Metal ion interactions with thiamine. Crystal structures of Co(thiamine)$Cl_3 \cdot 0.4H_2O$ and Zn(thiamine)$Br_3 \cdot 0.2H_2O$: metal bonding to the base

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Abstract

The crystal structures of Co(thiamine)$Cl_3 \cdot 0.4H_2O$ (**1**) and Zn(thiamine)$Br_3 \cdot 0.2H_2O$ (**2**) have been determined by X-ray diffraction. The compounds are isomorphous to each other. Each compound forms a discrete M(thiamine)X_3 (M = Co(II) and X = Cl^-; M = Zn(II) and X = Br^-) structure with the tetrahedral M(II) atom being bonded by the three halide atoms and the N(1′) atom of the pyrimidine ring. The thiamine ligand adopts the *S* conformation: ϕ_T and $\phi_P = 128.9(3)$ and 111.8(4)° for **1** and 130.5(9) and 113.5(9)° for **2**. A 'two-point' halide bridge between the pyrimidine and the thiazolium moieties of the same molecule through an N(4′α)–H···X(1) hydrogen bond and an X(2)···thiazolium electrostatic contact is a factor that affects the *S* conformation. Crystal data: **1**, monoclinic, space group *C2/c*, $a = 25.767(9)$, $b = 8.490(2)$, $c = 17.539(6)$ Å, $\beta = 106.24(1)$°, $Z = 8$, $D_{calc} = 1.579$ g cm^{-3} and $R = 0.045$ for 3508 observed reflections; **2**, monoclinic, space group *C2/c*, $a = 26.388(5)$, $b = 8.563(1)$, $c = 17.753(3)$ Å, $\beta = 105.95(1)$°, $Z = 8$, $D_{calc} = 1.977$ g cm^{-3} and $R = 0.051$ for 1991 observed reflections.

Introduction

There has been considerable interest in metal ion interactions with thiamine (vitamin B_1) because thiamine (as a coenzyme) enzymes require a divalent metal ion, Mg^{2+}, for their functions [1]. In accordance with Schellenberger's suggestion from enzyme studies [2] that the Mg^{2+} ion is involved in the formation of the enzyme–coenzyme complex through the metal bonding to the base moiety of thiamine, probably at N(1′), six metal–thiamine structures with direct metal–N(1′) bonding have been reported [3]. We describe here crystal structures of two additional compounds showing the metal bonding to N(1′), Co(thiamine)$Cl_3 \cdot 0.4H_2O$ (**1**) and Zn(thiamine)$Br_3 \cdot 0.2H_2O$ (**2**). The significance of a 'two-point' halide bridge between the pyrimidine and the thiazolium rings of the same thiamine through an N(4′α)–H···X(1) hydrogen bond and an X(2)···thiazolium ring electrostatic interaction is emphasized as a factor affecting the *S* conformation of thiamine. The compounds are isomorphous to each other and also to Cd(thiamine)$Cl_3 \cdot 0.4H_2O$ [3a] and Zn(thiamine)$Cl_3 \cdot 0.4H_2O$ [3b].

Experimental

Co(thiamine)$Cl_3 \cdot 0.4H_2O$ (**1**) and Zn(thiamine)$Br_3 \cdot 0.2H_2O$ (**2**) were prepared by reacting (Hthiamine)Cl_2 and $Co(CH_3CO_2)_2 \cdot 4H_2O$ and (Hthiamine)Br_2 and $Zn(CH_3CO_2)_2 \cdot 2H_2O$, respectively, each with 2:1 molar ratio in an aqueous solution at room temperature.

X-ray structure determination

Details of crystal data and data collection together with refinement are summarized in Table 1. Intensities were corrected for Lp effects; absorption corrections were applied for **2** but not for **1** because of the small variation in intensity of an axial reflection (at $\chi \sim 90$°) with the spindle angle ϕ.

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TABLE 1. Crystal and refinement data

Compound	**1**	**2**
Formula	$C_{12}H_{17.8}CoCl_3N_4O_{1.4}S$	$C_{12}H_{17.4}ZnBr_3N_4O_{1.2}S$
Molecular weight	437.86	574.05
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*
a (Å)	25.767(9)	26.388(5)
b (Å)	8.490(2)	8.563(1)
c (Å)	17.539(6)	17.753(3)
β (°)	106.24(1)	105.95(1)
V (Å^3)	3683(2)	3857(1)
Z	8	8
D_{calc} (g cm^{-3})	1.58	1.98
F(000)	1784	2224
Crystal size (mm)	0.14×0.23×0.35	0.17×0.37×0.38
Crystal shape	plate	rectangular
Crystal colour	deep blue	light yellow
Diffractometer	Enraf-Nonius CAD4	Rigaku-AFC5
Radiation used	graphite-monochromated Mo Kα	(0.71073 Å)
μ(Mo Kα) (cm^{-1})	14.85	75.72
Transmission factors	0.94–1.08[a]	0.17–0.57[b]
T (K)	293	293
Data measured	$\pm h$, $+k$, $+l$	$\pm h$, $+k$, $+l$
Scan type	ω–2θ	ω–2ϕ
2ϕ Range (°)	3.0–55.0	3.0–45.0
Scan speed (°; 2ϕ min^{-1})	1.27–4.12	4
Scan range (°)	$0.80+0.35 \tan \phi$	$1.5+0.5 \tan \phi$
No. standard reflections	3	3
Variation in intensity (%)	±2.3	±2.9
No. reflections measured	4378	2614
No. observed unique reflections (*m*) $[F_o > 3\sigma(F_o)]$	3508	1991
Variables (*n*)	281	203
Weighting scheme (*w*)	$\sigma(F_o)^{-2}$	$0.2+0.005F_o$ for $F_o \leqslant 70$ 1.0 for $70 < F_o \leqslant 200$ $(0.1+10^{-3}F_o+3\times10^{-5}F_o^2)^{-1}$ for $F_o > 200$
R[c]	0.045	0.051
R_w[d]	0.051	0.054
S[e]	3.45	5.81
$(\Delta/\sigma)_{max}$	0.29	0.31
$(\Delta\rho)_{max}$ (e Å^{-3})	0.80	0.75

[a] Scan method, normalized to an average of unity. [b] Calculated by using the Gaussian integration (grid 8×8×8) method [4]. [c] $R=\Sigma|F_o-|F_c||/\Sigma F_o$. [d] $R_w=[\Sigma w(F_o-|F_c|)^2/\Sigma wF_o^2]^{1/2}$. [e] $S=[\Sigma w(F_o-|F_c||)^2/(m-n)]^{1/2}$.

The structures were solved by heavy-atom methods and refined by block-diagonal least-squares methods minimizing the function $\Sigma w(F_0-|F_c|)^2$. Water molecules O(W1) and O(W2) in **1** and O(W) in **2** were disordered each with the occupancy factor of 0.2 estimated on the basis of its electron density; a separation of 1.13(3) Å between the water molecules in **1** is prohibitively short, thus the water positions may be half-occupied at most. All H atoms were located from difference Fourier maps, except for those attached to water molecules. Thermal parameters of all non-hydrogen atoms were refined anisotropically, including the disordered waters O(W1) and O(W2) in **1**, except for O(W) in **2** which was refined isotropically. The H atom positions and their isotropic thermal parameters were included in the structure-factor calculations in the final cycles of the refinements, where these parameters were refined for **1** but fixed for **2** ($B=5.0$ Å^2). The final R and R_w values were 0.045 and 0.051 for **1** and 0.051 and 0.054 for **2**, for 3508 and 1991 observed reflections, respectively. The final atomic parameters for the non-hydrogen atoms are listed in Tables 2 and 3.

Neutral atomic scattering factors and anomalous-dispersion corrections for Br, Cl, Zn, Co and S were taken from the International Tables for X-ray Crystallography [5]. All calculations were performed with the UNICSIII program system [6] on a FACOM 780 computer.

TABLE 2. Final atomic coordinates ($\times 10^5$ for Co, Cl and S, $\times 10^3$ for O(W1) and O(W2), and $\times 10^4$ for others) for **1**

Atom	x	y	z
Co	33382(2)	67522(6)	33940(3)
Cl(1)	32463(5)	40775(12)	33929(6)
Cl(2)	27763(4)	79589(13)	40006(6)
Cl(3)	41950(5)	73969(18)	40659(8)
N(1′)	3225(1)	7336(4)	2227(2)
C(2′)	3205(2)	8816(5)	1938(2)
N(3′)	3185(2)	9181(4)	1195(2)
C(4′)	3190(2)	8010(4)	682(2)
C(5′)	3224(2)	6421(4)	930(2)
C(6′)	3231(2)	6166(4)	1702(2)
C(2′α)	3212(2)	10147(5)	2498(3)
N(4′α)	3162(2)	8441(4)	−68(2)
C(3,5′)	3233(2)	5057(5)	388(2)
S(1)	41953(5)	15699(14)	13276(8)
C(2)	3614(2)	2546(5)	970(3)
N(3)	3690(1)	3983(4)	736(2)
C(4)	4228(2)	4375(5)	825(2)
C(5)	4565(2)	3174(5)	1165(3)
C(4α)	4366(2)	5921(6)	533(3)
C(5α)	5172(2)	3131(7)	1350(3)
C(5β)	5387(2)	1694(7)	1048(4)
O(5γ)	5273(2)	409(5)	1495(3)
O(W1)[a]	0	237(2)	250
O(W2)[a]	32(1)	148(3)	247(1)

[a]O(W1) and O(W2) are disordered each with occupancy factor of 0.2.

TABLE 3. Final atomic coordinates ($\times 10^5$ for Zn and Br, $\times 10^3$ for O(W), and $\times 10^4$ for others) for **2**

Atom	x	y	z
Zn	33488(4)	67462(12)	33749(6)
Br(1)	32507(5)	39562(13)	33651(6)
Br(2)	27622(5)	79716(13)	39897(6)
Br(3)	42242(5)	74404(18)	40659(8)
N(1′)	3242(3)	7337(8)	2226(4)
C(2′)	3219(3)	8815(11)	1945(5)
N(3′)	3199(3)	9175(9)	1211(4)
C(4′)	3197(3)	8006(10)	697(5)
C(5′)	3239(3)	6446(10)	939(5)
C(6′)	3246(4)	6182(10)	1711(5)
C(2′α)	3233(4)	10132(11)	2494(6)
N(4′α)	3159(4)	8446(9)	−45(5)
C(3,5′)	3258(4)	5084(10)	409(5)
S(1)	4179(1)	1591(3)	1314(2)
C(2)	3617(4)	2571(11)	964(5)
N(3)	3701(3)	4007(9)	759(4)
C(4)	4219(4)	4397(11)	877(5)
C(5)	4541(4)	3211(13)	1185(6)
C(4α)	4370(5)	5971(14)	630(8)
C(5α)	5146(5)	3142(17)	1394(9)
C(5β)	5344(5)	1701(17)	1123(9)
O(5γ)	5237(4)	461(13)	1581(8)
O(W)[a]	30(3)	248(9)	269(5)

[a]O(W) is disordered with occupancy factor of 0.2.

TABLE 4. Bond distances (Å) and angles (°) for **1** and **2**

	1	**2**
Coordination sphere[a]		
M–N(1′)	2.046(3)	2.044(7)
M–X(1)	2.283(1)	2.403(2)
M–X(2)	2.267(1)	2.370(2)
M–X(3)	2.260(1)	2.374(2)
N(1′)–M–X(1)	104.7(1)	104.7(2)
N(1′)–M–X(2)	115.4(1)	114.9(2)
N(1′)–M–X(3)	107.9(1)	107.6(2)
X(1)–M–X(2)	111.7(1)	111.2(1)
X(1)–M–X(3)	109.1(1)	109.9(1)
X(2)–M–X(3)	107.8(1)	108.5(1)
M–N(1′)–C(2′)	125.5(3)	125.3(6)
M–N(1′)–C(6′)	118.4(3)	118.0(6)
Thiamine molecule		
N(1′)–C(2′)	1.350(5)	1.36(1)
C(2′)–N(3′)	1.326(6)	1.33(1)
N(3′)–C(4′)	1.344(5)	1.35(1)
C(4′)–C(5′)	1.413(5)	1.40(1)
C(5′)–C(6′)	1.368(6)	1.39(1)
C(6′)–N(1′)	1.357(5)	1.35(1)
C(2′)–C(2′α)	1.495(6)	1.48(1)
C(4′)–N(4′α)	1.347(5)	1.35(1)
C(5′)–C(3,5′)	1.503(6)	1.51(1)
C(3,5′)–N(3)	1.479(5)	1.49(1)
S(1)–C(2)	1.672(4)	1.67(1)
C(2)–N(3)	1.319(5)	1.32(1)
N(3)–C(4)	1.392(6)	1.37(1)
C(4)–C(5)	1.364(6)	1.34(1)
C(5)–S(1)	1.730(5)	1.74(1)
C(4)–C(4α)	1.488(7)	1.50(2)
C(5)–C(5α)	1.506(7)	1.54(2)
C(5α)–C(5β)	1.497(9)	1.47(2)
C(5β)–O(5γ)	1.421(8)	1.41(2)
N(1′)–C(2′)–N(3′)	125.0(4)	124.4(8)
C(2′)–N(3′)–C(4′)	118.7(3)	118.8(8)
N(3′)–C(4′)–C(5′)	120.8(4)	121.0(8)
C(4′)–C(5′)–C(6′)	116.0(4)	116.0(8)
C(5′)–C(6′)–N(1′)	123.8(4)	123.4(8)
C(6′)–N(1′)–C(2′)	115.7(3)	116.3(8)
N(1′)–C(2′)–C(2′α)	117.7(4)	118.4(8)
N(3′)–C(2′)–C(2′α)	117.3(4)	117.1(8)
N(3′)–C(4′)–C(4′α)	116.4(4)	116.0(8)
C(5′)–C(4′)–N(4′α)	122.8(4)	123.1(8)
C(4′)–C(5′)–C(3,5′)	123.5(4)	124.1(8)
C(6′)–C(5′)–C(3,5′)	120.5(3)	119.9(8)
C(5′)–C(3,5′)–N(3)	111.4(3)	112.1(6)
C(3,5′)–N(3)–C(2)	121.9(3)	121.5(8)
C(3,5′)–N(3)–C(4)	123.5(3)	123.5(8)
S(1)–C(2)–N(3)	112.4(3)	111.9(7)
C(2)–N(3)–C(4)	114.6(3)	115.0(8)
N(3)–C(4)–C(5)	111.3(4)	111.9(9)
C(4)–C(5)–S(1)	110.4(3)	110.5(8)
C(5)–S(1)–C(2)	91.4(2)	90.8(5)
N(3)–C(4)–C(4α)	120.0(4)	120.5(8)
C(5)–C(4)–C(4α)	128.8(4)	127.6(10)

(*continued*)

TABLE 4. (*continued*)

	1	**2**
S(1)-C(5)-C(5α)	122.1(4)	120.7(9)
C(4)-(C5)-C(5α)	127.4(4)	128.8(11)
C(5)-C(5α)-C(5β)	114.1(4)	113.1(11)
C(5α)-C(5β)-O(5γ)	106.0(6)	107.3(13)

[a] M and X denote Co and Cl for **1** and Zn and Br for **2**, respectively.

Results

Interatomic distances and angles are listed in Table 4. Molecular structures of **1** and **2** are shown in Fig. 1(a) and (b), respectively, and their crystal-packing arrangements are in Fig. 2(a) and (b).

The compounds are isomorphous to each other and thus there are many common structural features. (i) The metal atom is tetrahedrally coordinated by the pyrimidine base N(1′), the most basic site [7], and by three halide atoms. (ii) The thiamine moiety is in the uncommon *S* conformation: ϕ_T = C(5′)-C(3,5′)-N(3)-C(2) and ϕ_P = N(3)-C(3,5′)-C(5′)-C(4′) are 128.9(3) and 111.8(4)° for **1** and 130.5(9) and 113.5(9)° for **2**, respectively (these conformational terms were defined by Pletcher and Sax [8]); the dihedral angle between the pyrimidine and the thiazolium rings = 86.8(2)° for **1** and 88.5(4)° for **2**. (iii) The C(5) hydroxyethyl side chain folds back towards the thiazolium moiety to make a close contact between the electro-negative O(5γ) and the electro-positive [8, 9] S(1): O(5γ)···S(1) = 2.884(5) Å for **1** and 2.87(1) Å for **2** (sum of van der Waals radii for O···S = 3.32 Å [10]); $\phi_{5\alpha}$ = S(1)-C(5)-C(5α)-C(5β) = 47.3(6)° for **1** and 44(1)° for **2** and $\phi_{5\beta}$ = C(5)-C(5α)-C(5β)-O(5γ) = −67.4(6)° for **1** and −70(1)° for **2** (conformational terms by Pletcher and Sax [8]). (iv) The bond distances and angles of the thiamine molecule are normal for the N(1′)-metalated or the neutral thiamines [3a] (Table 4); the N(1′) ligation does not affect the C(2′)-N(1′)-C(6′) bond angle and the opposite C(4′)-N(4′α) bond length, in contrast to appreciable effects of the N(1′) protonation. (v) The values of the C(2)-N(3)-C(3,5′) and C(4)-N(3)-C(3,5′) bond angles, which are sensitive to the molecular conformation [3a], are those expected for the C(2)-substituent free of thiamine in the *S*-form, where the C(4)-N(3)-C(3,5′) angle is always larger (3–9°) than the C(2)-N(3)-C(3,5′) angle [3a, b, 11], while they are nearly equal or rather opposite (0–2°) for the C(2)-substituted thiamine in the *S*-form [12], and the C(2)-N(3)-C(3,5′) angle is usually larger (1–4°) than the C(4)-N(3)-C(3,5′) angle for the *F*-form thiamine with a sole exception [13].

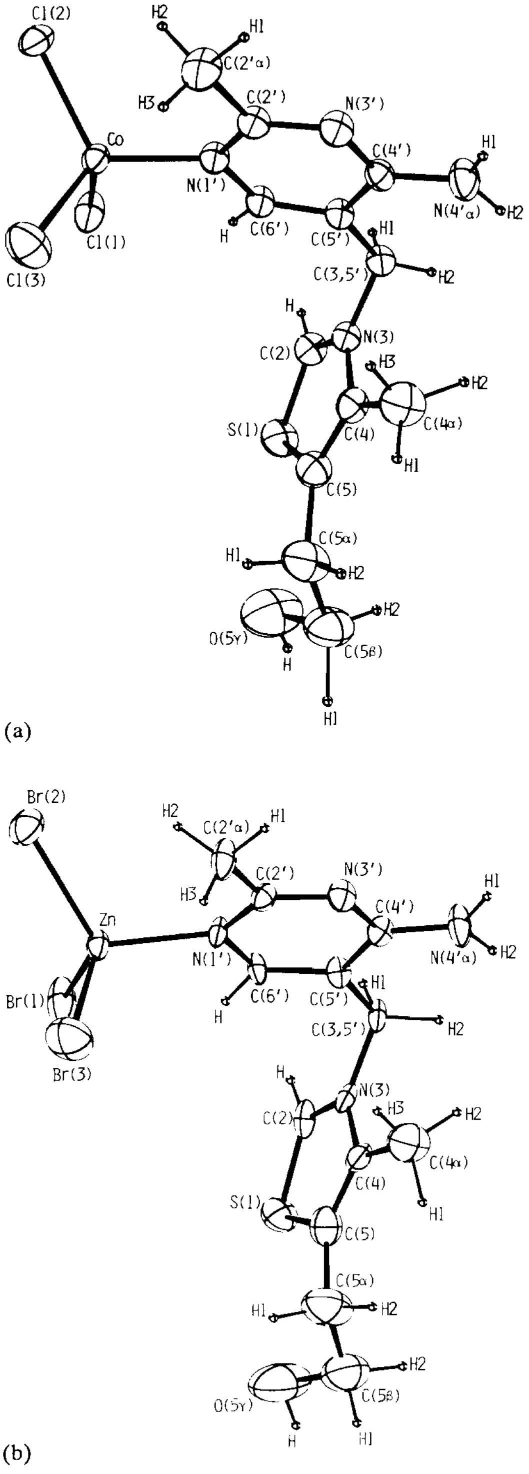

Fig. 1. Molecular structures of (a) Co(thiamine)Cl_3 (**1**) and (b) Zn(thiamine)Br_3 (**2**).

Crystal packings are also alike in **1** and **2** (Tables 5 and 6 and Fig. 2). Hydrogen bonds and electrostatic contacts are major intermolecular interactions. All three hydrogen atoms attached to the O(5γ) or N(4′α)

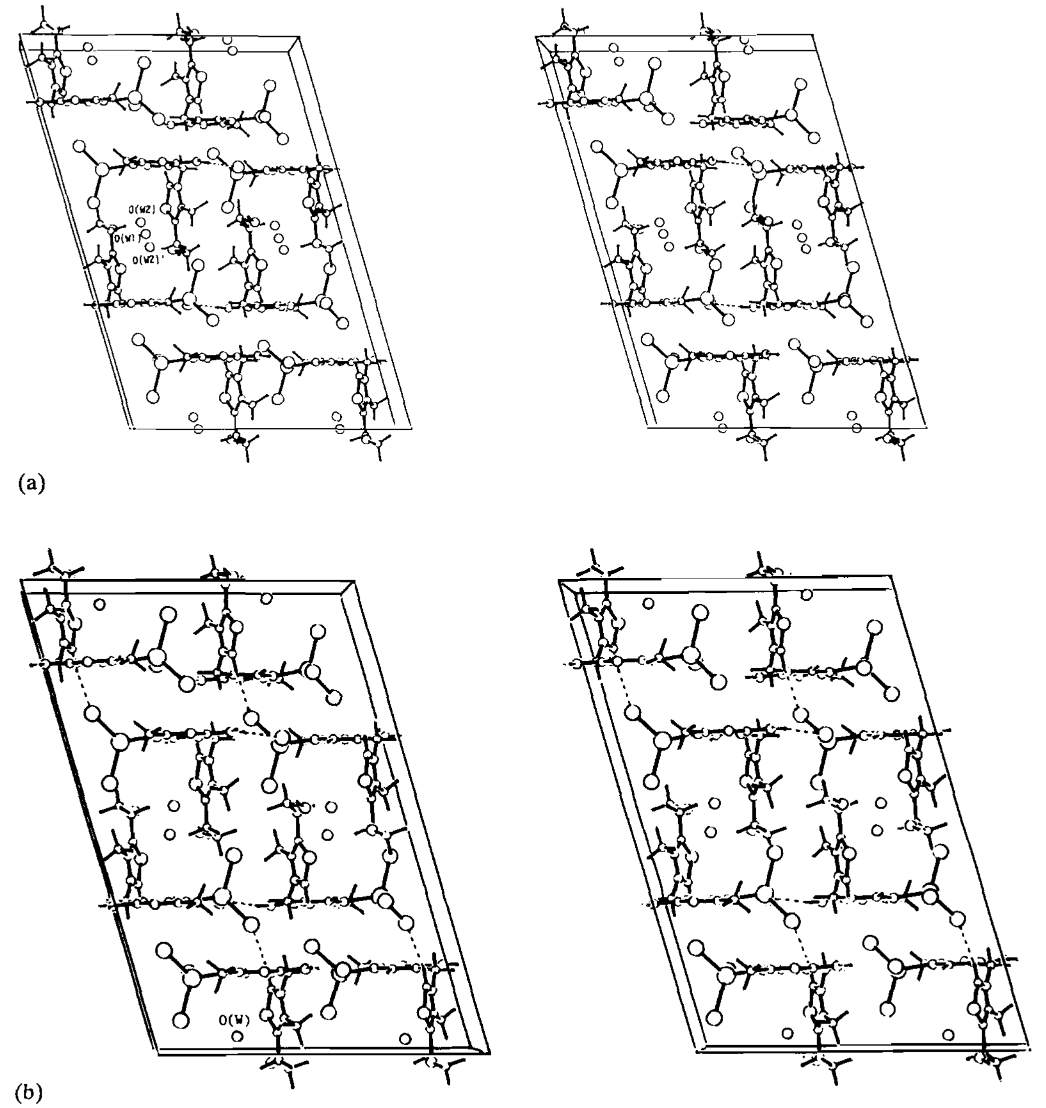

Fig. 2. Crystal-packing arrangements of (a) Co(thiamine)Cl$_3$ (**1**) and (b) Zn(thiamine)Br$_3$ (**2**), each viewed down the *b* axis with the *c* axis horizontal and *a* axis vertical. Broken lines denote hydrogen bonds.

atoms are hydrogen-bonded to halide acceptors. As observed in many thiamine structures [11a], the acidic [14] C(2)-hydrogen also takes part in hydrogen bonding, here with the pyrimidine N(3') of a neighbouring thiamine molecule (not shown in Fig. 2) and a halide ligand (a bifurcated hydrogen bond). Dipolar interactions occur between halide ions and the pyrimidine ring (not shown in Fig. 2) or the thiazolium ring.

Discussion

Crystals of Co(thiamine)Cl$_3$ (**1**) and Zn(thiamine)Br$_3$ (**2**) are isomorphous with those of Cd(thiamine)Cl$_3$ [3a] and Zn(thiamine)Cl$_3$ [3b]. Thus the structural features (i)–(v) noted above are also common to the four M(thiamine)X$_3$ compounds; Table 7 compares some relevant structural parameters. Including the present work, nine structures of thiamine [3] or tetrahydrothiamine [15] are available, in which a metal ion (Cd(II) [3a], Zn(II) [3b], Cu(I) [3c,f], Rh(II) [3d], Pt(II) [3e], or Co(II) [15]) is bonded to the pyrimidine N(1'). It is of interest to note here that Co(II), Zn(II) and even Cd(II) ions are among those ions which activate pyruvate carboxylase [16] (Cu(I), Rh(II) or Pt(II) have not been examined). Thus the involvement of N(1') in the metal coordination seems to certainly play some roles in enzymic processes. For example, Schellenberger suggests that the metal acts as a bridge between the apoenzyme and the thiamine cofactor [2].

TABLE 5. Hydrogen-bonding and other short contacts in **1**[a, b]

Hydrogen bonding contacts

Donor (D)–H	Acceptor (A)	D–H (Å)	D...A (Å)	H...A (Å)	D–H...A (°)
N(4′α)–H1	Cl(2^{i})	0.75(7)	3.477(4)	2.79(7)	153(6)
N(4′α)–H2	Cl(1^{ii})	0.94(6)	3.498(4)	2.56(6)	178(4)
O(5γ)–H	Cl(3^{iii})	0.94(12)	3.184(5)	2.25(12)	170(8)
C(2)–H	N(3′^{iv})	0.93(4)	3.128(5)	2.57(4)	118(3)
C(2)–H)	Cl(2^{v})		3.615(5)	2.81(4)	145(3)

Other short contacts (less than 3.7 Å for contacts with Cl and less than 3.5 Å for other contacts)

A	B	A...B (Å)	A	B	A...B (Å)
Cl(1)	C(2′α^{iv})	3.678(5)	Cl(3)	O(W2^{vii})	3.36(2)
Cl(1)	C(3,5′^{vi})	3.584(4)	N(3′)	S(1^{viii})	3.257(4)
Cl(1)	C(2′^{v})	3.627(4)	C(5′)	N(4′α^{ix})	3.468(5)
Cl(2)	C(3,5′^{vi})	3.501(4)	S(1)	O(5γ)	2.884(5)
Cl(2)	C(3,5′^{vii})	3.557(4)	C(4)	O(W2^{vii})	3.40(2)
Cl(2)	C(2^{vi})	3.550(4)	C(4α)	O(W2^{vii})	3.40(2)
Cl(2)	N(3^{vi})	3.676(3)	C(5α)	O(W2^{x})	3.42(2)
Cl(3)	C(4^{vi})	3.412(5)	O(5γ)	O(W1^{xi})	3.31(1)
Cl(3)	C(5^{vi})	3.568(5)			

[a] Symmetry operations: (none) x, y, z; (i) $x, 2-y, -\frac{1}{2}+z$; (ii) $x, 1-y, -\frac{1}{2}+z$; (iii) $1-x, -1+y, \frac{1}{2}-z$; (iv) $x, -1+y, z$; (v) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (vi) $x, 1-y, \frac{1}{2}+z$; (vii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (viii) $x, 1+y, z$; (ix) $\frac{1}{2}-x, \frac{3}{2}-y, -z$; (x) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (xi) $\frac{1}{2}+x, -\frac{1}{2}+y, z$. [b] Since hydrogen atoms on the disordered water molecules were not located, interactions involving O(W1) or O(W2) are listed here rather than as hydrogen bonds.

TABLE 6. Hydrogen-bonding and other short contacts in **2**[a, b]

Hydrogen-bonding contacts

Donor(D)–H	Acceptor (A)	D–H (Å)	D...A (Å)	H...A (Å)	D–H...A (°)
N(4′α)–H1	Br(2^{i})	1.00	3.530(8)	2.58	158
N(4′α)–H2	Br(1^{ii})	1.01	3.555(9)	2.56	168
O(5γ)–H	Br(3^{iii})	1.03	3.31(1)	2.29	168
C(2)–H	N(3′^{iv})	1.02	3.18(1)	2.60	116
C(2)–H	Br(2^{v})		3.68(1)	2.81	143

Other short contacts (less than 3.7 Å for contacts with Br and less than 3.5 Å for other contacts)

A	B	A...B (Å)	A	B	A...B (Å)
Br(1)	C(2′^{iv})	3.62(1)	Br(3)	O(W^{vii})	3.66(9)
Br(2)	C(3,5′^{vi})	3.618(8)	N(3′)	S(1^{viii})	3.277(8)
Br(2)	C(3,5′^{vii})	3.64(1)	S(1)	O(5γ)	2.87(1)
Br(2)	C(2^{vi})	3.640(8)	C(4α)	O(W^{vii})	3.15(8)
Br(3)	C(4^{vi})	3.58(1)	O(5γ)	O(W^{ix})	3.20(8)
Br(3)	C(5^{vi})	3.66(1)	O(5γ)	O(W^{v})	3.36(8)

[a] Symmetry operations: (none) x, y, z; (i) $x, 2-y, -\frac{1}{2}+z$; (ii) $x, 1-y, -\frac{1}{2}+z$; (iii) $1-x, -1+y, \frac{1}{2}-z$; (iv) $x, -1+y, z$; (v) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (vi) $x, 1-y, \frac{1}{2}+z$; (vii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (viii) $x, 1+y, z$; (ix) $\frac{1}{2}+x, -\frac{1}{2}+y, z$. [b] Since the hydrogen atoms on the disordered water molecule were not located, interactions involving O(W) are listed here rather than as hydrogen bonds.

The conformation of thiamine is important for its functions [2, 17]. Table 8 compiles the structural parameters in polyhalogenometal ion–thiamine compounds. Sax [18], Richardson *et al.* [11b, 19] and Cramer *et al.* [3e] have noticed that the double interaction of the halide ion with the amino group and the thiazolium ring via a N(4′α)–H$\cdots$X$^-$ (X$^-$ = halide ion) hydrogen bond and X$^-\cdots$thiazolium electrostatic interaction is a factor affecting the conformation of thiamine, where the larger size of the anion is responsible for the *S*-form while the smaller size is responsible for the *F*-form, basically due to crystal-packing requirements. The present complexes **1** and **2** also hold for this rule judging

TABLE 7. Comparison of relevant structural parameters in M(thiamine)X_3 (M = Co, Zn, or Cd; X = Cl or Br) compounds

	Co(thiamine)Cl_3	Zn(thiamine)Br_3	Cd(thiamine)Cl_3	Zn(thiamine)Cl_3
M-N(1') (Å)	2.046(3)	2.044(7)	2.239(2)	2.040(3)
M-X_{av} (Å)	2.27(2)	2.38(3)	2.451(9)	2.259(9)
ϕ_T[a] (°)	128.9(3)	130.5(9)	111.6	113.4
ϕ_P[a] (°)	111.8(4)	113.5(9)	129.8	130.4
Conformation[a]	*S*	*S*	*S*	*S*
$\phi_{5\alpha}$[a] (°)	47.3(6)	44(1)	46.5	45.0
$\phi_{5\beta}$[a] (°)	−67.4(6)	−70(1)	−68.8	−67.6
S(1)···O(5γ) (Å)	2.884(5)	2.87(1)	2.879(3)	2.878(4)
Reference	this work	this work	3a	3b

[a] Definition of the conformational terms by Pletcher and Sax [8].

TABLE 8. X···X non-bonded, N(4'α)-H···X hydrogen bond, X···thiazolium distances (Å) (X = Cl or Br) in the polyhalogenometal anion–thiamine compounds

Compound	Conformation of thiamine	Geometry of anion	X···X	N(4'α)···X···thiazolium[a]		Reference
Cu(thiamine)Cl_2	*F*	trigonal planar	3.867	3.251(2)	3.29	3c
Cu(thiamine)Br_2	*F*	trigonal planar	3.995(2)	3.39(1)	3.41	3f
Pt(thiamine)Cl_3	*F*	square planar	3.27	3.28(2)	3.30	3e
(Hthiamine)$PtCl_4$	*F*	square planar	3.243(6)	3.18(2)	3.36	3e
$(Hthiamine)_2(PtCl_4)Cl_2$	*F*	square planar	3.262	3.173(5)	3.32	3e
(Hthiamine)$CuCl_4$	*F*	tetrahedral	3.42(2)	3.44(1)	3.39	13
				N(4'α)···X1-M-X2···thiazolium[a]		
(Hthiamine)$CdCl_4$	*S*	tetrahedral	4.00(5)	3.306(3)	3.20	11a
(Hthiamine)$CoCl_4$	*S*	tetrahedral	3.72(4)	3.323	3.19	11b
(Hthiamine)$HgCl_4$	*S*	tetrahedral	–[b]	–[b]	–[b]	11c
Cd(thiamine)Cl_3	*S*	tetrahedral	4.0(1)	3.395(2)	3.39	3a
Zn(thiamine)Cl_3	*S*	tetrahedral	3.7(5)	3.473	3.42	3b
Co(thiamine)Cl_3	*S*	tetrahedral	3.71(6)	3.498(4)	3.41	this work
Zn(thiamine)Br_3	*S*	tetrahedral	3.90(4)	3.555(9)	3.55	this work

[a] Perpendicular distances to the ring plane. [b] No atomic coordinates are given.

from the non-bonded X···X distances. Cu(thiamine)Cl_2 [3c] and Cu(thiamine)Br_2 [3f] are exceptions, since their non-bonded X···X distances are rather large for the *F*-form thiamine. Previously we have pointed out [3f] that 'one-point' and 'two-point' halide bridges are characteristic of halogenometal compounds involving *F*-form and *S*-form thiamines, respectively, where the 'one-point' and 'two-point' bridges mean that the same halide atom bridges between the pyrimidine and the thiazolium rings in the former while a halide atom forms a hydrogen bond with N(4'α) and another halide of the same anion stacks on the thiazolium ring in the latter. This is also true for the present complexes **1** and **2**, which both contain *S*-form thiamines and 'two-point' halide bridges. It is most probable that crystal-packing forces determine the 'one-point' or the 'two-point' bridge, but further investigation is needed to clarify this suggestion.

Supplementary material

Listings of the thermal parameters for the non-hydrogen atoms, hydrogen atom coordinates, bond lengths and angles involving hydrogen atoms, least-squares planes, and of observed and calculated structure factors are available from the authors on request.

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