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

Co1—O2	2.114 (2)	N1—C5	1.365 (4)
Co1—O3	2.100 (2)	N3—C2	1.321 (3)
Co1—N3	2.103 (2)	N3—C4	1.390 (3)
O1—C8	1.223 (3)	C4—C5	1.361 (4)
O2—C8	1.280 (3)	C4—C6	1.500 (3)
O3—C7	1.434 (3)	C6—C7	1.530 (3)
N1—C2	1.342 (3)	C7—C8	1.533 (3)
O2—Co1—O3	75.37 (8)	N3—C4—C6	123.0 (2)
O2—Co1—N3	86.3 (1)	C5—C4—C6	128.8 (2)
O3—Co1—N3	87.6 (1)	N1—C5—C4	107.2 (2)
Co1—O2—C8	114.1 (2)	C4—C6—C7	113.9 (2)
Co1—O3—C7	109.0 (1)	O3—C7—C6	111.1 (2)
C2—N1—C5	107.4 (2)	O3—C7—C8	107.7 (2)
Co1—N3—C2	126.3 (2)	C6—C7—C8	111.3 (2)
Co1—N3—C4	126.8 (2)	O1—C8—O2	125.1 (2)
C2—N3—C4	106.0 (2)	O1—C8—C7	118.5 (2)
N1—C2—N3	111.3 (2)	O2—C8—C7	116.3 (2)
N3—C4—C5	108.2 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.948	1.937	2.800 (3)	150.30
O3—H7···O2^{ii}	0.893	1.749	2.631 (3)	168.76

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

H atoms were generated by calculation, except for the hydroxyl H7 atom, which was located from a difference Fourier map and included in the structure-factor calculations at a fixed position.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1037). Services for accessing these data are described at the back of the journal.

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Interactions of thiamine with anions: (Hthiamine)(thiamine) heptaiododimercurate dihydrate and its dimethanol monohydrate

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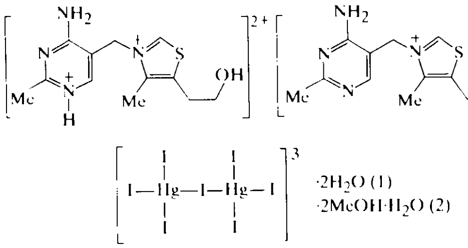
Abstract

In the title compounds, 3-[(4-amino-2-methyl-5-pyrimidinio)methyl]-5-(2-hydroxyethyl)-4-methylthiazolium(2+) 3-[(4-amino-2-methyl-5-pyrimidinyl)methyl]-5-(2-hydroxyethyl)-4-methylthiazolium(1+) heptaiododimercurate dihydrate, $(C_{12}H_{18}N_4OS)(C_{12}H_{17}N_4OS)[Hg_2I_7]\cdot 2H_2O$, (1), and its dimethanol monohydrate, $(C_{12}H_{18}N_4OS)(C_{12}H_{17}N_4OS)[Hg_2I_7]\cdot 2CH_3OH\cdot H_2O$, (2), a crystallographic centre of symmetry in (1) or a twofold axis in (2) is imposed between the protonated and deprotonated thiamine molecules, resulting in a statistically half-occupied proton attached at N1′ of the pyrimidine ring. The $Hg_2I_7^{3-}$ anion, residing on the centre of symmetry in (1) or on the twofold axis in (2), interacts with two thiamine molecules, each through a C2—H···I···pyrimidine-ring interaction. This bridging interaction is a characteristic of thiamine in the *F* conformation.

Comment

In the form of its pyrophosphate ester, thiamine {vitamin B_1; 3-[(4-amino-2-methyl-5-pyrimidinio)methyl]-5-(2-hydroxyethyl)-4-methylthiazolium} is a coenzyme for several enzyme systems (Krampitz, 1969). As a naturally occurring cationic host, thiamine interacts with different anion groups through characteristic hydrogen bonds and electrostatic contacts to form host–guest-like complexes (Aoki *et al.*, 1993). Thiamine compounds containing monovalent or divalent anions have been extensively studied by X-ray diffraction (Louloudi & Hadjiliadis, 1994). In these salts, thiamine exists in two forms, *i.e.* the protonated form with a proton attached to the pyrimidine N1′ site and the deprotonated form. It is of interest how thiamine interacts with high-valent anions and this work aims at examining the interactions of thiamine with the $Hg_2I_7^{3-}$ anion. To our knowledge, this is the first structural report of a thiamine salt with a trivalent anion.

The basic structural unit in (1) and (2) consists of one protonated and one deprotonated thiamine cation, along with an $Hg_2I_7^{3-}$ anion (Figs. 1 and 2). The anion is made up of two Hg–I tetrahedra sharing a vertex located on a centre of symmetry in (1), and on a twofold axis with an Hg—I1—Hg angle of 129.09 (7)° in (2). Although the protonated and deprotonated forms of thiamine exist simultaneously in the structure, one cannot distinguish between them because of the crystallographic symmetry. Since there is half an anion and one thiamine cation in the asymmetric unit, the pyrimidine ring must be half-protonated so that each thiamine molecule carries a statistical charge of +1.5 in order to meet the charge-balance requirements. This implies a disordered H atom with an occupancy factor of 0.5 attached to N1′. The close distance [2.85 (2) Å] between the N1′ atoms of the two centrosymmetrically related thiamine molecules in (1) indicates that a disordered hydrogen bond forms between them. This supports the inference of half-protonation at N1′ because such a close contact has never been observed in protonated or deprotonated thiamine compounds. There is no N1′···N1′ close contact in (2), but a disordered hydrogen bond may form between N1′ and O53(1 − *x*, 1 − *y*, 1 − *z*), with an N···O separation of 2.82 (2) Å. As previous observations (Cramer *et al.*, 1981; Aoki *et al.*, 1988) have shown, the C2′—N1′—C6′ angle, which is sensitive to the protonation at N1′, is about 115° for the free pyrimidine ring and about 120° for the protonated one. This angle appears to have an intermediate value [117.1 (11)° in (1) and 119.2 (13)° in (2)] consistent with a half-occupied proton at N1′, though the limited accuracy precludes a detailed comparison.



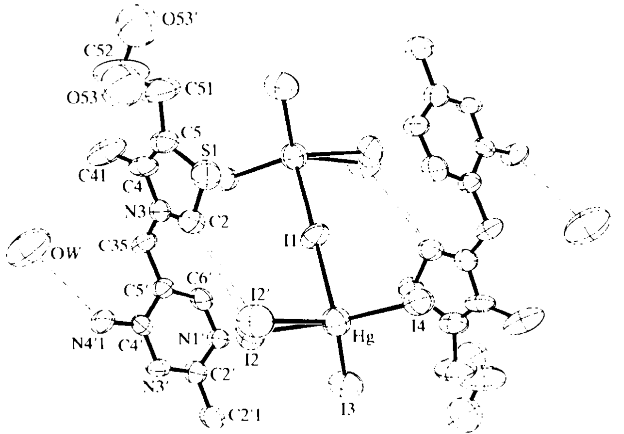


Fig. 1. The structure of (1) showing 50% probability displacement ellipsoids. The I2 and O53 atoms are disordered with occupancy factors of 0.75 and 0.25 for I2 and I2′, and 0.65 and 0.35 for O53 and O53′, respectively. Broken lines denote hydrogen bonds.

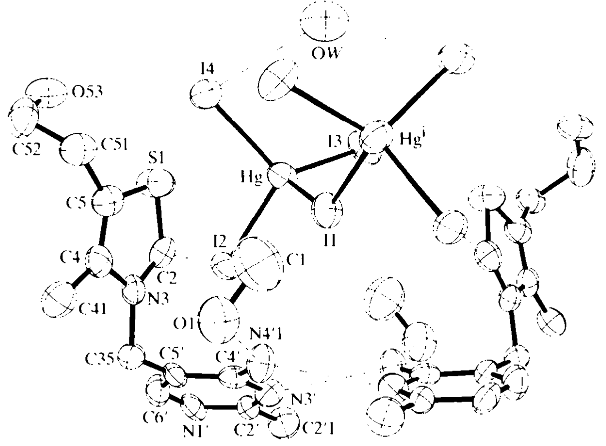


Fig. 2. The structure of (2) showing 50% probability displacement ellipsoids. Broken lines denote hydrogen bonds and C2—H2···I2 interactions. [Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.]

In both compounds, the thiamine molecule assumes the usual *F* conformation, as shown by the torsion angles (Pletcher *et al.*, 1977): φ_T (C5′—C35—N3—C2) = 3 (2)° in (1) and 13 (2)° in (2); φ_P (N3—C35—C5′—C4′) = 91 (2)° in (1) and 71 (2)° in (2). The I2 atom in (1) bridges the two aromatic rings of a thiamine molecule through a C2—H···I2 hydrogen bond and a loose contact between I2 and the pyrimidine ring, the closest distance, I2···N3′, being 4.13 (1) Å. Thus, an $Hg_2I_7^{3-}$ anion is held by two symmetrically related thiamine molecules (Fig. 1). This type of bridging interaction is a characteristic of thiamine compounds in the *F* conformation (Aoki *et al.*, 1991). The case of (2) is similar (Fig. 2), but with a weak C2—H···I2 interaction (H2···I2 3.22 Å and C2—H2···I2 159°; the sum of the van der Waals radii for I and H is 3.18 Å) and an I2···pyrimidine-ring close contact [the closest distance, I2···N1′, is 3.76 (1) Å]. Another kind of bridging interaction, which is also a structural feature of thiamine compounds with the *F* conformation, is found in both compounds. A methanol molecule is involved in an N4′1—H···O1 hydrogen bond and an O1···thiazolium-ring close contact in (2) [the closest distance, O1···N3, is 3.17 (2) Å], while a water molecule plays this role in (1), where there is also a loose contact between *OW* and the thiazolium ring [the closest distance, *OW*···N3, is 3.87 (2) Å]. As shown in Figs. 3 and 4, the base pairs in (1) and (2) are formed through N4′1—H···N3′ hydrogen bonds and they are further associated into a chain. This occurs *via* disordered hydrogen bonds between the N1′ atoms in (1) and *via* a pair of disordered hydrogen bonds between N1′ and O53 atoms in (2).

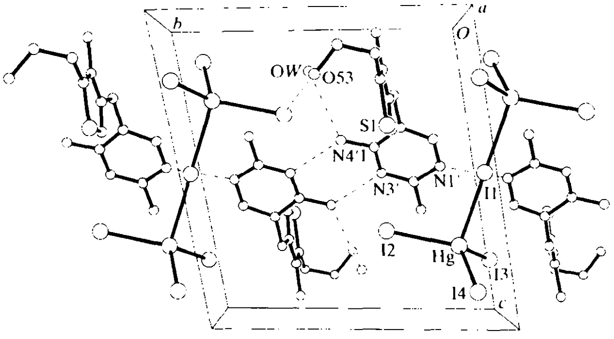


Fig. 3. A view of the crystal packing for (1) showing the association between the molecules by hydrogen bonds. The minor disordered positions are not shown.

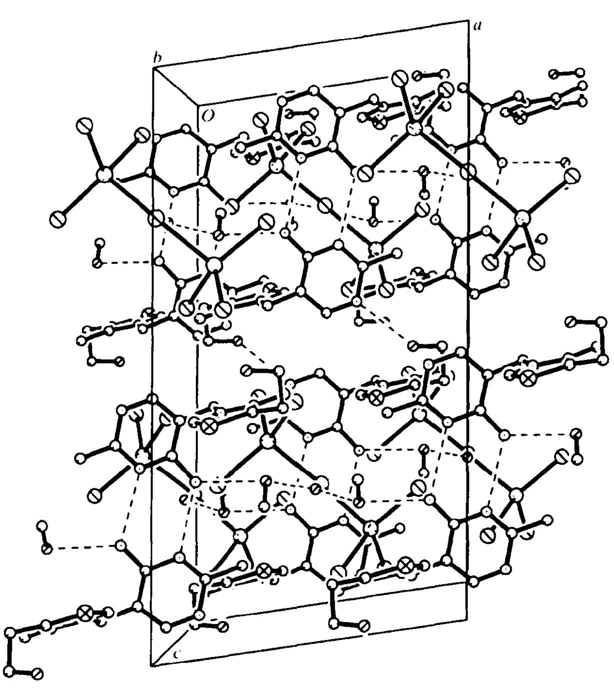


Fig. 4. A view of the crystal packing for (2) showing the hydrogen-bonding system.

Experimental

Thiamine·Cl·HCl (69.2 mg, 0.2 mmol) was reacted with $Ag(CH_3COO)$ (66.8 mg, 0.4 mmol) in water. The AgCl which formed was filtered off. The mother liquor was then mixed with an aqueous solution containing NaI (119.9 mg, 0.8 mmol) and $Hg(CH_3COO)_2$ (63.8 mg, 0.2 mmol). The resulting solution with a yellow precipitate was filtered and crystals of (1) were obtained from the filtrate after a day. The precipitate collected was dissolved in methanol (5 ml) and crystals of (2) appeared after a week. Compound (1) was unstable in air and a crystal was sealed in a glass capillary tube for the X-ray measurements.

Compound (1)

Crystal data

$(C_{12}H_{18}N_4OS)(C_{12}H_{17}N_4OS)[Hg_2I_7]{\cdot}2H_2O$
$M_r = 1857.26$
Triclinic
$P\overline{1}$
$a = 9.257\ (1)$ Å
$b = 10.947\ (3)$ Å
$c = 11.911\ (1)$ Å
$\alpha = 96.86\ (1)°$
$\beta = 108.997\ (7)°$
$\gamma = 96.59\ (1)°$
$V = 1117.8\ (3)$ Å^3
$Z = 1$
$D_x = 2.759$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 5.0$–$11.0°$
$\mu = 11.823$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.20 × 0.16 × 0.08 mm
Light yellow

Data collection

Siemens *R*3*m*/*E* four-circle diffractometer
ω scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{min} = 0.170$, $T_{max} = 0.507$
4856 measured reflections
3912 independent reflections
1953 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 25°$
$h = -1 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 13$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.147$
$S = 0.924$
3912 reflections
224 parameters
H atoms: see below
$w = \exp[3.00(\sin\theta/\lambda)^2]/[\sigma^2(F_o^2) + (0.10P)^2]$ where $P = 0.33F_o^2 + 0.67F_c^2$
$(\Delta/\sigma)_{max} = -0.008$
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.96$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Hg—I1	2.9705 (8)	C2′—N3′	1.32 (2)
Hg—I2	2.751 (5)	N3′—C4′	1.36 (2)
Hg—I3	2.6811 (15)	C4′—N4′1	1.33 (2)
Hg—I4	2.7361 (13)	C4′—C5′	1.41 (2)

N1′—C2′	1.33 (2)	C5′—C6′	1.38 (2)
N1′—C6′	1.33 (2)		
I1—Hg—I2	99.24 (12)	N3′—C2′—N1′	123.9 (13)
I1—Hg—I3	107.10 (4)	C2′—N3′—C4′	118.6 (12)
I1—Hg—I4	105.17 (3)	N4′1—C4′—N3′	115.8 (12)
I2—Hg—I3	112.26 (10)	N4′1—C4′—C5′	123.0 (12)
I2—Hg—I4	114.96 (10)	N3′—C4′—C5′	121.1 (11)
I3—Hg—I4	116.03 (5)	C6′—C5′—C4′	114.2 (12)
C2′—N1′—C6′	117.1 (11)	N1′—C6′—C5′	124.7 (12)

Table 2. *Hydrogen-bonding geometry (Å, °) for (1)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···I2	0.93	3.04	3.89 (2)	152
C2—H2···I2′	0.93	3.10	3.88 (3)	143
N4′1—H4′1···N3′^{i}	0.86	2.22	3.06 (2)	168
N4′1—H4′2···O*W*	0.86	2.27	3.02 (2)	147
O53···I2^{ii}			3.47 (3)	
O*W*···O53^{iii}			3.13 (4)	
O*W*···O53′^{iv}			3.06 (6)	
N1′···N1′^{v}			2.85 (2)	

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

Compound (2)

Crystal data

$(C_{12}H_{18}N_4OS)(C_{12}H_{17}N_4OS)[Hg_2I_7]\cdot 2CH_4O\cdot H_2O$
$M_r = 1903.33$
Monoclinic
*C*2/*c*
$a = 11.797$ (1) Å
$b = 19.238$ (2) Å
$c = 22.012$ (4) Å
$\beta = 98.57$ (1)°
$V = 4939.9$ (11) Å^3
$Z = 4$
$D_x = 2.559$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 5.5$–12.5°
$\mu = 10.706$ mm^{-1}
$T = 293$ (2) K
Block
0.42 × 0.38 × 0.36 mm
Light yellow

Data collection

Siemens *R*3*m*/*E* four-circle diffractometer
ω scans
Absorption correction: by integration (*SHELXTL*; Siemens, 1994*a*)
$T_{min} = 0.368$, $T_{max} = 0.434$
5545 measured reflections
4344 independent reflections

2379 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 25$°
$h = -1 \rightarrow 14$
$k = -1 \rightarrow 22$
$l = -26 \rightarrow 26$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.161$
$S = 1.108$
4344 reflections
230 parameters
H atoms: see below
$w = \exp[3.00(\sin\theta/\lambda)^2]/[\sigma^2(F_o^2) + (0.10P)^2]$ where $P = 0.33F_o^2 + 0.67F_c^2$

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.01$ e Å^{-3}
$\Delta\rho_{min} = -1.31$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (2)*

Hg—I1	2.9385 (11)	C2′—N3′	1.31 (2)
Hg—I2	2.7792 (12)	N3′—C4′	1.35 (2)
Hg—I3	2.6956 (14)	C4′—N4′1	1.34 (2)
Hg—I4	2.7848 (14)	C4′—C5′	1.38 (2)
N1′—C2′	1.37 (2)	C5′—C6′	1.35 (2)
N1′—C6′	1.34 (2)		
I1—Hg—I2	98.15 (4)	N3′—C2′—N1′	120.1 (14)
I1—Hg—I3	106.93 (4)	C2′—N3′—C4′	120.4 (12)
I1—Hg—I4	109.51 (5)	N4′1—C4′—N3′	115.1 (13)
I2—Hg—I3	121.62 (5)	N4′1—C4′—C5′	122.8 (14)
I2—Hg—I4	106.04 (4)	N3′—C4′—C5′	122.0 (13)
I3—Hg—I4	113.23 (5)	C6′—C5′—C4′	115.3 (14)
Hg^{i}—I1—Hg	129.09 (7)	N1′—C6′—C5′	122.9 (14)
C2′—N1′—C6′	119.2 (13)		

Symmetry code: (i) $1-x, y, \frac{1}{2}-z$.

Table 4. *Hydrogen-bonding geometry (Å, °) for (2)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4′1—H4′1···N3′^{i}	0.86	2.15	3.00 (2)	170
N4′1—H4′2···O1	0.86	1.95	2.78 (2)	161
O1—H1···O*W*^{ii}	0.82	2.09	2.84 (2)	152
O*W*···I4			3.660 (9)	
N1′···O53^{iii}			2.82 (2)	

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

For (1), the empirical absorption corrections were based on reflections measured at different azimuthal angles. Ten reflections were measured using ω scans with an increment of 10° in φ. Six parameters were refined to define a pseudo-ellipsoid which was used to calculate the corrections. For (2), the Gaussian integration method of absorption correction was applied. The precision and the number of grid points were automatically selected by the program *SHELXTL* (Siemens 1994*a*). The I2 and O53 atoms in (1) are disordered with occupancy factors of 0.75 and 0.25 for I2 and I2′, and 0.65 and 0.35 for O53 and O53′, respectively. The occupancy factors were estimated from the electron densities and fixed in the refinements. Anisotropic displacement parameters were refined for all non-H atoms except the disordered O53 and O53′ atoms in (1). The C5 side chain in (1) shows rather high displacement parameters and large uncertainties on some bond distances, mostly due to the disorder. The disordered H atoms attached to N1′, C52 and O53 in (1), and N1′ and O53 in (2) were not included in the refinements. The H atoms of water molecules in (1) and (2) were not located. The other H atoms were added at ideal positions and their coordinates refined.

For both compounds, data collection: *XSCANS* (Siemens, 1994*b*); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXTL* (Siemens, 1994*a*); program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1259). Services for accessing these data are described at the back of the journal.

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(Acetato-*O*,*O*′)(acetato-*O*)(2,9-dimethyl-1,10-phenanthroline-*N*,*N*′)zinc(II)

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Abstract

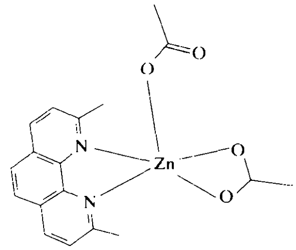
In diacetato-*O*,*O*′;*O*-(2,9-dimethyl-1,10-phenanthroline-*N*,*N*′)zinc(II), $[Zn(C_2H_3O_2)_2(C_{14}H_{12}N_2)]$, the zinc cation has a pentacoordinated environment consisting of the two N atoms of 2,9-dimethyl-1,10-phenanthroline, one O atom from a monodentate acetate group and two O atoms from a bidentate acetate group.

Comment

The study of zinc(II) complexes with *N*- and *O*-donor ligands is of current interest due to their potential use as models for zinc-containing active sites in enzymes (Creighton, 1984).

The carboxylate group, present in many of these active sites, has been found to behave as a monodentate, bidentate or bridging ligand, and many zinc acetate complexes with phenanthroline or bipyridine have been found to display these different modes of coordination (Chen, Tong & Mak, 1994; Chen, Xu *et al.*, 1994).

In this paper, we present the structure of the novel complex $[Zn(MeCO_2)_2(dmph)]$ (dmph is dimethylphenanthroline), (I), the first report of a complex in which the anion displays two different modes of coordination to the same metal centre. The Zn^{2+} ion is coordinated by two N atoms from dmph (N1 and N2), two O atoms from a bidentate acetate ion (O1*B* and O2*B*) and one O atom from the remaining acetate ion, which is monodentate; the second O atom of the monodentate acetate ion, though not formally bonded to zinc, is at a distance of 2.768 (4) Å, slightly shorter than the sum of the corresponding van der Waals radii.



(I)

The array around the cation can be described as a distorted square pyramid, the planar base being determined by atoms N1, N2, O1*B* and O2*B* [maximum deviation from the mean plane: 0.011 (4) Å for O1*B*], with the Zn^{2+} ion 0.870 (1) Å from this plane towards the apical site. The latter is occupied by the O1*A* atom from the monodentate acetate group, the bond to zinc [Zn—O1*A* 1.919 (3) Å] being tilted by 13.7 (1)° from the base normal (Fig. 1).

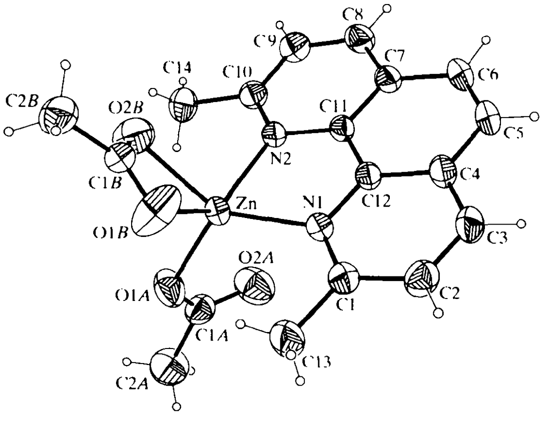


Fig. 1. The molecular diagram of (I) showing the numbering of atoms. Displacement ellipsoids are drawn at the 30% probability level.

A search in the Cambridge Structural Database (CSD; Allen & Kennard, 1993) showed that this is the first compound containing a Zn^{2+} ion complexed to acetate

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