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Interactions of thiamine with polymeric halogenocadmate anions in the organic–inorganic hybrid compound (thiaminium)[$Cd_3Br_{4.4}Cl_{3.6}$]

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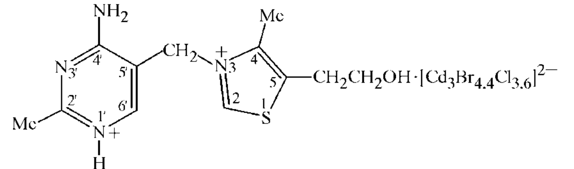
The structure of poly[3-[(4-amino-2-methylpyrimidin-1-ium-5-yl)methyl]-5-(2-hydroxyethyl)-4-methylthiazolium octa-μ-bromo/chloro(4.4/3.6)-tricadmate(II)], {($C_{12}H_{18}N_4OS$)[$Cd_3Br_{4.41}Cl_{3.59}$]}$_n$ consists of hydrogen-bonded thiamine molecules and polymeric cadmium bromide/chloride anions in an organic–inorganic hybrid fashion. The one-dimensional anion ribbons are formed by edge-sharing octahedra and vertex-sharing tetrahedra. Thiamine molecules adopting the *S* conformation are linked to anions *via* three types of interactions, namely an N(amino)—H···anion···thiazolium bridging interaction, an N(pyrimidine)—H···anion hydrogen bond and an O(hydroxy)—H···anion hydrogen bond.

Comment

Interest in the interactions of thiamine (vitamin B_1) with anions has been prompted by their relevance to biological catalytic processes because the enzymatic action of the coenzyme, thiamine pyrophosphate, involves a direct reaction of a substrate anion such as pyruvate at the C2 site of the thiazolium moiety (Breslow, 1958; Krampitz, 1969). Structural studies have revealed that the manner in which the thiamine is associated with the anions is closely related to the molecular conformation (Cramer *et al.*, 1988; Aoki *et al.*, 1993). There are two distinct types of anion bridging interactions, which link the thiazolium and pyrimidine rings of a thiamine molecule *via* hydrogen bonds and electrostatic contacts. They are of the forms C2—H···anion···pyrimidine ring and N(amino)—H···anion···thiazolium ring, and are defined as type I and II anion bridges, respectively (Hu *et al.*, 1999). The interaction of thiamine with discrete anions, from 'simple' anions such as halogen (Thompson & Richardson, 1977; Lee & Richardson, 1976), SCN^-, BF_4^- (Aoki *et al.*, 1990), ClO_4^- or PF_6^- (Aoki *et al.*, 1988), to metal complex anions such as $[PtCl_4]^{2-}$ (Cramer *et al.*, 1988), $[PtCl_6]^{2-}$ (Aoki *et al.*, 1993), $[Pt(NO_2)_4]^{2-}$ (Hu *et al.*, 2001*b*) and $[Pt(SCN)_6]^{2-}$ (Aoki *et al.*, 1999), have been widely investigated. However, reports describing thiamine compounds containing infinite polymeric anions are very rare.



(I)

In our previous work, we have examined the interaction of thiamine monophosphate (TMP) with polymeric halogenomercurate anions in (TMP)(Hg_2Br_5)·0.5H_2O and $(TMP)_2$(Hg_3I_8) (Hu *et al.*, 2002). Both compounds show organic–inorganic hybrid layered structures, consisting of sheets of polymeric mercury halide separated by hydrogen-bonded TMP cation layers. The TMP molecule adopting the usual *F* conformation (torsion angles φ_T = C5′—C35′—N3—C2 is approximately 0° and φ_P = N3—C35′—C5′—C4′ is approximately ±90°) (Pletcher *et al.*, 1977) is attached to the anion layer through a type I anion bridge, *i.e.* a C2—H···Br(or I)···pyrimidine ring interaction. As an extension of these studies, we were interested in examining how thiamine interacts with polymeric halogenometal anions and whether the anions impose effects on the conformation of thiamine. We report here the structure of (thiaminium)($Cd_3Br_{4.4}Cl_{3.6}$), (I),

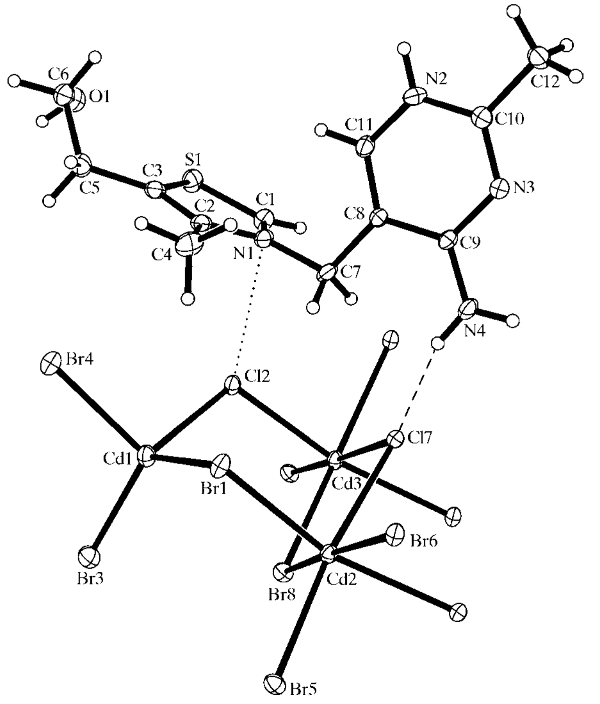


Figure 1
The structure of (I), showing the atom-labelling scheme and the two-point anion bridge. The dashed line denotes a hydrogen bond and the dotted line denotes the close contact. Displacement ellipsoids are drawn at the 30% probability level. Occupancy factors for Br/Cl: 0.683 (3):0.317 (3) for the Br1 site, 0.169 (3):0.831 (3) for the Cl2 site, 0.834 (3):0.166 (3) for the Br3 site, 0.810 (4):0.190 (4) for the Br4 site, 0.571 (3):0.429 (3) for the Br5 site, 0.635 (3):0.365 (3) for the Br6 site, 0.066 (3):0.934 (3) for the Cl7 site and 0.641 (3):0.359 (3) for the Br8 site.

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in which thiamine adopts the *S* conformation (φ_T is approximately ±100° and φ_P ±150°) and interacts with one-dimensional halogenocadmate anions in a manner different from that found in the TMP halogenomercurate compounds.

The structure of (I) consists of hydrogen-bonded thiamine molecules and polymeric cadmium bromide/chloride anions in an organic–inorganic hybrid fashion (Mitzi *et al.*, 1995). Fig. 1 shows the molecular structure of thiamine and three crystallographically independent Cd^{2+} centres. The crystal structure analysis indicated that Br and Cl atoms share the halogen sites. The atom names in the atomic numbering scheme are assigned as the major disordered component. As shown in Table 1, the average Cd—μ_3-Cl7 bond length is 2.711 (7) Å, apparently shorter than the average value of Cd—μ_3-Br6 [2.80 (2) Å]. This is also the case for the Cd1—μ_2-Cl2 and Cd1—μ_2-Br1 bond lengths and for the Cd3—μ_2-Cl2 and Cd2—μ_2-Br1 bond lengths (Table 1), consistent with the result that Cl is the major component at the Cl2 and Cl7 sites. Atoms Cd2 and Cd3 are both coordinated in an octahedral geometry, each by three μ_3-Br/Cl atoms and three μ_2-Br/Cl atoms. Each octahedral unit is connected to the four neighbouring units by sharing edges. These edge-sharing octahedra propagate in the [100] direction to form a one-dimensional ribbon. Atom Cd1 is tetrahedral and attached to the ribbon by sharing a vertex with Cd2 and Cd3 octahedra, respectively. The Cd1 tetrahedron acts as a tooth, with terminal atoms Br3 and Br4 pointing outside of the ribbon, thus producing a saw-like anion structure (Fig. 2). The anion ribbons are further arranged in the *ac* plane into layers at $b = 0$ and $\frac{1}{2}$.

The thiamine molecule exists as a divalent cation with N2 protonated; the H atom at N2 was clearly visible in a difference map and the C10—N2—C11 angle of 121.3 (4)° is larger than the corresponding value for an unprotonated pyrimidine ring (about 115°; Aoki *et al.*, 1990). The molecular dimensions are comparable with those of the reported divalent thiamine cation (Hu *et al.*, 2001*a*). The torsion angles, $\varphi_T = 90.3$ (5)° and $\varphi_P = 179.8$ (4)°, indicate that thiamine adopts the unusual *S* conformation. The *S* conformation makes the C11—H bond point over the N1 atom of the thiazolium ring (Fig. 1), while the *F* conformation is characterized by the C1—H bond pointing over the C8 atom of the pyrimidine ring. For C1-unsubstituted thiamine, the *F* form is overwhelmingly preferable to the *S* form (Shin *et al.*, 1993). Cramer *et al.* (1988) have pointed out that the polychlorometal anion can affect the conformation of thiamine through a bridging interaction (*i.e.* anion bridge II), and thus the *F* conformation is favoured by smaller anions and the *S* conformation by larger anions. Aoki *et al.* (1991) have further noticed that, for the *F* conformation, the type II anion bridge formed by a smaller anion is a one-point attachment, being of the form N(amino)—H···*X*···thiazolium ring, while for the *S* conformation, the type II anion bridge formed by a larger anion is a two-point attachment, being of the form N(amino)—H···*X*—*M*—*X*···thiazolium ring (*X* is an electronegative atom and *M* is a metal). This 'two-point' anion bridge has been observed again in the present structure containing thiamine in the *S* conformation, *i.e.* an N4—H···Cl7—Cd3—Cl2···thiazolium ring interaction, where the closest contact between Cl2 and the thiazolium ring is Cl2···N1 = 3.386 (3) Å. In contrast, the TMP molecule adopts the *F* conformation in $(TMP)(Hg_2Br_5)\cdot 0.5H_2O$ and $(TMP)_2(Hg_3I_8)$, despite the existence of large halogenometal anions. This is due to the anionic phosphate group of the TMP molecule, which is evidently smaller than the halogenometal anion measured by the non-bonded *X*···*X* distance and taking part in the formation of a 'one-point' anion bridge. Interestingly, in (I), strongly electronegative Cl atoms compete with Br atoms for the two-point anion bridge, as Cl is the major component at the Cl2 and Cl7 sites (Fig. 1).

Fig. 3 shows that the crystal packing of (I) exhibits a layer-like structure consisting of alternating cationic sheets of the hydrogen-bonded thiamine molecules and anionic sheets of the polymeric halogenocadmate. Thiamine molecules self-associate through N4—H···O1 hydrogen bonds into a chain structure (Fig. 4), which is tilted relative to the anion ribbon at

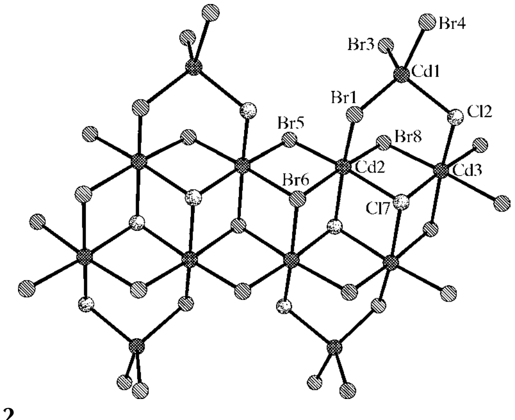

Figure 2
A view of the one-dimensional anion ribbon in (I).

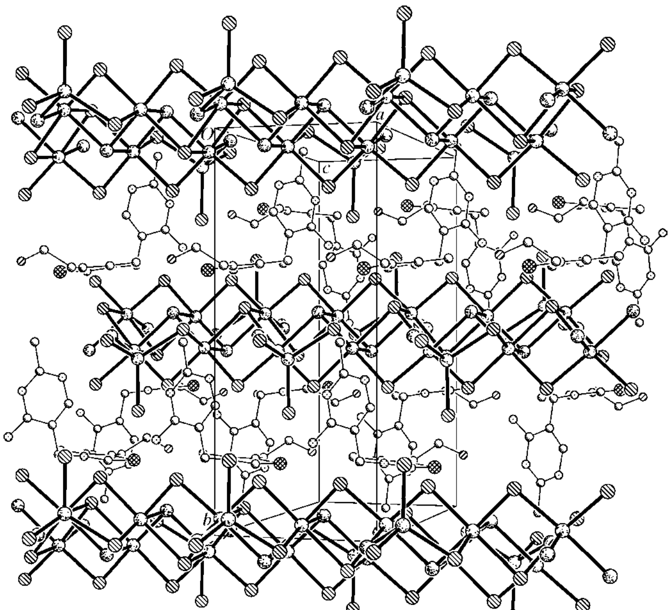

Figure 3
A view of the organic–inorganic hybrid layered structure. H atoms have been omitted.

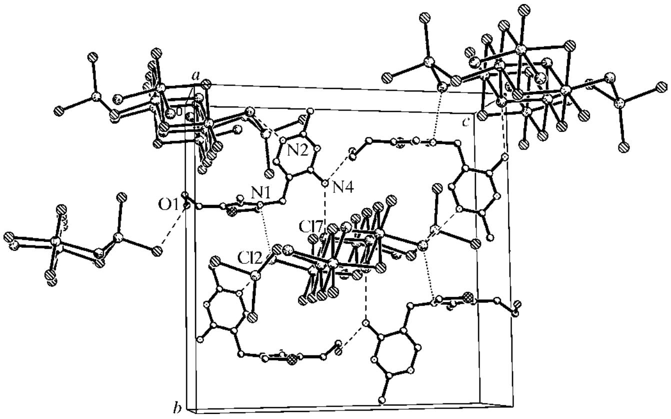

Figure 4
Part of the crystal structure of (I), showing the formation of a molecular chain of thiamine and the interactions of a thiamine molecule with three anion ribbons around it. For the sake of clarity, H atoms have been omitted.

an angle of 54.0 (4)°. Each thiamine molecule is bound to three anion ribbons. As seen in Fig. 4, the thiamine molecule at (x, y, z) is attached to one anion ribbon through the type II anion bridge described above. Atom O1 of this molecule acts as hydrogen-bond donor to atom Br4 at $(-x, 1 - y, -z)$ of a second ribbon, and the pyrimidine ring of this molecule is located between the teeth of a third ribbon lying in the above layer to form an N2—H···Cl2$(-x, y - \frac{1}{2}, \frac{1}{2} - z)$ hydrogen bond (Table 2). This binding mode is quite different from that observed in the structures of (TMP)(Hg_2Br_5)·0.5H_2O and $(TMP)_2(Hg_3I_8)$, where the TMP molecule binds to the polymeric anions mainly through the characteristic type I anion bridge for the *F* conformation. Therefore, the sole existence of large halogenocadmate anions results in the *S* conformation of thiamine and thus determines the binding mode of thiamine to the anions.

Experimental

Compound (I) was prepared by reacting thiamine chloride hydrochloride (0.2 mmol) and cadmium bromide (0.4 mmol) in water (20 ml). The solution was set aside to crystallize at ambient temperature and the resulting crystals were washed with water and methanol.

Crystal data

$(C_{12}H_{18}N_4OS)[Cd_3Br_{4.41}Cl_{3.59}]$
$M_r = 1083.23$
Monoclinic, $P2_1/c$
$a = 7.7492$ (4) Å
$b = 18.3881$ (10) Å
$c = 18.6756$ (11) Å
$\beta = 96.1870$ (10)°
$V = 2645.6$ (3) Å^3
$Z = 4$

$D_x = 2.720$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4585 reflections
$\theta = 2.5$–26.0°
$\mu = 9.51$ mm^{-1}
$T = 187$ (1) K
Tabular, colourless
0.21 × 0.15 × 0.09 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SAINT*; Bruker, 2003)
$T_{\min} = 0.202$, $T_{\max} = 0.431$
13339 measured reflections

5211 independent reflections
4331 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$
$\theta_{\max} = 26.0°$
$h = -9 \rightarrow 9$
$k = -22 \rightarrow 21$
$l = -23 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.060$
$S = 1.02$
5211 reflections
275 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0272P)^2 + 0.1435P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.008$
$\Delta\rho_{\max} = 0.64$ e Å^{-3}
$\Delta\rho_{\min} = -0.51$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

Cd1—Br3	2.5148 (6)	Cd2—Cl7^{i}	2.7178 (9)
Cd1—Br4	2.5480 (6)	Cd2—Br6	2.8058 (6)
Cd1—Cl2	2.5654 (9)	Cd3—Br5^{ii}	2.6389 (6)
Cd1—Br1	2.5986 (6)	Cd3—Br8	2.6497 (6)
Cd2—Br5	2.6442 (6)	Cd3—Cl2	2.6585 (9)
Cd2—Br8	2.6663 (6)	Cd3—Cl7	2.7183 (9)
Cd2—Cl7	2.6976 (9)	Cd3—Br6^{i}	2.7535 (6)
Cd2—Br1	2.6985 (6)	Cd3—Br6^{ii}	2.8285 (6)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*A*···O1^{iii}	0.88	2.28	2.991 (5)	138
N4—H4*B*···Cl7	0.88	2.47	3.298 (4)	157
N2—H2···Cl2^{iv}	0.88	2.36	3.216 (3)	164
O1—H1···Br4^{v}	0.84	2.76	3.542 (3)	156

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

Preliminary structure refinements were carried out with all halogen sites assigned to Br atoms ($R_1 = 0.080$). Examination of the refined structure using *PLATON* (Spek, 2003) showed large differences between the $U_{\rm eq}$ values of these atoms and a residual density minimum larger than expected, which might be caused by wrongly assigned atom types. This implies that the halogen sites might be statistically occupied by Br and Cl. Thus, the refinements of the structure were carried out again using an algorithm to refine the occupancy factors of Br and Cl and to keep the summation of the two components to 1 for each site. The refinements led to a markedly reduced R_1 value of 0.027. The final occupancy factors correspond in total to 4.41 Br atoms and 3.59 Cl atoms per molecular formula unit. All H atoms were treated as riding atoms, with C—H distances of 0.98 (CH_3), 0.99 (CH_2) or 0.95 Å (CH), and N—H distances of 0.88 Å, and with $U_{\rm iso}({\rm H}) = U_{\rm eq}$(parent).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); 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: FG1881). Services for accessing these data are described at the back of the journal.

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