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Thiamine–Metal Ion and Thiamine–Anion Interactions. Crystal Structure of Cu(thiamine)Br_2

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Abstract

The reaction of $Cu(OAc)_2$ and thiamine hydrobromide in water produced Cu(thiamine)Br_2. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.383(2)$, $b = 15.061(3)$, $c = 6.241(2)$ Å, $\alpha = 103.43(2)$, $\beta = 85.25(3)$, $\gamma = 106.87(1)°$, $Z = 2$, $D_{calc} = 1.977$ g cm^{-3} and $R = 0.046$ for the 199 variables and the 1666 data. The complex forms a discrete Cu(thiamine)Br_2 structure in which the two Br atoms and the N(1′) atom of the pyrimidine ring are bonded to the trigonal-planar Cu(I) atom. The thiamine ligand is in the usual *F* conformation with torsion angles $\phi_T = -12(1)°$ and $\phi_P = 82(1)°$. An anion bridge between the thiazolium and the pyrimidine moieties of the same molecule through a C(2)–H···Br hydrogen bonding and a pyrimidine···Br electrostatic contact is a factor that affects the *F* conformation.

Introduction

Thiamine–metal ion interactions have received considerable attention because thiamine pyrophosphate (as a coenzyme)-containing enzymes also require a divalent metal ion, Mg^{2+}, for their functions [1], where Mg^{2+} is suggested to be involved in the formation of the enzyme–coenzyme complex [2, 3]. To our knowledge, there have been reported fourteen crystal structures of thiamine, its monophosphate, or its pyrophosphate involving metal ions [4–6], the majority of which are salt type [4], *i.e.* no direct bonding between them; only Cd(thiamine)Cl_3 [5a], Cu(thiamine)Cl_2 [5b], Rh_2(acetato)$_4$(thiamine monophosphate)$_2$ [5c], Zn(thiamine)Cl_3 [5d] and Pt(thiamine)Cl_3 [4g] show metal binding to the pyrimidine moiety through the N(1′) site and Cu(thiamine pyrophosphate)(1,10-phenanthroline)(H_2O) [6] solely to the pyrophosphate group.

We report here the crystal structure of Cu(thiamine)Br_2, which provides an additional example showing metal bonding to N(1′). The significance of an anion bridge between the thiazolium ring and the pyrimidine moiety of the same molecule through C(2)–H···Br hydrogen bonding and an electrostatic Br···pyrimidine ring interaction is emphasized, as a factor affecting the conformation of thiamine. The complex is isostructural to Cu(thiamine)Cl_2 [5b].

Experimental

Preparation of Cu(thiamine)Br_2

(Hthiamine)Br_2 (4 mmol) and $Cu(CH_3CO_2)_2 \cdot H_2O$ (2 mmol) were dissolved in a minimum quantity of water to give a light blue solution. It gradually turned light orange on standing at room temperature. Dark yellow plates formed after four days. *Anal.* Calc. for $C_{12}H_{17}Br_2CuN_4OS$: C, 29.49; H, 3.51; N, 11.46; Cu, 13.06. Found: C, 30.14; H, 3.42; N, 11.49; Cu, 12.67%.

X-ray Structure Determination

Details of crystal data and data collection together with refinement are summarized in Table 1. Intensities were corrected for Lorentz and polarization effects as well as for absorption. The positions of the copper and the two bromine atoms were determined in a Patterson map and those of all the other non-hydrogen atoms were located in a subsequent Fourier map, involving the C(5β) atom that is disordered into two positions with occupancy factors of 0.65 for C(5β) and 0.35 for C(5β)′, the values of occupancy factors being estimated on the basis of the values of electron densities. The structure was refined by the block-diagonal least-squares method, minimizing the function $\Sigma w(F_o - |F_c|)^2$. Thermal parameters of all the non-hydrogen atoms including the disordering atoms (C(5β) and C(5β)′) were refined anisotropically while the positions of hydrogen atoms located from difference Fourier maps and their isotropic thermal parameters were

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TABLE 1. Crystal and Refinement Data

Formula	$C_{12}H_{17}Br_2CuN_4OS$
M	488.72
a (Å)	9.383(2)
b (Å)	15.061(3)
c (Å)	6.241(2)
α (°)	103.43(2)
β (°)	85.25(3)
γ (°)	106.87(1)
V (Å^3)	820.9(4)
Space group	$P\bar{1}$
Z	2
No. reflections used to determine cell constants	20 ($21 < 2\theta < 31°$)
D_{calc} (g cm^{-3})	1.977
Radiation used	graphite-monochromated Mo Kα (0.71073 Å)
Linear absorption coefficient (cm^{-1})	62.8
Crystal dimensions (mm)	{100}, 0.98; {010}, 0.176; {001}, 0.326
Transmission factors[a]	0.33–0.57
Diffractometer	Rigaku AFC-5
Data collection method	ω–2θ
2θ Range (°)	$3 < 2\theta < 45$
Scan range (°)	$1.5 + 0.5 \tan\theta$
Scan speed (2θ/min, °)	4.0
Background (s)	5 at the lower and upper limits of each scan
Temperature (K)	293
Data collected	$\pm h$, $\pm k$, $+l$
No. standard reflections	3
Variation in standard intensity (%)	±1.7
No. unique data collected	2077
No. data used in refinement (m)	1666 [$F_o > 3\sigma(F_o)$]
No. variables (n)	199
Data: parameter ratio	8.4
R[b]	0.046
R_w[b]	0.051
$G.O.F.$[b]	2.02
Weighting scheme	$w = \sigma(F_o)^{-2}$
Largest shift/e.s.d.	0.22
Highest peak in final difference map (e Å^{-3})	0.82 near to Cu (1.2 Å)

[a] Calculated by using the Gaussian integration (grid 8 × 8 × 8) method [7]. [b] $R = \Sigma|F_o - |F_c||/\Sigma F_o$; $R_w = [\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2]^{1/2}$; $G.O.F. = [\Sigma w(F_o - |F_c|)^2/(m - n)]^{1/2}$.

included in the structure factor calculations in the final cycles of the refinement but fixed ($B = 5.0$ Å^2); missing hydrogen atoms were those attached to the C(5α), C(5β) and C(5β)′ atoms. The final R, R_w and $G.O.F.$ values were 0.046, 0.051 and 2.0, respectively, for 1666 observed reflections. The final atomic parameters for the non-hydrogen atoms are listed in Table 2.

Neutral atomic scattering factors were used with Br, Cu and S corrected for anomalous dispersion [8]. All calculations were performed with the UNICS III program system [9] on a FACOM 380 computer.

Results

Figure 1 shows the molecular structure of the complex, which is isostructural to Cu(thiamine)Cl_2 [5b]. The trigonal-planar Cu(I) ion is bonded directly to thiamine through N(1′) of the pyrimidine moiety and to two Br atoms. The coordination plane, comprized of Cu, Br(1), Br(2) and N(1′) atoms, is almost coplanar with the pyrimidine plane; the tilt angle between them is 2.7(2)° and the torsion angle C(2′)–N(1′)–Cu–Br(1) is –0.6(9)°. The Cu–N(1′) bond length of 2.003(8) Å is comparable to the value 1.993(2) Å in the chloride derivative [5b]. Due to a

TABLE 2. Positional Parameters ($\times 10^4$) and Equivalent Isotropic Temperature Factors^a for Cu(thiamine)Br_2

Atom	*x*	*y*	*z*	B_{eq} ($Å^2$)
Cu	3500(1)	1855(1)	2764(2)	2.9
Br(1)	5768(1)	1545(1)	1622(2)	3.9
Br(2)	2904(1)	2982(1)	1024(2)	3.7
N(1′)	1916(8)	1464(5)	4988(13)	2.4
C(2′)	1956(10)	881(6)	6291(15)	2.1
N(3′)	886(8)	618(5)	7737(12)	2.3
C(4′)	−293(10)	986(6)	8010(15)	2.3
C(5′)	−419(10)	1606(6)	6681(15)	2.3
C(6′)	745(10)	1823(7)	5224(16)	2.6
C(2′α)	3257(11)	503(7)	6168(17)	2.9
N(4′α)	−1320(9)	699(6)	9500(15)	3.5
C(3, 5′)	−1703(10)	2016(7)	6812(16)	2.7
S(1)	−871(3)	4099(2)	12113(5)	3.9
C(2)	−623(11)	3165(8)	10245(18)	3.4
N(3)	−1595(8)	2887(5)	8651(13)	2.4
C(4)	−2595(10)	3420(6)	8836(15)	2.4
C(5)	−2343(11)	4132(7)	10680(18)	3.1
C(4α)	−3791(11)	3189(8)	7197(19)	3.8
C(5α)	−3230(14)	4848(8)	11408(22)	5.0
C(5β)^b	−2508(25)	5686(13)	13259(30)	5.2
C(5β)′^{b}	−3522(36)	5069(25)	13623(60)	4.9
O(5γ)	−2192(15)	5429(9)	15024(18)	9.9

$^a B_{eq} = (4/3)\Sigma_i \Sigma_j \beta_{ij} \mathbf{a}_i \mathbf{a}_j$. ^{b}Disordered: occupancy factors 0.65 for C(5β) and 0.35 for C(5β)′.

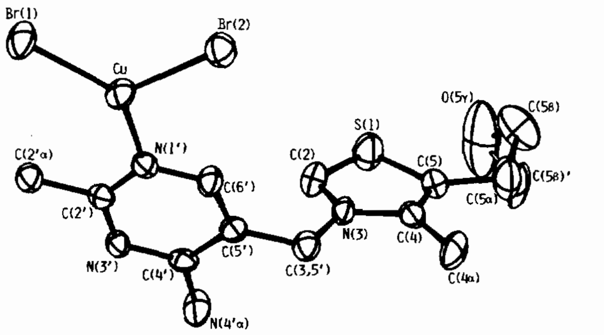

Fig. 1. Molecular structure of Cu(thiamine)Br_2 with the numbering scheme.

steric interaction between Br(1) and the C(2′α) substituent, angles about the Cu and the N(1′) atoms are asymmetrical: the angles N(1′)–Cu–Br(1) and Cu–N(1′)–C(2′) [135.6(2)° and 124.4(7)°] are significantly larger than the corresponding angles N(1′)–Cu–Br(2) and Cu–N(1′)–C(6′) [110.0(3)° and 118.1(7)°] (Table 3); this in turn lengthens the Cu–Br(2) bond distance to result in equal van der Waals contacts between the Br(1) and H3(C2′α) atoms (2.97 Å) and between the Br(2) and H(C6′) atoms (2.90 Å) (van der Waals radii for Br and H (for C–H) are 1.85 and 1.20 Å, respectively [10]). The Cu–Br(1) bond distance of 2.329(2) Å is somewhat shorter than that (2.346(2) Å) observed in $(PPh_3)_2CuBr$ [11], which is, to our knowledge, a sole trigonal-planar Cu(I) compound involving Br, while the Cu–Br(2) distance of 2.425(2) Å is considerably longer.

The bond distances and angles of the thiamine molecule (Table 3) are mostly as expected for the N(1′)-metalated or the neutral thiamines [5a], except for a few bond lengths involving the disordering C(5β) atom; the N(1′) ligation does not affect the C(2′)–N(1′)–C(6′) angle and the opposite C(4′)–N(4′α) bond length, in contrast to appreciable effects of the N(1′) protonation, that is, the increase of the angel and the decrease of the bond length. The torsion angles defining the conformation of thiamine with respect to the C(3, 5′) methylene bridge atom [12], ϕ_P = N(3)–C(3, 5′)–C(5′)–C(4′) = 82(1)° and ϕ_T = C(5′)–C(3, 5′)–N(3)–C(2) = −12(1)°, correspond to the usual *F* conformation; the dihedral angle between the pyrimidine and the thiazolium rings is 104.7(3)° (Table 4). The C(5)–hydroxyethyl side chain is folded back toward the thiazolium ring to make a short contact of 2.87(1) Å between the O(5γ) and S(1) atoms (sum of van der Waals radii for S···O = 3.32 Å [10]): $\phi_{5\alpha}$ = S(1)–C(5)–C(5α)–C(5β) = 13(2)°, $\phi_{5\beta}$ = C(5)–C(5α)–C(5β)–O(5γ) = −54(2)°, $\phi_{5\alpha'}$ = S(1)–C(5)–C(5α)–C(5β)′ = −39(2)° and $\phi_{5\beta'}$ = 56(3)°. Disorder of the C(5)–hydroxyethyl side chain sometimes occurs, e.g., in Cu(thiamine)Cl_2, 2-(α-hydroxyethyl)thiamine·Cl·HCl [13], or thiamine naphthalene-1,5-disulfonate [14].

The crystal packing (Fig. 2) is mainly dominated by a hydrogen bonding network (Table 5), ring–ring stacking, and electrostatic interactions. Two

TABLE 3. Bond Distances (Å) and Angles (°) in Cu(thiamine)Br_2

Coordination sphere			
Bond distances			
Cu–N(1′)	2.003(8)	Cu–Br(2)	2.425(2)
Cu–Br(1)	2.329(2)		
Bond angles			
N(1′)–Cu–Br(1)	135.6(3)	Cu–N(1′)–C(2′)	124.4(7)
N(1′)–Cu–Br(2)	110.0(3)	Cu–N(1′)–C(6′)	118.1(7)
Br(1)–Cu–Br(2)	114.32(7)		
Thiamine molecule			
Bond distances			
N(1′)–C(2′)	1.34(1)	C(2)–N(3)	1.32(1)
C(2′)–N(3′)	1.33(1)	N(3)–C(4)	1.38(1)
N(3′)–C(4′)	1.36(1)	C(4)–C(5)	1.36(1)
C(4′)–C(5′)	1.42(2)	C(5)–S(1)	1.72(1)
C(5′)–C(6′)	1.38(1)	C(4)–C(4α)	1.49(2)
C(6′)–N(1′)	1.34(1)	C(5)–C(5α)	1.51(2)
C(2′)–C(2′α)	1.48(2)	C(5α)–C(5β)	1.53(2)
C(4′)–N(4′α)	1.33(1)	C(5α)–C(5β)′	1.37(4)
C(5′)–C(3, 5′)	1.49(2)	C(5β)–O(5γ)	1.33(3)
C(3, 5′)–N(3)	1.51(1)	C(5β)′–O(5γ)	1.48(4)
S(1)–C(2)	1.67(1)		
Bond angles			
N(1′)–C(2′)–N(3′)	123.7(9)	C(3, 5′)–N(3)–C(4)	121.2(8)
C(2′)–N(3′)–C(4′)	119.3(9)	S(1)–C(2)–N(3)	112.1(9)
N(3′)–C(4′)–C(5′)	120.2(8)	C(2)–N(3)–C(4)	115.0(8)
C(4′)–C(5′)–C(6′)	115.4(10)	N(3)–C(4)–C(5)	111.1(9)
C(5′)–C(6′)–N(1′)	123.8(10)	C(4)–C(5)–S(1)	110.4(8)
C(6′)–N(1′)–C(2′)	117.4(8)	C(5)–S(1)–C(2)	91.5(5)
N(1′)–C(2′)–C(2′α)	119.5(8)	N(3)–C(4)–C(4α)	121.9(8)
N(3′)–C(2′)–C(2′α)	116.7(9)	C(5)–C(4)–C(4α)	127.0(10)
N(3′)–C(4′)–N(4′α)	116.3(10)	S(1)–C(5)–C(5α)	124.2(8)
C(5′)–C(4′)–N(4′α)	123.5(10)	C(4)–C(5)–C(5α)	125.4(10)
C(4′)–C(5′)–C(3, 5′)	123.9(8)	C(5)–C(5α)–C(5β)	114(1)
C(6′)–C(5′)–C(3, 5′)	120.7(10)	C(5)–C(5α)–C(5β)′	116(2)
C(5′)–C(3, 5′)–N(3)	114.0(7)	C(5α)–C(5β)–O(5γ)	114(2)
C(3, 5′)–N(3)–C(2)	123.7(9)	C(5α)–C(5β)′–O(5γ)	115(2)

TABLE 4. Least-squares Planes[a] and Atomic Deviations (Å)

Plane 1: the coordination plane (0.3129x + 0.4921y + 0.6021z = 3.446)					
Cu	−0.0053(5)	Br(1)	0.0018(2)	Br(2)	0.0011(1)
N(1′)	0.076(7)				
Plane 2: the pyrimidine ring (−0.3245x − 0.5191y − 0.5640z = −3.487)					
N(1′)	0.004(5)	C(2′)	−0.012(7)	N(3′)	0.011(5)
C(4′)	−0.014(7)	C(5′)	0.007(7)	C(6′)	−0.003(8)
Cu*	0.00(1)	C(2′α)*	−0.07(2)	N(4′α)*	0.00(1)
C(3, 5′)*	0.03(2)				
Plane 3: the thiazolium ring (0.4252x + 0.5873y − 0.6295z = −1.480)					
S(1)	−0.0004(6)	C(2)	0.006(9)	N(3)	−0.002(5)
C(4)	−0.001(6)	C(5)	0.004(8)		
C(3, 5′)*	−0.09(2)	C(4α)*	−0.04(2)	C(5α)*	0.00(2)
Dihedral angles (°) between the planes					
Planes 1 and 2	177.3(2)		Planes 2 and 3	104.7(3)	

[a] In the equation of the plane, x, y and z are coordinates measured in Å units along the crystallographic a, b and c axes, respectively. Atoms designated by an asterisk (*) were given zero weight in calculating the planes.

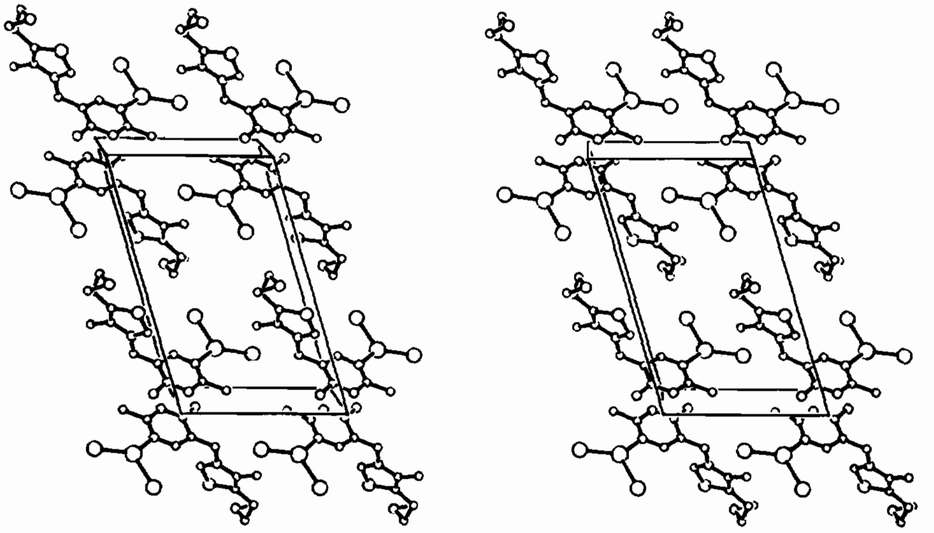

Fig. 2. A stereopair of the crystal packing viewed down the *c* axis with the *a* axis horizontal and the *b* axis vertical.

TABLE 5. Hydrogen Bonding Interactions and Other Short Contacts

A	B	Equivalent position for B	A···B (Å)	H···B (Å)	A–H···B (°)
Hydrogen bonds					
N(4′α)	Br(1)	$x-1, y, 1+z$	3.39(1)	2.43	173
N(4′α)	N(3′)	$-x, -y, 2-z$	3.04(1)	1.97	171
O(5γ)	Br(2)	$-x, 1-y, 2-z$	3.19(1)	2.11	157
C(2)	Br(2)	$x, y, 1+z$	3.48(1)	2.59	142
Other short contacts (less than 3.7 Å for contacts with Br atoms and less than 3.5 Å for other contacts)					
S(1)	O(5γ)	x, y, z	2.87(1)		
S(1)	O(5γ)	$-x, 1-y, 2-z$	3.32(1)		
C(2′)	C(4′)	$-x, -y, 1-z$	3.49(1)		
C(5β)′	C(5β)′	$-x-1, 1-y, 3-z$	3.12(5)		
N(3)	Br(1)	$x-1, y, 1+z$	3.424(8)		
C(4)	Br(1)	$x-1, y, 1+z$	3.56(1)		

types of pyrimidine–pyrimidine interactions occur (Fig. 3): one is a hydrogen-bonded base-pair formed by a pair of N(4′α)H···N(3′) hydrogen bonds across a crystallographic center of inversion and the other is a ring–ring stacking with an average spacing of 3.46 Å across another center of symmetry. The amino N(4′α) donates the other proton to the Br(1) anion (at $-1+x$, y, $1+z$), which further participates in an electrostatic interaction with the thiazolium ring of the same molecule, the closest contact being 3.424(8) Å with the quarternary nitrogen N(3) (Fig. 4 and Table 5) (sum of van der Waals radii for Br···aromatic ring = 3.62 Å [10]). The acidic C(2) hydrogen takes part in the hydrogen bonding formation with Br(2) of the neighboring molecule (at x, y, $1+z$) and the pyrimidine ring caps on this bromine atom with the distance of 3.609(4) Å between Br(2) and the pyrimidine plane (Fig. 3). We can see that the rotation of the $CuBr_2$ group around the Cu–N(1′) vector is prohibited because of this Br(2)···pyrimidine contact at one side (Fig. 3) and a Br(2)···O(5γ) contact [3.19(1) Å] (a hydrogen bond, not shown in Figs.) at the other side; this may be a reason for the coplanarity of the $CuBr_2$ group with the pyrimidine plane in spite of an unfavorable steric constraint between Br(1) and the methyl substituent C(2′α), as noticed by Cramer *et al.* in the chloride derivative [5b].

Discussion

The conformation of thiamine is of importance for its catalytic functions [2]. Table 6 examines the structures of polyhalogenometal ion–thiamine compounds. Cramer *et al.* [4g] have pointed out that an anion bridge between the pyrimidine and the thiazolium moieties of the same molecule via an N(4′α)–H···Cl hydrogen bond and Cl···thiazolium

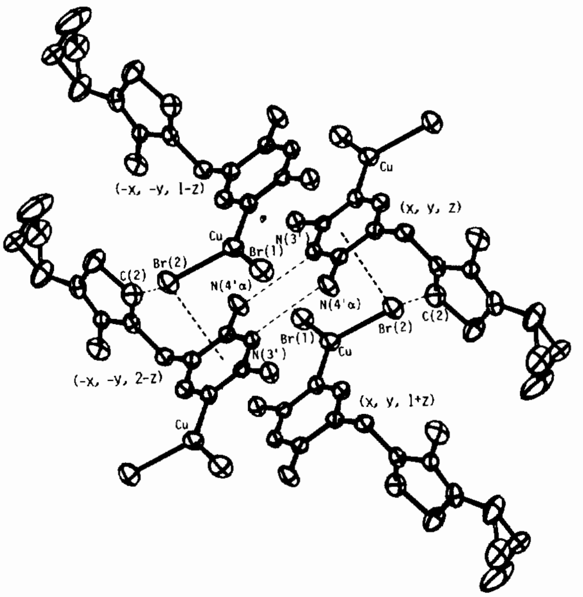

Fig. 3. A plot of four adjacent units of Cu(thiamine)Br$_2$, showing pyrimidine–pyrimidine stacking, a pair of interbase N(4'α)–H···N(3') hydrogen bonds, C(2)–H···Br(2) hydrogen bonds and Br(2)···pyrimidine close contacts.

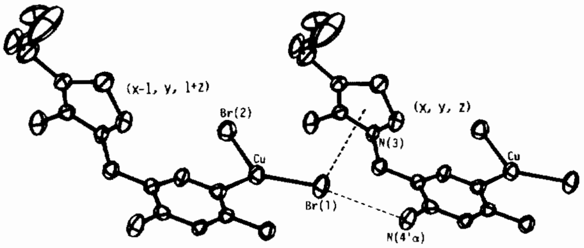

Fig. 4. A plot of two adjacent units of Cu(thiamine)Br$_2$, showing an N(4'α)–H···Br(1) hydrogen bond and a Br(1)··· thiazolium close contact.

electrostatic interaction is a factor that affects the conformation of thiamine for the polychlorometal ion salt or complex system, where the *F* conformation is favored by smaller metal anions with shorter Cl···Cl non-bonding distances (average 3.4(3) Å) while the *S* conformation by larger metal anions with longer ones (average 3.9(2) Å). The present complex, in which this anion bridge is formed again and thiamine assumes the *F* conformation, deviates from this rule, however, since the corresponding Br···Br distance is 3.995(2) Å. Rather, a common feature to thiamines with the *F* conformation is the 'one-point' halide bridge, that is, the same halide atom bridges between the pyrimidine and the thiazolium rings, while that to thiamines with the *S* conformation is the 'two-point' halide bridge, namely, a halide atom forms a hydrogen bond with N(4'α) and another halide of the same anion stacks on the thiazolium ring. This is rationalized from the distance between the pyrimidine and the thiazolium rings, since in the *F* thiamine it is too near for the 'two-point' bridge while in the *S* thiamine it is too far for the 'one-point' bridge. However, what is a factor(s) determining the 'one-point' or the 'two-point' bridge is still unclear. We suggest here an additional factor that affects the *F* but not the *S* conformation, that is, another anion bridge C(2)–H···X···pyrimidine (X = Br or Cl). It appears from Table 6 that both a C(2)–H···X hydrogen bond and an X···pyrimidine stacking are almost always formed in thiamines with the *F* conformation, one exception being (Hthiamine)$_2$(PtCl$_4$)Cl$_2$ [4g] which has a too distant Cl···pyrimidine contact, while they are not for thiamines with the *S* conformation. As Cramer *et al.* have suggested, such anion bridges by carboxylate anions of aspartic acid and/or glutamic acid residues in the apoenzyme may contribute to the recognition or the stabilization of a particular thiamine conformation suitable for catalytic reactions. When thiamine pyrophosphate coenzyme is stabilized by such a pair of separated carboxylate anions into the *S* conformation, the distance between the two anions is, as we can expect, *ca.* 4.0 Å.

TABLE 6. X···X Nonbonded, N(4'α)–H···X Hydrogen Bond, X···Thiazolium, C(2)–H···X Hydrogen Bond, and X···Pyrimidine Distances (Å) (X = Br or Cl) in the Polyhalogenometal Anion–Thiamine Compounds

Compound	Conformation	X···X[a]	N(4'α)···X···thiazolium[b,c]		C(2)···X···pyrimidine[b,c]		Reference
Cu(thiamine)Br$_2$	*F*	3.995(2)	3.39(1)	3.41	3.48(1)	3.609(4)	this work
Cu(thiamine)Cl$_2$	*F*	3.867	3.251(2)	3.29	3.400(2)	3.47	5b
Pt(thiamine)Cl$_3$	*F*	3.27	3.28(2)	3.30	3.43(2)	3.17	4g
(Hthiamine)PtCl$_4$	*F*	3.243(6)	3.18(2)	3.36	3.59(2)	3.26	4g
(Hthiamine)$_2$(PtCl$_4$)-Cl$_2$	*F*	3.262	3.173(5)	3.32	3.318(6)	5.39	4g
(Hthiamine)CuCl$_4$	*F*	3.42(2)	3.44(1)	3.39	3.64(1)	3.19	4b
			N(4'α)···X1–M–X2···thiazolium[b,c]				
(Hthiamine)CdCl$_4$	*S*	4.00(5)	3.306(3)	3.20			4c
Cd(thiamine)Cl$_3$	*S*	4.0(1)	3.395(2)	3.39			5a
Zn(thiamine)Cl$_3$	*S*	3.7(5)	3.473(4)	3.42			5d

[a] Values from ref. 4g. [b] Perpendicular distances to the ring plane. [c] van der Waals radii from ref. 9: Br = 1.85, Cl = 1.75 and aromatic ring = 1.77 Å.

This is, to our knowledge, the sixth thiamine–metal complex that involves metal bonding to the pyrimidine base of thiamine, N(1′) being the common binding site, in accordance with Schellenberger's suggestion [2] from enzyme studies. However, they are all anionic polyhalogenometal complexes, except a rhodium(II) complex [5c], among which Cd(thiamine)Cl_3 [5a] and Zn(thiamine)Cl_3 [5d] and Cu(thiamine)Cl_2 [5b] and Cu(thiamine)Br_2 are isostructural to each other, respectively, as expected from the similar chemical nature between Cd(II) and Zn(II) and between Cl^- and Br^-. Therefore, it will be useful to further examine the metal–N(1′) bonding for other metal ion systems, especially for a cationic $[Mg(H_2O)_6]^{2+}$, in the future.

Supplementary Material

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

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