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THE $CdCl_2$/THIAMINE (VITAMIN B_1) SYSTEM: CRYSTAL STRUCTURE AND SPECTROSCOPIC PROPERTIES OF THE NEW COMPLEX *trans*-[Cd(THIAMINE)$_2$Cl$_4$]

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Abstract—The structure of the title compound was determined by X-ray diffraction. The cadmium atom is coordinated to the four chlorine ligands and to two N(1′)-bound thiamines in S conformation that occupy *trans* positions in a distorted octahedral kernel. The structural details and the solid state (CP/MAS ^{13}C and ^{113}Cd) and solution (^{13}C, ^{15}N and ^{113}Cd) NMR spectroscopic properties of the complex are compared with those of previously isolated cadmium(II)/thiamine compounds.

Cadmium has played an important role in the understanding of the coordination chemistry of vitamin B_1 (thiamine, T^+). The compound [$CdTCl_3$]·$0.6H_2O$ was the first 'true' thiamine complex (that is, a compound containing thiamine–metal bonds) to be studied by X-ray diffraction.[1] This study showed a trichlorocadmate(II) anion bound to the thiamine cation *via* its N(1′) pyrimidine atom. Later, an X-ray diffraction study of the complex [$CdT(SCN)_3$] showed that in this case the metal is bound to the vitamin through the O(5γ) atom belonging to the hydroxyethyl side chain of the thiazolium ring.[2] More recently,[3] we prepared [$CdTCl_3$]$_2$·$2H_2O$, in which two N(1′),O(5γ)-bonded thiamines bridge between two cadmium atoms in a centrosymmetric dimer. During this work with $CdCl_2$/thiamine in water, we also isolated a solid with a formula showing it to be either a new complex [CdT_2Cl_4] or the salt $(T)_2$[$CdCl_4$]. In this paper we report X-ray diffraction data showing that this compound is a true complex with two thiamines bound to the cadmium atom *via* the N(1′) pyrimidine atoms. This is, as far as we know, the first 1:2 metal:thiamine complex ratio studied by X-ray diffraction.

EXPERIMENTAL

Crystals of [CdT_2Cl_4] were obtained as described elsewhere.[3] Intensity data for a colourless prismatic crystal with dimensions $0.15 \times 0.25 \times 0.25$ mm were obtained at room temperature (293 K) on an Enraf-Nonius CAD4 diffractometer using graphite monochromatized Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å). The $\omega/2\theta$ scan technique was employed to measure the intensities of 4718 reflections up to a maximum Bragg angle of 30°. Cell parameters were refined by a least-squares procedure from the setting angles of 25 reflections ($6.4 \leqslant \theta \leqslant 16.8°$).[4a] No decomposition of the crystal occurred during data collection. Corrections were applied for Lorenz and polarization effects, and for absorption ($\mu = 1.04$ mm^{-1}).[4b] A total of 3355 unique reflections with $I \geqslant 3\sigma(I)$ were used in further calculations. The structure was solved by direct methods[4c] and refined by a full-matrix least-squares procedure based on F.[4a] Non-hydrogen atoms were refined with anisotropic displacement parameters. Seventeen hydrogen atoms were located by difference Fourier synthesis and refined with B_{iso} fixed at 4.0 Å^2, the remainder were placed in calculated positions (C—H = 0.95 Å) and added to the structure factor calculations with fixed isotropic B values ($B_{iso} = 4.0$ Å^2), but their positions were not refined. With the weighting scheme $\omega = 1/\sigma^2(F)$, the refinement pro-

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ceeded smoothly to convergence with a maximum Δ/σ of 0.57 for $R = 0.035$, $R_w = 0.037$ and goodness-of-fit (GOF) = 0.961 (368 variables). The secondary extinction coefficient refined to $g = 3.155 \times 10^{-7}\{F_c = F_c/[1+g(F_c)^2Lp]\}$. Analysis of the variance showed no special features, and the maximum and minimum residual electron density peaks in the final difference map were +0.54 and −0.50 e Å^{-3}, respectively. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from a standard source.[4d] Crystal data are listed in Table 1.

NMR experiments were performed as described elsewhere.[3]

RESULTS AND DISCUSSION

Crystal structure

Bond lengths and angles around the cadmium atom are listed in Table 2 together with other relevant structural data. The structure of the complex is shown in Fig. 1.

Crystals of [CdT$_2$Cl$_4$] consist of discrete units whose packing is governed by intermolecular hydrogen bonds (Fig. 2). The donor atoms surrounding the cadmium atom are located at the vertices of a distorted octahedron, with the two thiamines in *trans* position (Fig. 1).

The Cd—Cl and Cd—N distances in the three cadmium(II)–thiamine complexes so far isolated and in the cadmium(II)–thiaminium salt (HT)[CdCl$_4$]·H$_2$O[5] are compared in Table 3. As might be expected, the Cd—Cl distance increases as the coordination number of the metal increases; in [CdT$_2$Cl$_4$] it lies in the range observed for other hexacoordinate chlorocadmium complexes.[6] The Cd—N bond, however, is longer in [CdTCl$_3$]$_2$·2H$_2$O than in [CdT$_2$Cl$_4$], probably due to the thiamine being bidentate in the former complex.

Table 1. Crystal data of [CdT$_2$Cl$_4$]

Molecular formula	$C_{24}H_{34}CdCl_4N_8O_2S_2$
Formula mass	784.95
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.555 (1)
b (Å)	10.622 (1)
c (Å)	8.910 (2)
α (°)	98.16 (1)
β (°)	112.17 (1)
δ (°)	66.55 (1)
V (Å^3)	768.2 (2)
Z	1
D_x (g cm^{-1})	1.697
F(000)	398

The four chloride ligands adopt a planar arrangement ($\chi^2 = 60$) with the cadmium atom 0.06 Å above this plane. The best pyrimidine ring planes approximately bisect Cl—Cd—Cl angles but form dihedral angles of *ca* 78 (thiamine 1) and 76° (thiamine 2) with the equatorial plane, so that thiamine 2 is tilted towards Cl(1) and Cl(2) and thiamine 1 towards Cl(3) and Cl(4).

Other structural characteristics of T$^+$ are listed in Table 2. The values of Φ_T and Φ_P indicate that thiamine is in the less common S conformation,[7] but the non-bonding Cl···Cl distances [average 3.7(4) Å] are shorter than those observed in other thiamine compounds with S conformation (see ref. 3 and refs therein). Unlike most well-characterized thiamine derivatives, [CdT$_2$Cl$_4$] has clearly non-planar pyrimidine (P) and thiazolium (T) rings (χ^2 = 180 and 97 for P and T, respectively, in thiamine 1, and 622 and 560 in thiamine 2). Though the hydroxyl hydrogen atom was not located, the O—Cl distances [O(15γ)—Cl(2) = 3.19(1) Å, O(25γ)—Cl(3) = 3.13(1) Å] suggest the presence of two intramolecular hydrogen bonds. The values of the torsion angles $\Phi_{5\alpha}$ and $\Phi_{5\beta}$ (Table 2) prevent any significant intramolecular electrostatic link between the electronegative O(5γ) and the electron-deficient S atom.[8] In fact, the O—S distances are close to or above the sum of the van der Waals radii.[9]

Packing along the *a* axis is largely governed by intermolecular hydrogen bonds between thiamine-NH$_2$ groups and *cis* pairs of chloride ligands belonging to neighbouring [CdT$_2$Cl$_4$] units (Fig. 2). The thiazolium sulphur atoms have no close contacts, the closest atoms [Cl(2) for S(1) and Cl(3) for S(2)] lying at distances greater than the sum of the van der Waals radii.[9]

NMR study

Table 4 lists the chief solid state (^{13}C CP/MAS) and solution (^{13}C, ^{15}N and ^{113}Cd) NMR data. There are no significant differences between the ^{13}C CP/MAS NMR data for [CdT$_2$Cl$_4$] and [CdTCl$_3$]$_2$·2H$_2$O[3] even though thiamine has different conformations in the two complexes (S and F, respectively). The ^{13}C NMR spectra in D$_2$O solution are also very similar. The only noteworthy difference between the ^{15}N NMR spectra of the two compounds is that the N(1′) signal lies at slightly lower frequencies in the 1 : 2 complex, probably because in this compound the inductive influence of the metal is drawn on by two pyrimidine rings, resulting in less deshielding of each nitrogen.

The ^{113}Cd isotropic chemical shift of [CdT$_2$Cl$_4$]

Table 2. Structural parameters of $[CdT_2Cl_4]$

Bond distances (Å)

Cd—Cl(1)	2.561 (2)	Cd—Cl(4)	2.590 (2)
Cd—Cl(2)	2.713 (1)	Cd—N(11′)	2.475 (6)
Cd—Cl(3)	2.719 (1)	Cd—N(21′)	2.418 (6)

Bond angles (°)

Cl(1)—Cd—Cl(2)	88.82 (5)	Cl(2)—Cd—N(21′)	95.2 (2)
Cl(1)—Cd—Cl(3)	91.54 (5)	Cl(3)—Cd—Cl(4)	88.67 (6)
Cl(1)—Cd—Cl(4)	179.41 (7)	Cl(3)—Cd—N(11′)	94.9 (1)
Cl(1)—Cd—N(11′)	93.7 (1)	Cl(3)—Cd—N(21′)	84.7 (2)
Cl(1)—Cd—N(21′)	88.1 (1)	Cl(4)—Cd—N(11′)	85.8 (1)
Cl(2)—Cd—Cl(3)	179.63 (6)	Cl(4)—Cd—N(21′)	92.4 (1)
Cl(2)—Cd—Cl(4)	90.97 (5)	N(11′)—Cd—N(21′)	178.2 (2)
Cl(2)—Cd—N(11′)	85.2 (1)		

Torsion angles

Thiamine 1 $\Phi_T = -92.3$, $\Phi_P = 171.1$, $\Phi_{5\alpha} = 93.5$, $\Phi_{5\beta} = -71.8$

Thiamine 2 $\Phi_T = 93.4$, $\Phi_P = 179.1$, $\Phi_{5\alpha} = -76.0$, $\Phi_{5\beta} = 54.1$

Intermolecular hydrogen bonding

A—H···B	A—H (Å)	H···B (Å)	A···B (Å)	A—H—B (°)
N(14′α)—H(14′α1)—Cl(1^i)^a	0.88 (8)	2.44 (9)	3.268 (5)	157
N(14′α)—H(14′α2)—Cl(2^i)^a		2.55 (14)	3.196 (8)	139
N(24′α)—H(24′α1)—Cl(4^{ii})^a	0.87 (8)	2.49 (9)	3.286 (5)	151
N(24′α)—H(24′α2)—Cl(3^{ii})^a		2.46 (13)	3.276 (8)	140

[a] Symmetry codes: i = $x+1, y, z$; ii = $x-1, y, z$.

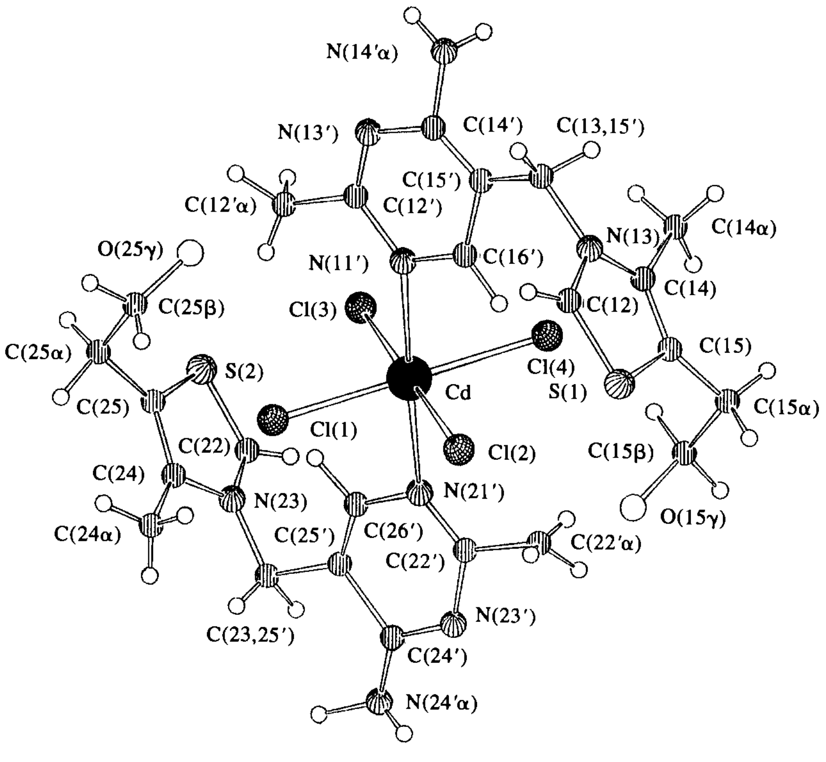

Fig. 1. SCHAKAL[13] view of $[CdT_2Cl_4]$, with atomic numbering scheme.

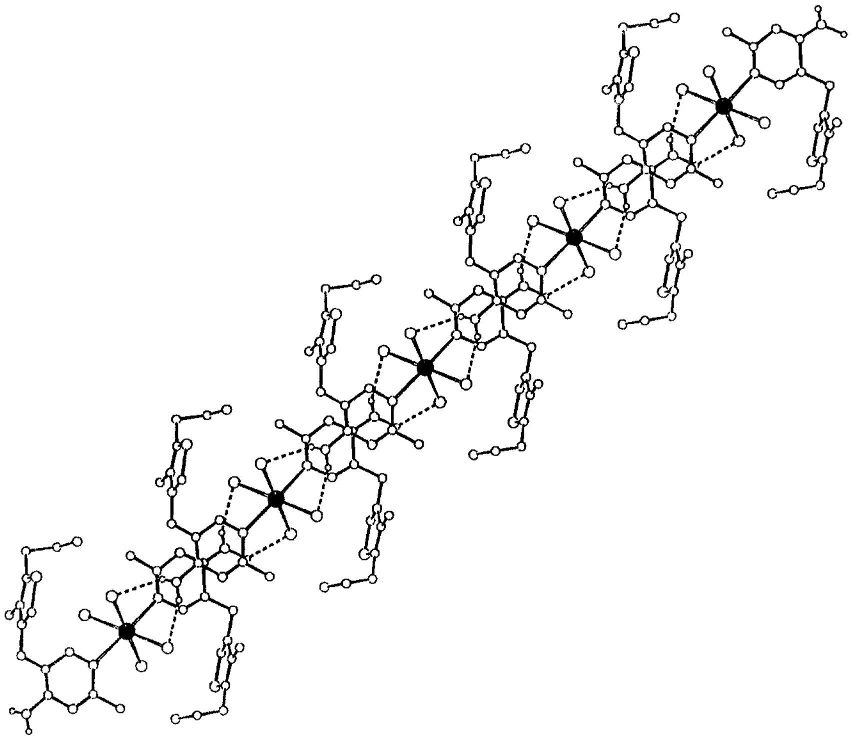

Fig. 2. Partial view of the crystal packing, showing the intermolecular hydrogen bonds along the *a* axis.

Table 3. Cd—Cl and Cd—N distances in the cadmium(II)/thiamine compounds

	CdCl	CN[a]	Cd—N(1′)	Ref.
(HT)[CdCl$_4$]·H$_2$O	2.465 (1) 2.453 (1) 2.432 (1) 2.461 (1) 2.453 (av.)	4	—	5
[CdTCl$_3$]·0.6H$_2$O	2.441 (1) 2.451 (1) 2.457 (1) 2.451 (av.)	4	2.239 (2)	1
[CdTCl$_3$]$_2$·2H$_2$O	2.435 (2) 2.567 (2) 2.421 (2) 2.474 (av.)	5	2.264 (5)	3
[CdT$_2$Cl$_4$]	2.561 (2) 2.713 (1) 2.719 (1) 2.590 (1) 2.646 (av.)	6	2.475 (6) 2.418 (6) 2.447 (av.)	This work

[a] CN = coordination number.

in the solid state is considerably smaller than those of (Et$_4$N)$_2$[CdCl$_4$] (483 ppm[10]) or (HT)[CdCl$_4$]·H$_2$O (451 ppm[11]), as is only to be expected[10] from the increase in coordination number from four to six. In D$_2$O solution the Cd nuclide in [CdT$_2$Cl$_4$] is slightly more deshielded than in [CdTCl$_3$]$_2$·2H$_2$O (74.7 ppm[3]), probably because the additional N and Cl ligands of the former have a greater deshielding effect[12] than the oxygen ligands (from chemical exchange with solvent[3]) of the latter, and the differ-

Table 4. ^{13}C, ^{15}N and ^{113}Cd NMR chemical shifts of $[CdT_2Cl_4]$[a]

	C(2′)	C(4′)	C(2)	C(6′)	C(4)	C(5)	C(5′)	C(5β)	C(3,5′)	C(5α)	C(2′α)	C(4α)
D_2O/H_2O solution (1 : 2)[b]	169.0	162.0	154.0 153.8t[c]	157.0	143.0	136.2	104.6	60.6	51.2	29.4	24.4	11.4
Solid state[d]	167.8	160.5	151.9	159.3	142.0	136.8	107.6	60.6	49.3	29.4	27.6	12.9

	N(3)	N(1′)	N(3′)	N(4′α)	$^{113}Cd(W_{1/2})$
D_2O/H_2O solution (1 : 2)[e]	−143.7	−139.9	−168.6	−297.2	100.3 (217)
Solid state	—	—	—	—	177.3

[a] δ in ppm.

[b] Referred to external dioxane (67.3 ppm).

[c] Attributable to C(2)—D ; t = triplet

[d] Referred to external glycine (176.25 ppm).

[e] Referred to external CH_3NO_2 neat.

ence outweighs any possible change in the cadmium coordination number.

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