A novel metal–thiamine complex with a cyclic dimer formed by metal-bridged two thiamine ligands. Crystal structure of $[Mn(thiamine)Cl_2(H_2O)]_2[thiamine]_2Cl_4 \cdot 2H_2O$

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Abstract

The crystal structure of $[Mn(thiamine)Cl_2(H_2O)]_2[thiamine]_2Cl_4 \cdot 2H_2O$ has been determined by X-ray diffraction methods. The compound contains a cyclic dimer of a complex cation with two thiamine ligands bridged by two Mn(II) ions across a crystallographic center of symmetry. Each Mn(II) is coordinated by two chloride atoms, a water molecule, a N(1') atom of the pyrimidine from a thiamine and an O(53) atom of the hydroxyethyl side chain from another thiamine. There are two free-base thiamine molecules related by a center of symmetry in the unit cell, which form a base-pair through the hydrogen bonds. Both the independent thiamine molecules in the asymmetric unit assume the common *F* conformation with $\phi_T = 10.0(9)$ and 3.6(10) and $\phi_P = 85.6(7)$ and 79.6(7), respectively. The compound provides a possible model for a metal-bridged enzyme–coenzyme complex in thiamine catalysis. Crystallographic data: triclinic, space group $P\bar{1}$, $a = 12.441(4)$, $b = 13.572(4)$, $c = 11.267(3)$ Å, $\alpha = 103.15(2)$, $\beta = 89.03(3)$, $\gamma = 115.64(2)°$, $Z = 1$, $D_{calc} = 1.524$ g cm^{-3}, and $R = 0.050$ for 3019 observed reflections with $I > 3\sigma(I)$.

Introduction

Thiamine (vitamin B_1), in the form of the pyrophosphate ester, is a coenzyme in several enzyme systems catalyzing the decarboxylation of α-keto acids and the transfer of aldehyde or acyl groups [1]. Divalent metal ions such as Mg(II) or Mn(II) are believed to act as a bridge involved in the formation of the enzyme–coenzyme complex [2, 3]. Much attention has been paid to metal–thiamine complexes in order to understand the interactions between the metal ion and thiamine. In 1981, Cramer *et al.* [4a] presented the first X-ray evidence of a metal–thiamine complex with the metal bonding to the thiamine base nitrogen N(1'), in accordance with Schellenberger's proposal from enzyme studies [3]. Ten crystal structures of metal complexes of thiamine or its derivatives have been reported so far [4–6], the majority of which show metal bonding to the pyrimidine N(1') site and a sole example to the pyrophosphate group [6].

In the reaction of thiamine with a metal acetate, the complexes of formula $M(thiamine)X_n$ formed, where M = Cd(II) [4a], Zn(II) [4d, g], Co(II) [4g] and Cu(I) [4b, f]; X = Cl or Br and $n = 3$ or 2. This prompted us to further investigate the reactions of thiamine with other metal acetates. Manganese was chosen because of the fact that it is one of the essential elements in living organisms and because of its high activity, next only to that of magnesium [2a] in the thiamine-dependent enzyme system. In this contribution we report the crystal structure of $[Mn(thiamine)Cl_2(H_2O)]_2[thiamine]_2Cl_4 \cdot 2H_2O$, which shows the Mn(II) ion bonding to two thiamine ligands at the pyrimidine N(1') and the hydroxyethyl O(53), respectively. This is the first example of a metal ion bridging two thiamine molecules.

Experimental

Preparation of the compound

$[Mn(thiamine)Cl_2(H_2O)]_2[thiamine]_2Cl_4 \cdot 2H_2O$ was prepared by reacting (thiamine)Cl·HCl and $Mn(CH_3CO_2)_2 \cdot 4H_2O$ in a 2:1 molar ratio in an aqueous solution at room temperature. The plate-like crystals of the compound were produced by allowing vapor diffusion of acetone into the resulting solution. Crystals formed after about two weeks. *Anal.* Calc. for $C_{48}H_{76}N_{16}Mn_2Cl_8O_8S_4$: C, 37.76; H, 5.02; N, 14.68. Found: C, 37.26; H, 5.02; N, 14.46%.

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X-ray structure determination

A Nicolet R3m/E four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) was used for structure determination. Cell parameters were refined by a least-squares program using 22 centred reflections in the range of $23 < 2\theta < 30°$. The intensity checks of two standard reflections showed no significant variation. Intensity data were corrected for Lp factors and for empirical absorption. Details of crystal data, data collection and structure refinement are summarized in Table 1.

The structure was solved by the direct methods program [7] and difference Fourier syntheses followed by refinement using a block-diagonal least-squares method which minimized the function $\Sigma w(F_o - |F_c|)^2$. The space group $P\bar{1}$ was confirmed by the solution and satisfactory refinement of the structure. The non-hydrogen atoms were assigned anisotropic thermal parameters. All hydrogen atoms, except for those of the methyl groups, were located on a difference Fourier map with the references to their stereochemistry and hydrogen-bonding interactions. U was fixed in the final cycles to a value of 0.06 Å^2. Hydrogen atoms of the methyl groups were added at idealized positions. The final R value was 0.050 and R_w 0.070 for 3019 observed reflections. The final atomic coordinates are given in Table 2.

Neutral atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography [8]. All

TABLE 1. Summary of crystal data and structure determination

Formula	$C_{48}H_{76}N_{16}Mn_2Cl_8O_8S_4$
Molecular weight	1526.97
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	12.441(4)
b (Å)	13.572(4)
c (Å)	11.267(3)
α (°)	103.15(2)
β (°)	89.03(3)
γ (°)	115.64(2)
V (Å^3)	1662.8(8)
Z	1
D_{calc} (g cm^{-3})	1.524
$F(000)$	790
μ(Mo Kα) (cm^{-1})	8.68
Crystal size (mm)	0.12 × 0.27 × 0.47
Transmission factors	0.748–0.815
Scan mode	ω
2θ Range (°)	0–48
Scan speed (°/min)	4.88
Scan width (°)	1.5
Unique data measured	5150
Unique data used (m) ($I > 3\sigma(I)$)	3019
Variables (n)	388
Weighting scheme (w)	$1/[\sigma^2(F_o) + 0.0018(F_o)^2]$
R^a	0.050
$R_w{}^b$	0.070
S^c	1.24
$(\Delta/\sigma)_{max}$	0.01
$(\Delta\rho)_{max}$ (e Å^{-3})	0.61

[a] $R = \Sigma||F_o| - |F_c||/\Sigma F_o$. [b] $R_w = [\Sigma w(F_o - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$. [c] $S = [\Sigma w(F_o - |F_c|)^2/(m - n)]^{1/2}$.

TABLE 2. Final atomic coordinates (×10^5 for Mn and ×10^4 for others) for $[Mn(thiamine)Cl_2(H_2O)]_2[thiamine]_2Cl_4 \cdot 2H_2O$

Atom	x	y	z
Mn	35591(8)	16820(8)	7472(8)
Cl(1)	2410(2)	2706(2)	1298(2)
Cl(2)	3998(2)	1923(1)	−1296(1)
Cl(3)	6612(2)	3774(2)	4154(2)
Cl(4)	8312(2)	1761(2)	8271(2)
O(w1)	2449(4)	−70(3)	93(3)
O(w2)	11873(5)	3614(5)	4309(5)
S(1A)	5172(2)	4992(1)	7155(2)
C(2A)	4502(5)	3760(5)	6132(5)
N(3A)	3446(4)	3108(4)	6415(4)
C(4A)	3113(5)	3594(5)	7495(5)
C(5A)	3970(5)	4622(5)	8031(5)
C(41A)	1935(6)	2967(6)	7955(6)
C(51A)	3967(6)	5405(5)	9212(5)
C(52A)	3663(5)	6322(5)	9074(6)
O(53A)	4573(4)	7080(3)	8509(4)
C(35′A)	2658(5)	1952(5)	5667(5)
N(1′A)	3681(4)	1268(4)	2549(4)
C(2′A)	4322(5)	747(5)	2798(5)
N(3′A)	4467(4)	570(4)	3889(4)
C(4′A)	4000(5)	994(4)	4842(4)
C(5′A)	3294(5)	1531(4)	4669(5)
C(6′A)	3159(5)	1635(4)	3509(5)
C(21′A)	4895(6)	310(6)	1772(5)
N(41′A)	4208(4)	823(4)	5917(4)
S(1B)	10474(2)	4969(2)	6972(2)
C(2B)	9788(5)	3761(5)	5911(6)
N(3B)	8642(4)	3213(4)	6060(4)
C(4B)	8252(5)	3773(5)	7022(5)
C(5B)	9150(6)	4761(5)	7620(6)
C(41B)	6982(5)	3281(6)	7280(6)
C(51B)	9088(6)	5589(6)	8734(7)
C(52B)	10002(8)	6707(8)	8954(9)
O(53B)	11156(5)	6718(7)	9156(7)
C(35′B)	7817(5)	2085(5)	5287(6)
N(1′B)	8702(5)	986(4)	2247(4)
C(2′B)	9337(5)	520(5)	2613(5)
N(3′B)	9547(4)	511(4)	3763(4)
C(4′B)	9075(5)	1027(5)	4638(5)
C(5′B)	8419(5)	1567(5)	4345(5)
C(6′B)	8254(5)	1527(5)	3135(5)
C(21′B)	9870(6)	−39(5)	1643(5)
N(41′B)	9287(5)	984(5)	5788(5)

calculations were performed using the SHELXTL program system [7].

Results

The crystal structure consists of the discrete complex cation $[Mn(thiamine)Cl_2(H_2O)]_2^{2+}$, a $[thiamine]_2^{2+}$ unit, four chloride anions and two water molecules in the unit cell. The asymmetric unit contains two independent thiamine molecules, A and B. The structures of the $[Mn(thiamine)Cl_2(H_2O)]_2^{2+}$ unit containing A and the $[thiamine]_2^{2+}$ unit composed of B are shown in Figs. 1 and 2, respectively, and the crystal packing diagram is shown in Fig. 3. Bond lengths and angles are listed in Table 3.

The Mn(II) ion is five-coordinated in a distorted square-pyramidal geometry with the basal plane defined by the chloride Cl(2), the water O(w1), the pyrimidine N(1′) of the thiamine A and the hydroxyethyl O(53) of its centrosymmetric partner; the axial position is occupied by the chloride Cl(1). Thus the two Mn(II) ions bridge the two thiamine molecules in a head-to-tail fashion across a center of symmetry to produce a cyclic dimer. The Mn(II) ion is displaced 0.542 Å from the basal plane, which is planar only within 0.150 Å, toward the axial Cl(1). The Mn–Cl and Mn–N bond lengths are somewhat

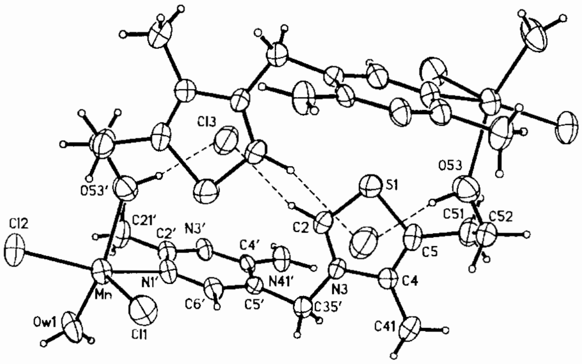

Fig. 1. Structure of the $[Mn(thiamine)Cl_2(H_2O)]_2^{2+}$ cation, which resides on a center of symmetry. The numbering of the thiamine molecule corresponds to that labelled A in the text. Broken lines denote hydrogen bonds.

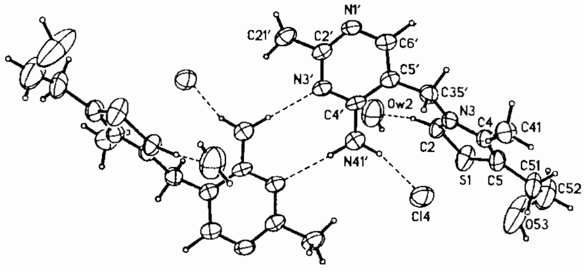

Fig. 2. Structure of the $[thiamine]_2^{2+}$ cation. Two thiamine molecules are related by a center of symmetry. The numbering of the thiamine molecule corresponds to that labelled B. Broken lines denote hydrogen bonds.

TABLE 3. Bond lengths (Å) and angles (°) for $[Mn(thiamine)Cl_2(H_2O)]_2[thiamine]_2Cl_4 \cdot 2H_2O$[a]

Coordination sphere			
Mn–N(1′A)	2.250(5)	Mn–Cl(2)	2.419(2)
Mn–O(53A^i)	2.229(4)	Mn–O(w1)	2.121(4)
Mn–Cl(1)	2.379(3)		
N(1′A)–Mn–O(53A^i)	78.8(2)	O(53A^i)–Mn–Cl(1)	104.4(1)
N(1′A)–Mn–O(w1)	85.2(2)	O(53A^i)–Mn–Cl(2)	91.1(1)
N(1′A)–Mn–Cl(1)	98.5(2)	O(w1)–Mn–Cl(1)	111.6(2)
N(1′A)–Mn–Cl(2)	159.4(2)	O(w1)–Mn–Cl(2)	92.5(1)
O(53A^i)–Mn–O(w1)	142.3(2)	Cl(1)–Mn–Cl(2)	101.4(1)

Thiamine molecules	A	B
N(1′)–C(2′)	1.342(10)	1.325(10)
C(2′)–N(3′)	1.334(8)	1.330(8)
N(3′)–C(4′)	1.345(7)	1.352(8)
C(4′)–C(5′)	1.402(10)	1.397(11)
C(5′)–C(6′)	1.367(8)	1.367(9)
C(6′)–N(1′)	1.360(8)	1.361(9)
C(2′)–C(21′)	1.491(9)	1.498(10)
C(4′)–N(41′)	1.333(8)	1.346(8)
C(5′)–C(35′)	1.511(9)	1.507(9)
C(35′)–N(3)	1.493(6)	1.490(6)
S(1)–C(2)	1.664(5)	1.666(5)
C(2)–N(3)	1.311(7)	1.322(7)
N(3)–C(4)	1.394(7)	1.382(8)
C(4)–C(5)	1.341(7)	1.348(7)
C(5)–S(1)	1.729(6)	1.725(7)
C(4)–C(41)	1.495(8)	1.479(9)
C(5)–C(51)	1.503(8)	1.508(10)
C(51)–C(52)	1.488(12)	1.415(10)
C(52)–O(53)	1.418(7)	1.451(14)
N(1′)–C(2′)–N(3′)	125.0(6)	125.8(6)
C(2′)–N(3′)–C(4′)	118.6(6)	117.2(6)
N(3′)–C(4′)–C(5′)	120.5(5)	121.2(5)
C(4′)–C(5′)–C(6′)	116.5(5)	117.0(6)
C(5′)–C(6′)–N(1′)	123.8(7)	122.1(7)
C(6′)–N(1′)–C(2′)	115.4(5)	116.7(5)
N(1′)–C(2′)–C(21′)	117.6(6)	116.9(6)
N(3′)–C(2′)–C(21′)	117.4(7)	117.3(7)
N(3′)–C(4′)–N(41′)	116.0(6)	115.6(7)
C(5′)–C(4′)–N(41′)	123.5(5)	123.2(6)
C(4′)–C(5′)–C(35′)	123.9(5)	122.4(6)
C(6′)–C(5′)–C(35′)	119.6(6)	120.4(7)
C(5′)–C(35′)–N(3)	112.4(4)	114.1(5)
C(35′)–N(3)–C(2)	124.1(5)	124.3(5)
C(35′)–N(3)–C(4)	122.2(4)	121.5(5)
S(1)–C(2)–N(3)	112.8(4)	112.3(5)
C(2)–N(3)–C(4)	113.7(4)	114.2(4)
N(3)–C(4)–C(5)	111.9(5)	111.7(5)
C(4)–C(5)–S(1)	110.4(4)	110.6(5)
C(5)–S(1)–C(2)	91.1(3)	91.2(3)
N(3)–C(4)–C(41)	120.8(4)	120.4(5)
C(5)–C(4)–C(41)	127.2(5)	127.8(6)
S(1)–C(5)–C(51)	121.3(4)	121.9(4)
C(4)–C(5)–C(51)	128.3(5)	127.4(6)
C(5)–C(51)–C(52)	115.0(6)	116.5(7)
C(51)–C(52)–O(53)	110.1(6)	109.7(10)

[a] Symmetry operations: (none) x, y, z; (i) $1-x, 1-y, 1-z$.

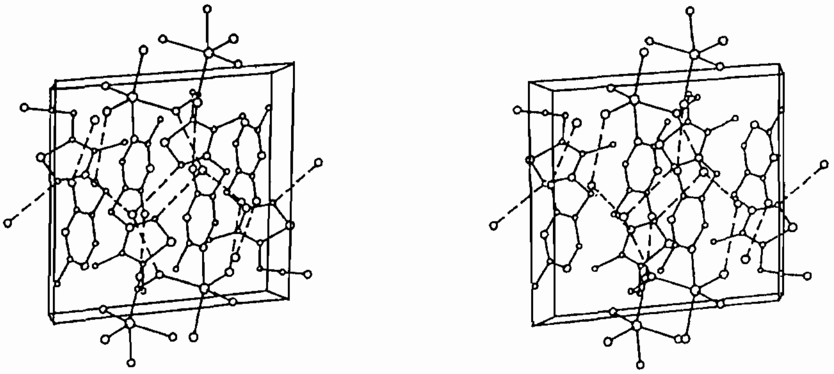

Fig. 3. Stereoview of the crystal packing along the *b* axis with the *a* axis horizontal and the *c* axis vertical. Broken lines denote hydrogen bonds.

shorter than those found in an octahedral N_4Cl_2 coordination sphere of Mn(II) ion [9].

There is a free-base thiamine B in the asymmetric unit. Both thiamines A and B assume the common *F* conformation in terms of the torsion angles defined by Pletcher and Sax [10]: ϕ_T = C(5′)–C(35′)–N(3)–C(2) and ϕ_P = N(3)–C(35′)–C(5′)–C(4′) are 10.0(9) and 85.6(7)° for A and 3.6(10) and 79.6(7)° for B, respectively. The dihedral angles between the pyrimidine and thiazolium rings are 91.3° for A and 103.6° for B. The hydroxyethyl side chain folds back toward the thiazolium moiety to make a short contact of 2.843(8) Å between O(53) and S(1) for B, but a rather long distance of 3.277(5) Å for A presumably due to the O(53A) ligation. The torsion angles defining the conformation of the hydroxyethyl side chain [11] are $\phi_{5\alpha}$ = 79.8(7)° for A and 23(1)° for B and $\phi_{5\beta}$ = −66.7(6)° for A and −62(1)° for B. The bond lengths and angles for the two thiamine molecules are similar to each other, and as expected for the N(1′)-metalated or free-base form of thiamine [4], except for some bond lengths involving the hydroxyethyl chain of thiamine B, where the high thermal parameters render the lengths somewhat uncertain. The present structure agrees with the conclusion [4a] that metal ion coordination at N(1′) has less effect on the C(2′)–N(1′)–C(6′) bond angle and opposite C(4′)–N(41′) bond length than does protonation, which makes the angle increase and the length decrease. The bond angles C(2)–N(3)–C(35′) and C(4)–N(3)–C(35′) fall on the values for the *F*-form, that is, the former is larger (1–4°) than the latter [4g], in contrast to what is observed in the *S*-form because of the more exposed C(2) position of the *S*-form.

Hydrogen-bonding and electrostatic interactions are the major packing forces (Table 4). The thiamines A and B are nearly parallel to each other in the cell and thus there are some common packing features for them. The amino N(41′) donates a hydrogen atom to N(3′) of the symmetrically related molecule to form a base-pair, and another to Cl(2) (at *x*, *y*, 1+*z*) for A or Cl(4) for B. This chloride atom further participates in an electrostatic interaction with the thiazolium ring of the same molecule with the distances of 3.357 Å for A and 3.224 Å for B between the Cl anion and electropositive thiazolium ring. The acidic C(2)-hydrogen [12] takes part in the hydrogen-bonding interaction with Cl(3) for A or water molecule O(w2) for B, which is located over the pyrimidine ring of the same thiamine with the rather long stacking distances being 3.683 Å for A and 3.729 Å for B, mostly because of the hydrogen-bonding interaction between O(w2) and Cl(3) in the opposite direction (Fig. 3). The O(w2) (at *x*−1, *y*, *z*) is hydrogen-bonded to Cl(1) at one end of the complex cation and to Cl(3) (at 1−*x*, 1−*y*, 1−*z*), which is in turn linked to O(53A) at the other end of the cation to further stabilize the cyclic complex. In addition, the N(1′) atom of thiamine B interacts indirectly with Mn(II) through an O(w1)H...N(1′) hydrogen bond.

Discussion

The understanding of the factors which determine the conformation of thiamine is important for the clarification of enzymic processes. Cramer *et al.* [4e] have noticed that the polychlorometal anion can act as a bridge between the pyrimidine and thiazolium rings via a N(41′)H...Cl hydrogen bond and a Cl...thiazolium electrostatic interaction to affect the conformation of thiamine. This results in the *F*-form being favored by smaller anions and the *S*-form by larger ones. Aoki and co-workers [4f, g] have further pointed out that 'one-point' and 'two-point' halide bridges are the features of the *F*- and *S*-form, respectively. The 'one-point' bridge means a

TABLE 4. Hydrogen bonds and other short contacts[a]

Hydrogen bonds

Donor	Acceptor	D...A (Å)	H...A (Å)	D–H...A (°)
C(2A)	Cl(3)	3.410(6)	2.48	161
O(53A)	Cl(3^{i})	3.100(4)	2.16	169
N(41′A)	N(3′A^{ii})	3.040(9)	2.06	177
N(41′A)	Cl(2^{iii})	3.214(5)	2.30	154
C(2B)	O(w2)	3.186(9)	2.32	148
O(53B)	Cl(4^{iv})	3.044(8)	2.13	153
N(41′B)	N(3′B^{v})	3.085(10)	2.12	170
N(41′B)	Cl(4)	3.171(6)	2.22	164
O(w1)	Cl(4^{ii})	3.090(5)	2.11	179
O(w1)	N(1′B^{vi})	2.764(6)	1.90	173
O(w2)	Cl(3^{vii})	3.264(5)	2.47	155
O(w2)	Cl(1^{viii})	3.494(6)	2.53	166

Other short contacts

A	B	A...B (Å)	A	B	A...B (Å)
S(1A)	O(53A)	3.277(5)	N(1′A)	Cl(4^{ii})	3.665(6)
S(1B)	O(53B)	2.843(8)	C(2′A)	Cl(4^{ii})	3.520(5)
S(1A)	Cl(1^{i})	3.378(2)	N(3B)	Cl(4)	3.429(6)
C(51B)	Cl(1^{i})	3.548(10)	C(4B)	Cl(4)	3.372(8)
C(52B)	Cl(1^{i})	3.452(12)	C(41B)	Cl(4)	3.508(10)
N(3A)	Cl(2^{iii})	3.553(7)	C(35′B)	Cl(4)	3.585(7)
C(4A)	Cl(2^{iii})	3.440(8)	C(52B)	Cl(4^{iv})	3.462(9)
C(41A)	Cl(2^{iii})	3.617(8)	C(5′B)	N(41′A^{ii})	3.423(7)
C(35′B)	Cl(3)	3.675(7)	C(52B)	N(1′B^{vii})	3.423(10)
S(1B)	Cl(3^{vii})	3.625(3)	O(53B)	C(52A^{viii})	3.382(8)

[a] Symmetry operations: (none) x, y, z; (i) $1-x, 1-y, 1-z$; (ii) $1-x, -y, 1-z$; (iii) $x, y, 1+z$; (iv) $2-x, 1-y, 2-z$; (v) $2-x, -y, 1-z$; (vi) $1-x, -y, -z$; (vii) $2-x, 1-y, 1-z$; (viii) $1+x, y, z$.

N(41′)H...X...thiazolium interaction whereas a 'two-point' bridge is a N(41′)H...X–M–X... thiazolium interaction (X = halide ion, M = metal). The present structure also holds for this rule. The coordinated Cl(2) and the free Cl(4) provide such 'one-point' bridges for the thiamines A and B. An additional characteristic for the *F*-form, but not for the *S*-form, suggested by Aoki and co-workers [4f] also exists in this structure, that is, the anion bridge C(2)H...X...pyrimidine, where X = Cl(3) for A and O(w2) for B, as mentioned above. This water bridge, albeit weak, seems to be first observed in thiamine structures. The structural parameters of several polyhalogenometal ion–thiamine compounds are summarized in Table 5. A careful inspection of these structures shows that the conformation is related not only to the size of metal anion measured by the X...X distance but also to the manner in which the anion approaches the thiazolium ring. When a tetrahedral metal anion approaches the thiazolium ring with a trigonal plane, the thiamine would orient the pyrimidine and thiazolium rings in the *S*-form to avoid the steric hindrance caused by such a manner and the 'two-point' bridge forms. In contrast, the less steric effect could result in the 'one-point' bridge and the *F*-form if the anion attacks the thiazolium ring with an edge (line) or a vertex (point) of the coordination polyhedron. It seems to be the case with the larger metal anion (e.g. X...X > 3.7 Å) from Table 5. For smaller anions, however, the approaching manner is not decisive, and so the *F*-form is preferred. Obviously the approaching manner can be restricted by the intermolecular interactions, especially for the metal anions with the bulky thiamine ligand. The *F*-form adopted in the present complex is thereby rationalized from the approach of the Cl(1)–Cl(2) edge of the coordination polyhedron (Fig. 3), though the anion size is large.

The interesting structural feature of the complex is the formation of the metal–ion bridge between two thiamines through Mn–N(1′) and Mn–O(53) bonds. The metal–N(1′) interaction was considered to be due mainly to the high basicity of this site [4c]. The O(53) coordination to Mn(II) is reasonable from the 'hard base' and 'hard acid' characters for the hydroxyethyl oxygen and the Mn(II) ion. This result provides evidence that the divalent metal ion can be simultaneously involved in bonding to the

TABLE 5. Comparison of the structural parameters affecting the conformation of thiamine in the polyhalogenometal anion–thiamine compounds

Compound	Conformation of thiamine	Anion geometry	X...X[a]	Approaching manner	Dihedral angle[b]	Reference
(Hthiamine)$CdCl_4$	*S*	tetrahedral	4.00(5)	plane	17.4	13a
Cd(thiamine)Cl_3	*S*	tetrahedral	4.0(1)	plane	9.9	4a
Cu(thiamine)Br_2	*F*	trigonal planar	3.995(2)	line	84.7	4f
Zn(thiamine)Br_3	*S*	tetrahedral	3.90(4)	plane	8.9	4g
Cu(thiamine)Cl_2	*F*	trigonal planar	3.867	line	84.7	4b
$[Mn(thiamine)Cl_2(H_2O)]_2^{2+}$	*F*	square pyramidal	3.714(3)	line	85.5	this work
Co(thiamine)Cl_3	*S*	tetrahedral	3.71(6)	plane	7.8	4g
Zn(thiamine)Cl_3	*S*	tetrahedral	3.7(5)	plane	9.0	4d
(Hthiamine)$CuCl_4$	*F*	tetrahedral	3.42(4)	plane	9.0	13b
Pt(thiamine)Cl_3	*F*	square planar	3.27	point		4e
(Hthiamine)$PtCl_4$	*F*	square planar	3.243(6)	plane	3.6	4e

[a] X = Cl or Br. Data from ref. 4e and g. [b] Angle between the approaching plane and thiazolium ring or angle between the approaching line and the normal of thiazolium plane.

base N(1′) and an electronegative atom, consistent with Schellenberger's model [3] in which the bonding between the pyrimidine N(1′) and the apoenzyme takes place through the intermediary of a metal ion. Moreover, the present complex exhibits a formally neutral $[MnCl_2(H_2O)]$ unit bonding to two cationic thiamine moieties, while the metal–thiamine complexes reported so far all have anionic polyhalogenometal units [4] except a rhodium(II) complex [4c], in which a neutral $[Rh_2(acetato)_4]$ is bonded to two neutral thiamine monophosphate zwitterions. In this regard, it would be of special interest to examine the possibility of thiamine coordination to cationic metal ion units such as $[Mg(H_2O)_6]^{2+}$ [4c].

Supplementary material

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

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