Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: CF1096). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Akhtar, B. & Drew, M. G. B. (1982). *Acta Cryst.* **B38**, 1149–1154.

Frenz, B. A. (1985). *Enraf–Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf–Nonius, Delft, The Netherlands.

Garnovskii, A. D., Nivorozhkin, A. L. & Minkin, V. I. (1993). *Coord. Chem. Rev.* **126**, 1–42.

Hall, S. R. & Stewart, J. M. (1990). Editors. *Xtal*3.0 *Reference Manual*. Universities of Western Australia, Australia, and Maryland, USA.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kopfmann, G. & Huber, R. (1968). *Acta Cryst.* **A24**, 348–351.

Labisbal, E., Romero, J., García-Vasquez, J. A., Sousa, A., Castellano, E. E. & Zukerman-Schpector, J. (1994). *Acta Cryst.* **C50**, 1043–1044.

Maggio, F., Pizzino, T. & Romano, V. (1974). *Inorg. Nucl. Chem. Lett.* **10**, 1005–1008.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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Sodium Bis(2,9-dimethyl-1,10-phenanthroline)-μ-hydroxo-di(thiosulfato)dizinc(II) Pentahydrate Methanol Solvate

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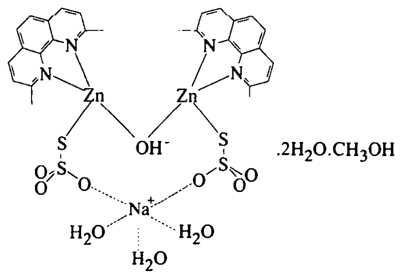
Abstract

The title complex, triaqua-1κ^3O-bis(2,9-dimethyl-1,10-phenanthroline)-2κ^2N,N';3κ^2N,N'-μ-hydroxo-2:3κ^2O-di-μ-thiosulfato-1:2$\kappa^2O:S$;1:3$\kappa^2O:S$-sodiumdizinc(II) dihydrate methanol solvate, $[Zn_2(C_{14}H_{12}N_2)_2(\mu\text{-}OH)(\mu\text{-}S_2O_3)_2Na(H_2O)_3].2H_2O.CH_3OH$, presents an unusual ten-membered ring containing three different metal centers, two zinc and one sodium, bridged by one hydroxo and two thiosulfate groups. The thiosulfate groups bridge through S and O atoms, with a mean S—S bond length which is longer than that found in the free anion, with the corresponding S—O distances shorter. Both zinc coordination spheres are tetrahedral, while that of the pentacoordinate sodium is distorted trigonal bipyramidal. The monomeric units are linked by strong hydrogen-bonding interactions into chains parallel to **z**, which in turn are held together by hydrogen-bonding contacts through some not fully occupied solvate molecule sites, as well as by van der Waals interactions.

Comment

Zn^{II} complexes including the thiosulfate ion as a ligand are not common. The few structures reported so far (Andreetti, Cavalca, Domiano & Musatti, 1968; Baggio, Baggio & de Perazzo, 1974; Baggio, Baggio, Pardo & Garland, 1996) invariably display very interesting coordination geometries, a characteristic shared by many d^{10} ions, where the coordination number is strongly influenced by the ligands involved, as well as by crystal-packing interactions and hydrogen-bonding forces. As part of a structural study of complexes of d^{10} ions containing the thiosulfate group, we report here the structure of $[Zn_2(dmph)_2(\mu\text{-}OH)(\mu\text{-}S_2O_3)_2Na(H_2O)_3]$.-$2H_2O.CH_3OH$ (where dmph is 2,9-dimethyl-1,10-phenanthroline), (I).



(I)

The molecule of (I) with the numbering scheme used is shown in Fig. 1. A striking feature in the compound is the presence of a ten-membered ring containing three metal atoms (Zn1, Zn2 and Na). The two independent Zn atoms in the cycle have a similar distorted tetrahedral environment, provided in each case by two N atoms from a dmph molecule, one S atom from a thiosulfate group and a bridging OH group, which is shared by the two Zn atoms. This type of Zn—(OH)—Zn bridge has already been reported in other compounds. The mean 'bridge' Zn—OH distance in the present structure [1.910 (3) Å] is at the shorter end of the reported range [shortest is 1.869 (6) Å (Guseinov *et al.*, 1987) and longest

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is 2.331 (5) Å (Arif, Cowley, Jones & Koschmieder, 1987)]. The mean values of the Zn—N and Zn—S bonds present no unusual features. The third metal center (Na) joins to two different thiosulfate groups through the O2 and O5 atoms. The latter groups, acting as a bridge between the two independent Zn atoms and sodium, finally close the ring. To our knowledge, this type of bridging of the thiosulfate anion has only been reported in $[Zn(etu)_2(S_2O_3)]$ (where etu is ethylenethiourea) (Baggio, Baggio & de Perazzo, 1974), with the sole difference being that in that case, the anion connected atoms of equal type (Zn). When compared with the free anion, the two independent thiosulfate groups show a slight lengthening of the S—S bond [2.058 (5) *versus* 1.987 (3)–2.031 (4) Å; Teng, Fuess & Bats, 1984, and references therein]. On the other hand, a shortening of the mean S—O distance was observed [1.443 (7) *versus* 1.473 (3)–1.489 (3) Å], though no difference among the endocyclic and exocyclic S—O bond lengths could be detected.

The Na atom completes its coordination sphere through bonding to the O1*W*, O2*W* and O3*W* atoms. This results in a distorted trigonal bipyramidal environment about sodium, with the equatorial plane defined by the O1*W*, O2*W* and O5 atoms, and the O3*W* and O2 atoms occupying the apical sites.

A packing view of the (101) plane, where both intra- and intermolecular hydrogen-bonding interactions are clearly seen is shown in Fig. 2. The former involves the hydroxyl H atom, which makes a bifurcated symmetrical bond to the O2 and O5 atoms from two different thiosulfate groups, thus contributing to the stability of the ten-membered cycle. On the other hand, the O2*W*, O3*W* and O4*W* atoms participate with their six available H atoms in a similar number of intermolecular bonds (Table 2) joining the structural units into a strong zigzag chain running along **z**. The only direct connectivity found between these one-dimensional structures consists of interactions mediated by the not fully occupied solvate molecules, mainly methanol, through a water(1)′···methanol···O1″ chain along [101], normal to the plane in the figure.

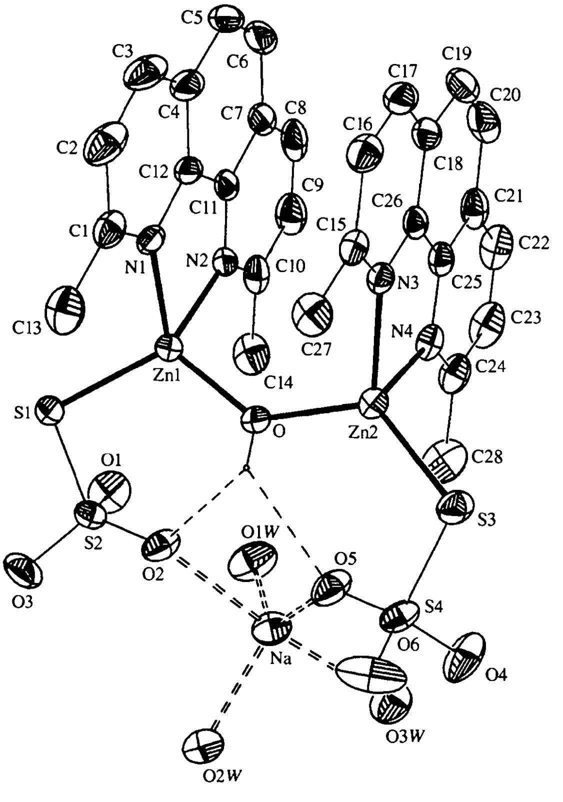

Fig. 1. View of the title molecule showing the numbering scheme used, as well as displacement ellipsoids drawn at the 30% probability level. For clarity, solvate molecules and H atoms are not shown, except for the hydroxyl H atoms involved in intramolecular hydrogen bonding to the O2 and O5 atoms. The coordination spheres of the Zn atoms are drawn in heavy full lines, while the coordination sphere of sodium is shown in heavy dashed lines.

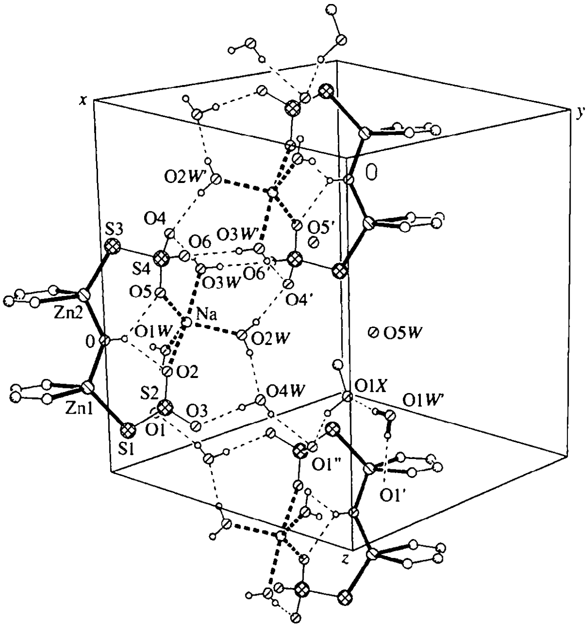

Fig. 2. A simplified packing diagram (large portions of the dmph molecules removed for clarity) showing the fairly complex hydrogen-bonding scheme leading to the formation of chains running along **c**. The link between chains taking place along [101] (out of the paper through the partially occupied methanol site) is suggested.

Experimental

The title compound was obtained by allowing a methanol solution of dmph to very slowly diffuse into an aqueous solution of sodium thiosulfate and zinc acetate (molar ratio 2:1:1). A few well developed pale yellow plates appeared at the liquid interface after the system had been allowed to stand unperturbed for two months.

Crystal data

$[NaZn_2(OH)(S_2O_3)_2$-
$(C_{14}H_{12}N_2)_2(H_2O)_3]$.-
$2H_2O.CH_4O$
$M_r = 933.6$
Triclinic
$P\bar{1}$
$a = 10.358$ (2) Å
$b = 13.627$ (3) Å
$c = 13.872$ (3) Å
$\alpha = 90.16$ (1)°
$\beta = 98.47$ (1)°
$\gamma = 103.23$ (1)°
$V = 1883.9$ (7) Å^3
$Z = 2$
$D_x = 1.646$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5$–$12.5°$
$\mu = 1.57$ mm^{-1}
$T = 293$ (2) K
Platelet
0.65 × 0.50 × 0.20 mm
Pale yellow

Data collection

Siemens *R*3*m* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*XEMP* in *SHELXTL/PC*; Sheldrick, 1991)
$T_{min} = 0.43$, $T_{max} = 0.73$
7329 measured reflections
6407 independent reflections

4699 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 24.8°$
$h = -12 \rightarrow 11$
$k = -16 \rightarrow 16$
$l = -1 \rightarrow 16$
2 standard reflections every 98 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R(F) = 0.039$
$wR(F^2) = 0.112$
$S = 0.96$
6375 reflections
512 parameters
H atoms riding with restrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0628P)^2 + 1.4P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Zn1—O	1.912 (3)	Zn2—O	1.908 (3)
Zn1—N2	2.067 (3)	Zn2—N3	2.077 (3)
Zn1—N1	2.094 (3)	Zn2—N4	2.088 (3)
Zn1—S1	2.2713 (12)	Zn2—S3	2.2688 (13)
S1—S2	2.054 (2)	S3—S4	2.062 (2)
S2—O2	1.437 (3)	S4—O5	1.434 (3)
S2—O3	1.448 (3)	S4—O4	1.443 (3)
S2—O1	1.455 (4)	S4—O6	1.443 (4)
O—Zn1—N2	106.24 (12)	O—Zn2—N4	113.15 (13)
O—Zn1—N1	111.27 (12)	N3—Zn2—N4	80.75 (13)
N2—Zn1—N1	81.65 (13)	O—Zn2—S3	121.23 (9)
O—Zn1—S1	116.44 (9)	N3—Zn2—S3	114.93 (9)
N2—Zn1—S1	123.81 (10)	N4—Zn2—S3	115.60 (10)
N1—Zn1—S1	112.30 (9)	S4—S3—Zn2	100.19 (6)
O2—S2—O3	113.7 (2)	O5—S4—O4	112.1 (2)
O2—S2—O1	110.7 (2)	O5—S4—O6	112.0 (3)
O3—S2—O1	110.4 (2)	O4—S4—O6	110.6 (3)
O2—S2—S1	109.02 (13)	O5—S4—S3	108.24 (14)
O3—S2—S1	104.9 (2)	O4—S4—S3	107.0 (2)
O1—S2—S1	107.8 (2)	O6—S4—S3	106.6 (2)
O—Zn2—N3	103.30 (12)	Zn2—O—Zn1	134.25 (15)

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

Values from the refinement are quoted with their e.s.d.'s and values normalized according to Jeffrey & Lewis (1978) and Taylor & Kennard (1983) are not.

D—H···*A*	*D*···*A*	*D*—H	*D*—H	H···*A*	*D*—H···*A*
O—H···O2	2.952 (5)	0.78 (1)	0.94	2.21	136
O—H···O5	2.930 (5)	0.78 (1)	0.94	2.24	130
O1*W*—H1*WA*···O1*X*	2.702 (7)	0.82 (2)	0.94	1.78	166
O1*W*—H1*WB*···O1	2.903 (6)	0.82 (5)	0.94	2.03	154
O2*W*—H2*WA*···O4*W*	2.766 (6)	0.81 (1)	0.94	1.84	171
O2*W*—H2*WB*···O4^{i}	3.025 (5)	0.81 (4)	0.94	2.13	160
O3*W*—H3*WA*···O6^{i}	2.877 (6)	0.82 (5)	0.94	1.95	171
O3*W*—H3*WB*···O4	2.894 (5)	0.82 (5)	0.94	1.97	170
O4*W*—H4*WA*···O1^{ii}	3.088 (6)	0.81 (5)	0.94	2.18	164
O4*W*—H4*WA*···O3^{ii}	3.198 (5)	0.81 (5)	0.94	2.48	133
O4*W*—H4*WB*···O3	2.824 (6)	0.82 (6)	0.94	1.95	155
O1*X*—H1*X*···O1^{iii}	2.733 (7)	0.83 (9)	0.94	2.32	106

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

The title structure was solved through a combination of Patterson methods and difference Fourier synthesis using the *SHELXTL/PC* package (Sheldrick, 1991). Refinement was performed with *SHELXL*93 (Sheldrick, 1993) on F^2. The hydroxylic H atom and those of the O1*W*–O4*W* water molecules were found in successive difference Fourier synthesis and refined with constrained distances to the host atom. Those attached to carbon were positioned theoretically. In all cases, displacement parameters were allowed to ride. When it was thought that all the expected diffraction power had already been accounted for, three large residual peaks (over 1.8 e Å^{-3} against an evenly distributed background below 0.45 e Å^{-3}) were still present in the difference Fourier synthesis. Two of these were found to be at a bonding distance of *ca* 1.4 Å and were consistent with a partially occupied methanol solvate molecule [occupation factor = 0.85 (5)], along with a methyl H atom amenable to restrained least-squares refinement. The remaining peak was associated with the O atom of a similarly depleted water molecule for which no associated H atoms could be found [occupation factor = 0.35 (7)]. With this assignment, the final difference Fourier map appeared featureless. Any independent determination (TGA, *etc.*) of the solvation contents was precluded by the exiguous quantity of material available. The mean σ(C—C) was 0.007 Å.

Data collection: *P3/P4-PC* (Siemens, 1991). Cell refinement: *P3/P4-PC*. Data reduction: *XDISK* in *SHELXTL/PC*. Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *CIFTAB* in *SHELXL*93, *PARST* (Nardelli, 1983) and *CSD* (Allen, Kennard & Taylor, 1983).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BK1290). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.

Andreetti, G. D., Cavalca, L., Domiano, P. & Musatti, A. (1968). *Ric. Sci.* **38**, 1100–1101.

Arif, A. M., Cowley, A. H., Jones, R. A. & Koschmieder, S. U. (1987). *J. Chem. Soc. Chem. Commun.* pp. 1319–1320.

Baggio, R., Baggio, S., Pardo, M. I. & Garland, M. T. (1996). *Acta Cryst.* C**52**, 820–823.

Baggio, S., Baggio, R. & de Perazzo, P. (1974). *Acta Cryst.* B**30**, 2166–2172.

Guseinov, G. A., Usubaliev, B. T., Musaev, F. N., Amiraslanov, I. R., Mamedov, Kh. S. & Agamalieva, E. A. (1987). *Zh. Neorg. Khim.* **32**, 1865–1871.

Jeffrey, G. A. & Lewis, L. (1978). *Carbohydr. Res.* **60**, 179–182.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Sheldrick, G. M. (1991). *SHELXTL/PC*. Version 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Siemens (1991). *P3/P4-PC Diffractometer Program*. Version 4.27. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Taylor, R. & Kennard, O. (1983). *Acta Cryst.* B**39**, 133–138.

Teng, S. T., Fuess, H. & Bats, J. W. (1984). *Acta Cryst.* C**40**, 1785–1787.

Acta Cryst. (1997). C**53**, 554–556

Bis(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-pentaoxabenzo[*b*]cyclopentadecene-*O*^{1},*O*^{4},*O*^{7},*O*^{10},*O*^{13})sodium(1+) 1,1,7,7-Tetracyano-3,5-dithiahepta-1,6-diene-2,6-dithiolate(2–) (2/1)

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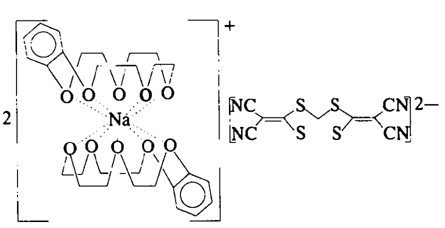
Abstract

The cation of the title compound, $2[Na(C_{14}H_{20}O_5)_2]^+.C_9H_2N_4S_4^{2-}$, comprises two configurations of benzo-15-crown-5–sodium complex cations in which the Na atoms are sandwiched by ligands through coordinated O atoms. The Na—O distances are in the range 2.443 (4)–3.004 (3) Å. The anion portion is a partially alkylated product of isomalononitriledithiolate ($C_4N_2S_2^{2-}$). The sulfide S—C distances are in the range 1.769 (4)–1.796 (4) Å, while those of the thiol moieties are in the range 1.667 (4)–1.671 (4) Å.

Comment

We have recently reported the non-linear optical properties of compounds related to isomalononitriledithiolato (*i*-mnt) metal complexes (Long *et al.*, 1996). The starting material for isomalononitriledithiolato metal complexes is usually the alkaline metal salt. When sodium isomalononitriledithiolate was refluxed in CH_2Cl_2 with 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-pentaoxabenzo-[*b*]cyclopentadecene (benzo-15-crown-5), not only was the crown ether–sodium complex formed, but an alkylation reaction also took place on the thiolato groups. The title compound, $2[Na(C_{14}H_{20}O_5)_2]^+.C_9H_2N_4S_4^{2-}$, (I), was obtained.



(I)

The molecular structure of (I) is shown in Fig. 1. The anion is the alkylation product of *i*-mnt. Two $C_4N_2S_2$ moieties are linked by a methylene group. Configurations of the moieties are similar to that found in $Pd(i\text{-mnt})_2^{2-}$ (Long *et al.*, 1996). The S—C distances for the sulfide are between 1.769 (4) and 1.796 (4) Å, while those of the thiol group are 1.667 (4) and 1.671 (4) Å; these distances are comparable to those found in $Pd(i\text{-mnt})_2^{2-}$. There are two types of S—C—S angles. One type involves the thiol S atom, with values of 123.5 (3) and 122.9 (2)°, while the other is the central S—C—S angle of 116.0 (2)°. The former is near the value of 122.8 (3)° found in sodium salts of *i*-mnt (Hummel, 1987), while the latter is close to the S—C—S angles found in the metal complexes $Pd(i\text{-mnt})_2^{2-}$ and $M(i\text{-mnt})_2^{2-}$ [M is Pt^{II} (Hummel, 1987), Cd^{II} (Li & Amma, 1990) and Pb^{II} (Hummel & Meske, 1989)]. The alkylation reaction of the thiol with *i*-mnt in CH_2Cl_2 is partial and leaves a half group free, which may be used as a coordination group for metal complexes.

The cations are in two configurations as shown in Fig. 1. The Na1 atom is coordinated by seven O atoms and Na2 by eight O atoms. These sandwich structures are comparable to those found in Na(benzo-15-crown-5)$_2$.ClO$_4$ (Owen, 1980). The crown rings are coordinated through the O atoms. The Na—O

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