordinated Zn. In each type of chain, the 4,4'-bipyridine units act as spacers, and the chains run along three non-intersecting almost orthogonal directions in space. The profusion of hydrogen-bond donors (all the H atoms of the water molecules) and acceptors (the thiosulfate O and S atoms) generates a very complex hydrogen-bonding scheme.

### Comment

Sulfur oxoanions (such as sulfate, sulfite and thiosulfate) are usually good ligands towards transition metal cations, and when used as the unique connecting agent their multidentate capacity makes them prone to generating tight and compact three-dimensional structures (*e.g.* Bear & Mumme, 1970; Bugli & Carré, 1980; Magnusson & Johansson, 1981). In order to 'open' the framework, it is possible to include bulkier (usually organic) ligands in the synthesis, whose connectivity properties might modify the final structural outcome. Thus, 'chelating' N-heterocyclic bases, such as 2,2'-bipyridine and 1,10-phenanthroline, tend to act as 'terminal' points in the connectivity chains, with a splitting action leading to monomers/dimers, chains or sheets, often tightly interdigitated and held together through aromatic  $\pi$ - $\pi$  interactions (Díaz de Vivar *et al.*, 2004, 2005, 2006).

On the other hand, when these chelating ligands are replaced by their 'bridging' counterparts, such as 4,4'-bi-

pyridine (4,4'-bipy), more open frameworks are often obtained; these compounds are becoming the object of active research owing to the interesting catalytic properties that some of them display (Wu *et al.*, 2002, and references therein). We report here an interesting structure, (I), which contains an open framework where 4,4'-bipyridine acts as a spacer. To our knowledge, this is the first Zn<sup>II</sup> complex containing thiosulfate and 4,4'-bipyridine.



In this structure, two different one-dimensional arrays co-exist, *viz.* a cationic chain consisting of one heterocyclic base unit and four water molecules bound to a six-coordinate Zn atom (Zn3), and a second array, describable as an anionic double chain providing for charge balance and built up around the two remaining four-coordinate Zn centres (Zn1 and Zn2), bound to two heterocyclic base units and to three thiosulfate anions (Fig. 1).

The environment around atom Zn3 is a nearly perfect octahedron, with the equatorial plane formed by four evenly distributed water molecules [O1W–O4W; the angular span around Zn3 is 86.32 (5)–95.53 (6)°; the mean deviation from the least-squares equatorial plane is 0.01 (1) Å]. Two N atoms [N5<sup>ii</sup> and N6; symmetry code: (ii)  $x - \frac{1}{2}, y + \frac{1}{2}, z$ ] from two symmetry-related 4,4'-bipy units occupy the axial positions [N5<sup>ii</sup>–Zn3–N6 = 176.36 (6)°; the largest deviation from the mean-plane normal is 3.5 (1)° for the Zn3–N5<sup>ii</sup> vector] and serve as the connector for the cationic one-dimensional structure that builds up along [110] and, as a result of the *c*-glide, also along  $[\bar{1}10]$ , *c*/2 apart from the former.

On the other hand, the coordination polyhedra around atoms Zn1 and Zn2 are similar to each other with regard to coordination number ( $n = 4$ ), but diverse both in their components and in their distortions with respect to an expected ideal tetrahedral geometry. Atom Zn1 coordinates to two donor N atoms [N1 and N2<sup>i</sup>; symmetry code: (i)  $x, -y, z + \frac{1}{2}$ ] from two symmetry-related 4,4'-bipy groups, and two S atoms (S2 and S4) from two different thiosulfate anions, determining a linear polymer where the organic ligand acts as a spacer between two symmetry-related metal ions. Atom Zn2 is also four-coordinate and bound to two symmetry-related

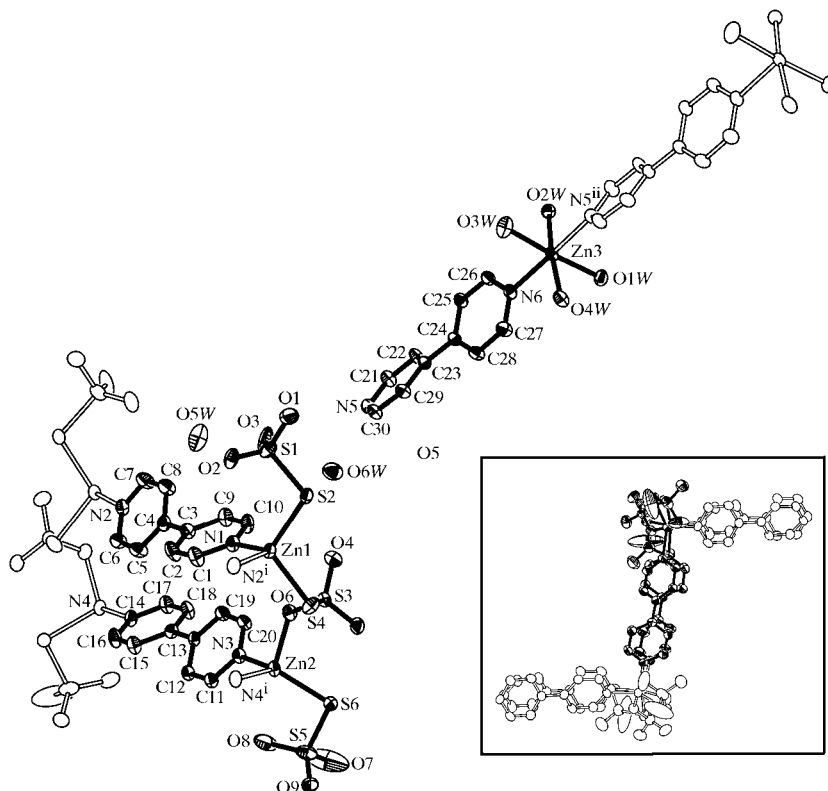
## metal-organic compounds

independent 4,4'-bipy groups *via* two N atoms (N3 and N4<sup>i</sup>) and to two thiosulfate anions, this time through one O (O6) and one S (S6) atom. When connected through the 4,4'-bipy molecule, these groups also define linear chains, parallel to the Zn1 counterpart. Each of the Zn1 and Zn2 centres is in turn connected by one of the thiosulfate anions (acting in a bridging mode), thus forming a two-dimensional net through the Zn1–S4–S3–O6–Zn2 bridge.

The result is that the anionic part of the structure can be seen as ribbons resembling a twisted ladder (Fig. 1), with the

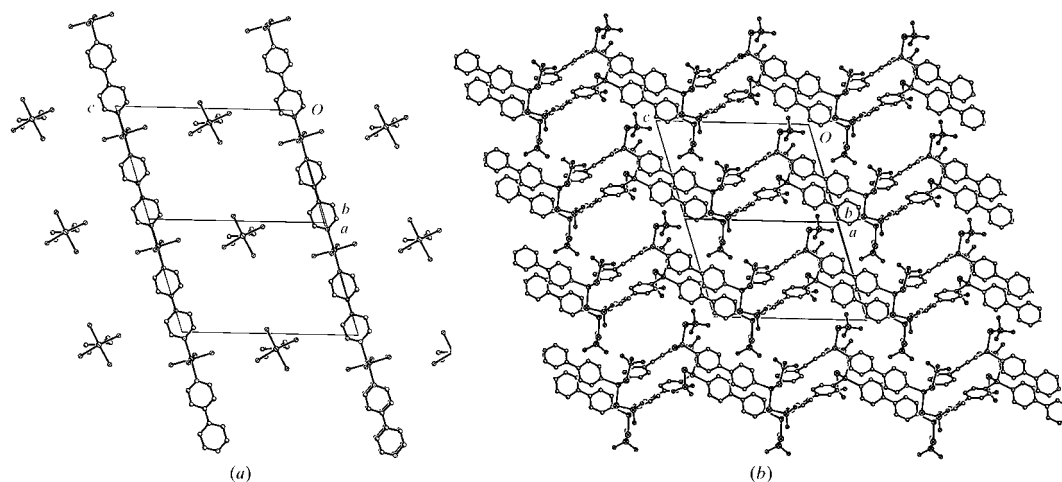
'uprights' defined by pairs of parallel 4,4'-bipy units and the 'steps' by extended Zn<sub>2</sub>(S<sub>2</sub>O<sub>3</sub>)<sub>3</sub> groups. At each 'step', the expected straight direction of the ladder 'breaks' in a 120° zigzag fashion (see the insert in Fig. 1). The strips evolve parallel to each other along the *c* axis.

The thiosulfate anions display two different coordination modes, *i.e.* monodentate ( $\mu$ -S) and bidentate ( $\mu$ -S,O), both of them quite frequent in the coordination behaviour of the anion. Both monodentate units present some kind of disorder (see *Experimental*).



**Figure 1**

The molecular structure of (I). The independent (symmetry-related) part is drawn in full (empty) lines and shows 60% probability displacement ellipsoids. The symmetry codes are as in Table 1. Insert: a lateral view of the anionic chain, showing its zigzag character; see *Comment* for details.



**Figure 2**

Partial (and superimposable) projections of the structure along  $[1\bar{1}0]$ . (a) The straight cationic chains, running along  $[110]$  (top to bottom) and  $[1\bar{1}0]$  (coming out of the figure); the anionic chains have been omitted for clarity. (b) The zigzag anionic chains, running parallel to  $[001]$ . The cationic chains have been omitted for clarity.

As already stated, the three independent 4,4'-bipy units in the structure act as spacers, and all of the individual 4,4'-bipy groups are oriented out of the common mean plane [the dihedral angles are 39.3 (1), 30.8 (1) and 32.1 (1)° for the 4,4'-bipy units in the Zn1, Zn2 and Zn3 chains, respectively].

Fig. 2 shows how the three individual one-dimensional structures pack, the straight cationic chains running parallel to the [110] and  $[\bar{1}10]$  diagonals (each family  $c/2$  away from one another; Fig. 2a), and the zigzag anionic ribbons running along [001] (Fig. 2b). The three types of chains evolve in space in much the same way as the three independent sets of screw axes do in space group  $P2_12_12_1$ , conforming a set of three non-intersecting one-dimensional structures. There is, however, a strong interaction between different chains, due to the very complex hydrogen-bonding scheme (Table 2), having the water molecules of the cationic chain as the donors and the thiosulfate units of the anionic chains as the acceptors.

## Experimental

4,4'-Bipyridine was dissolved in methanol and left to diffuse slowly at room temperature over an aqueous solution of  $\text{Na}_2\text{S}_2\text{O}_3$  and zinc acetate in a 1:1:1 molar ratio. Colourless crystalline aggregates of (I) appeared after ten days, from which crystals suitable for X-ray analysis could be separated.

### Crystal data

$[\text{Zn}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4][\text{Zn}_2(\text{S}_2\text{O}_3)_3(\text{C}_{10}\text{H}_8\text{N}_2)_2] \cdot 2\text{H}_2\text{O}$	$\beta = 115.340 (2)^\circ$
$M_r = 1109.12$	$V = 4176.4 (3) \text{ \AA}^3$
Monoclinic, $Cc$	$Z = 4$
$a = 16.6521 (8) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 15.5103 (7) \text{ \AA}$	$\mu = 2.08 \text{ mm}^{-1}$
$c = 17.8922 (8) \text{ \AA}$	$T = 292 (2) \text{ K}$
	$0.22 \times 0.10 \times 0.08 \text{ mm}$

### Data collection

Bruker SMART CCD area-detector diffractometer	29188 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	11611 independent reflections
$T_{\min} = 0.657$ , $T_{\max} = 0.851$	11255 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.019$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$	$\Delta\rho_{\text{max}} = 0.57 \text{ e \AA}^{-3}$
$wR(F^2) = 0.051$	$\Delta\rho_{\text{min}} = -0.41 \text{ e \AA}^{-3}$
$S = 0.90$	Absolute structure: Flack (1983),
11611 reflections	5223 Friedel pairs
601 parameters	Flack parameter: 0.006 (4)
H atoms treated by a mixture of independent and constrained refinement	

H atoms attached to C atoms were placed at calculated positions, with C—H distances of 0.93 Å, and allowed to ride. Those bound to O atoms were located in difference maps and then refined with the sole restraint of a common refinable O—H distance which converged to 0.78 (2) Å. For all H atoms,  $U_{\text{iso}}(\text{H})$  values were set at  $1.2U_{\text{eq}}(\text{carrier})$ . Both monocoordinated thiosulfate groups (S1/S2/O1—O3 and S5/S6/O7—O9) presented some kind of disorder in the non-coordinated atoms and were refined with split models. The occupation factors for the major/minor components in each group refined to 0.727 (2)/0.273 (2) and 0.746 (8)/0.254 (8), respectively. The correct orientation of the structure with respect to the polar-axis direction was determined by means of the Flack (1983) parameter.

**Table 1**  
Selected bond lengths (Å).

Zn1—N1	2.0411 (15)	Zn2—S6	2.2719 (5)
Zn1—N2 <sup>i</sup>	2.0577 (15)	Zn3—O4W	2.0924 (13)
Zn1—S2	2.2967 (5)	Zn3—O2W	2.0927 (13)
Zn1—S4	2.3332 (5)	Zn3—O3W	2.1090 (15)
Zn2—O6	2.0237 (13)	Zn3—N6	2.1446 (15)
Zn2—N3	2.0422 (14)	Zn3—N5 <sup>ii</sup>	2.1529 (15)
Zn2—N4 <sup>i</sup>	2.0457 (15)	Zn3—O1W	2.1705 (14)

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

**Table 2**  
Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1W—H1WA $\cdots$ S4 <sup>iii</sup>	0.797 (17)	2.71 (2)	3.4264 (14)	150 (2)
O1W—H1WB $\cdots$ O3 <sup>iv</sup>	0.794 (17)	1.909 (18)	2.700 (2)	175 (3)
O2W—H2WA $\cdots$ O5W <sup>v</sup>	0.790 (16)	1.865 (17)	2.649 (2)	171 (3)
O2W—H2WB $\cdots$ O8 <sup>vi</sup>	0.773 (16)	1.943 (18)	2.699 (3)	165 (2)
O3W—H3WA $\cdots$ O4 <sup>ii</sup>	0.759 (17)	2.088 (18)	2.8354 (19)	168 (3)
O3W—H3WB $\cdots$ O9 <sup>vi</sup>	0.794 (17)	1.889 (18)	2.678 (4)	173 (3)
O4W—H4WA $\cdots$ O2 <sup>iv</sup>	0.782 (17)	1.952 (18)	2.719 (2)	167 (3)
O4W—H4WB $\cdots$ O5 <sup>ii</sup>	0.806 (16)	2.045 (19)	2.815 (2)	160 (3)
O5W—H5WA $\cdots$ O2	0.799 (18)	2.06 (2)	2.815 (3)	157 (3)
O5W—H5WB $\cdots$ O5 <sup>vii</sup>	0.805 (18)	1.942 (18)	2.744 (2)	174 (3)
O6W—H6WA $\cdots$ O1	0.789 (18)	2.042 (18)	2.828 (3)	175 (3)
O6W—H6WB $\cdots$ O7 <sup>viii</sup>	0.789 (18)	1.950 (19)	2.722 (3)	166 (3)

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

Data collection: SMART-NT (Bruker, 2001); cell refinement: SAINT-NT (Bruker, 2001); data reduction: SAINT-NT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL-NT (Bruker, 2001); software used to prepare material for publication: SHELXTL-NT and PLATON (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3072). Services for accessing these data are described at the back of the journal.

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