Table 2. *Bond lengths* (Å) *and angles* (°)

Co—N(1)	2·032 (4)	Co—N(4)	2·043 (4)
Co—N(2)	1·929 (4)	Co—N(5)	1·927 (4)
Co—N(3)	1·913 (4)	Co—N(6)	1·918 (4)
N(1)—C(1)	1·353 (5)	N(4)—C(12)	1·348 (5)
C(1)—C(2)	1·375 (6)	C(12)—C(13)	1·371 (7)
C(2)—C(3)	1·369 (8)	C(13)—C(14)	1·362 (8)
C(3)—C(4)	1·367 (7)	C(14)—C(15)	1·376 (7)
C(4)—C(5)	1·388 (6)	C(15)—C(16)	1·407 (8)
C(5)—N(1)	1·363 (6)	C(16)—N(4)	1·353 (6)
C(5)—C(6)	1·493 (6)	C(16)—C(17)	1·496 (7)
C(6)—C(7)	1·526 (8)	C(17)—C(18)	1·522 (9)
C(7)—N(2)	1·459 (6)	C(18)—N(5)	1·470 (6)
N(2)—C(8)	1·292 (5)	N(5)—C(19)	1·290 (6)
C(8)—C(9)	1·442 (6)	C(19)—C(20)	1·454 (7)
C(8)—C(10)	1·493 (7)	C(19)—C(21)	1·501 (8)
C(9)—C(11)	1·491 (6)	C(20)—C(22)	1·506 (8)
C(9)—N(3)	1·323 (5)	C(20)—N(6)	1·320 (6)
N(3)—O(1)	1·268 (5)	N(6)—O(2)	1·265 (5)
Cl—O(3)	1·427 (6)	Cl—O(5)	1·414 (6)
Cl—O(4)	1·414 (6)	Cl—O(6)	1·438 (5)
N(1)—Co—N(2)	93·3 (2)	N(4)—Co—N(5)	94·1 (2)
N(1)—Co—N(3)	174·5 (2)	N(4)—Co—N(6)	175·2 (2)
N(1)—Co—N(5)	94·7 (1)	N(4)—Co—N(2)	94·3 (2)
N(1)—Co—N(6)	89·8 (2)	N(4)—Co—N(3)	90·5 (2)
N(1)—Co—N(4)	93·1 (1)	N(3)—Co—N(6)	86·9 (2)
N(2)—Co—N(3)	82·2 (2)	N(5)—Co—N(6)	81·8 (2)
N(2)—Co—N(6)	89·3 (2)	N(3)—Co—N(5)	89·2 (2)
N(2)—Co—N(5)	168·0 (2)		
Co—N(1)—C(1)	119·1 (3)	Co—N(4)—C(12)	118·9 (3)
Co—N(1)—C(5)	124·1 (2)	Co—N(4)—C(16)	123·5 (3)
Co—N(2)—C(7)	124·0 (3)	Co—N(5)—C(18)	122·5 (3)
Co—N(2)—C(8)	113·6 (3)	Co—N(5)—C(19)	114·2 (3)
Co—N(3)—C(9)	114·4 (3)	Co—N(6)—C(20)	115·0 (3)
Co—N(3)—O(1)	124·0 (3)	Co—N(6)—O(2)	122·9 (3)
N(1)—C(1)—C(2)	123·4 (5)	N(4)—C(12)—C(13)	122·8 (4)
C(1)—C(2)—C(3)	119·7 (4)	C(12)—C(13)—C(14)	121·0 (4)
C(2)—C(3)—C(4)	117·8 (4)	C(13)—C(14)—C(15)	117·1 (5)
C(3)—C(4)—C(5)	121·2 (5)	C(14)—C(15)—C(16)	120·8 (5)
C(4)—C(5)—N(1)	121·0 (4)	C(15)—C(16)—N(4)	120·7 (4)
C(1)—N(1)—C(5)	116·8 (4)	C(12)—N(4)—C(16)	117·6 (4)
N(1)—C(5)—C(6)	119·1 (4)	N(4)—C(16)—C(17)	118·9 (4)
C(4)—C(5)—C(6)	119·9 (5)	C(15)—C(16)—C(17)	120·4 (4)
C(5)—C(6)—C(7)	113·3 (4)	C(16)—C(17)—C(18)	114·1 (4)
C(6)—C(7)—N(2)	111·0 (4)	C(17)—C(18)—N(5)	110·6 (4)
C(7)—N(2)—C(8)	121·6 (4)	C(18)—N(5)—C(19)	122·4 (4)
N(2)—C(8)—C(9)	115·6 (4)	N(5)—C(19)—C(20)	115·3 (5)
N(2)—C(8)—C(10)	123·7 (4)	N(5)—C(19)—C(21)	124·9 (5)
C(9)—C(8)—C(10)	120·7 (4)	C(20)—C(19)—C(21)	119·8 (5)
C(8)—C(9)—C(11)	126·7 (4)	C(19)—C(20)—C(22)	125·9 (5)
C(8)—C(9)—N(3)	113·4 (4)	C(19)—C(20)—N(6)	112·8 (4)
C(11)—C(9)—N(3)	119·9 (4)	C(22)—C(20)—N(6)	121·3 (5)
C(9)—N(3)—O(1)	121·6 (4)	C(20)—N(6)—O(2)	122·1 (4)
O(3)—Cl—O(4)	108·6 (3)	O(4)—Cl—O(5)	111·5 (4)
O(3)—Cl—O(5)	108·0 (3)	O(4)—Cl—O(6)	110·0 (3)
O(3)—Cl—O(6)	109·5 (4)	O(5)—Cl—O(6)	109·3 (3)

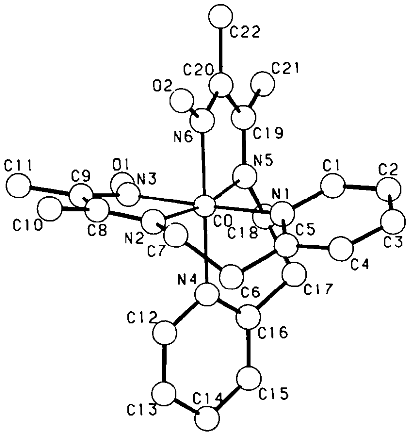

Fig. 1. Perspective view of the complex cation.

The perchlorate ion has an average Cl—O distance of 1·423 (3) Å and average O—Cl—O angle of 109·5 (1)°, both of which are normal for this ion.

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Thiaminium Tetrachlorocobaltate(II) Monohydrate,* $C_{12}H_{18}N_4OS^{2+}.CoCl^2{}_4^{-}.H_2O$

By Cindy L. MacLaurin and Mary Frances Richardson

*Department of Chemistry, Brock University, St. Catharines, Ontario, Canada L2S 3A*1

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Abstract. $M_r = 485·12$, monoclinic, $P2_1/n$, $a = 16·518$ (1), $b = 15·445$ (1), $c = 7·883$ (1) Å, $\beta = 97·55$ (1)°, $V = 1993·8$ Å^3, $Z = 4$, $D_m = 1·61$, $D_x = 1·62$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda(\alpha_1) = 0·70926$ Å, $\mu = 15·4$ cm^{-1}, $F(000) = 988$, room temperature, $R = 0·035$ for 3032 reflections with $I > 3\sigma(I)$, $R = 0·049$ for all 3507 reflections. The compound is isostructural with thiaminium tetrachlorocadmate monohydrate, with the thiaminium cation in the S conformation. The $CoCl_4^{2-}$ ion is tetrahedral with an average Co—Cl bond length of 2·276 (16) Å.

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* The thiamine cation is 3-[(4-amino-2-methyl-5-pyrimidinyl)methyl]-5-(2-hydroxyethyl)-4-methylthiazolium.

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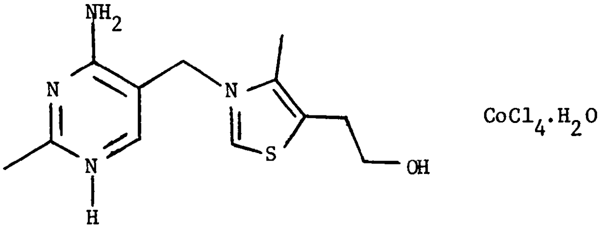
Introduction. Thiamine and its derivatives exhibit three different conformations relative to the bridging methylene group between the two rings (Pletcher, Sax, Turano & Chang, 1982; Shin, Pletcher & Sax, 1981). The *F* conformation is generally found for unsubstituted thiamines and the *S* conformation for substituted ones; the *V* conformation has so far only been observed for oxythiamin. Thiaminium tetrachlorocadmate monohydrate ($HThiCdCl_4.H_2O$) was the first example of an unsubstituted thiamine in the *S* conformation (Richardson, Franklin & Thompson, 1975). One other example of an unsubstituted thiamine in the *S* conformation is known (Cramer, Maynard & Ibers, 1981). It has been tentatively suggested (Sax, 1982) that the reason the thiaminium cation adopts the *S* conformation in this structure may be the large size of the tetrachlorocadmate anion, and that smaller tetrahedral anions may lead to the more common *F* formation. Since Lee (1975) had shown that the tetrachlorocobaltate(II) salt was isomorphous with the tetrachlorocadmate, we undertook the structure determination of $HThiCoCl_4.H_2O$ (I) in order to provide further experimental data for the development of a theory explaining thiamine conformations.



(I)

Experimental. Blue diamond-shaped crystals from aqueous equimolar thiaminium hydrochloride and cobalt(II) chloride, 0·28 × 0·29 × 0·34 mm, CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$, lattice parameters from 25 reflections with $16° < \theta < 29°$, one standard measured every hour (variation ±2%), 3984 $\pm hkl$ with $\theta < 25°$, 3507 independent, 3032 with $I > 3\sigma(I)$, Lp correction, no absorption correction, fractional coordinates taken from structure of $HThiCdCl_4.H_2O$ (Richardson, Franklin & Thompson, 1975) and refined by full-matrix least squares on *F*'s, H-atom positions calculated except for H_2O, $-NH_2$, and $-OH$, 232 parameters, $R_w = 0{\cdot}039$, $w = [\sigma^2(F) + 0{\cdot}0004\,F^2]^{-1}$, final difference map with no features greater than 0·3 e $Å^{-3}$ or less than −0·6 e $Å^{-3}$, ratio of maximum least-squares shift to error = 0·6, scattering factors from *International Tables for X-ray Crystallography* (1974), computer programs *SHELX76* (Sheldrick, 1976) and *ORTEP* (Johnson, 1976).

Discussion. The atomic coordinates are listed in Table 1, and bond distances and angles are given in Table 2. Fig. 1 shows the thiaminium and tetrachlorocobaltate(II) ions.*

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters for* $HThiCoCl_4.H_2O$, *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}(Å²)
Co	0·18627 (2)	0·17133 (2)	−0·12398 (4)	0·0251
Cl(1)	0·29197 (4)	0·08030 (5)	−0·03251 (11)	0·0448
Cl(2)	0·07808 (4)	0·09108 (4)	−0·24250 (10)	0·0375
Cl(3)	0·15017 (5)	0·24352 (5)	0·10335 (9)	0·0426
Cl(4)	0·22093 (4)	0·26501 (5)	−0·32837 (10)	0·0422
S	0·35728 (4)	0·43904 (5)	−0·00366 (9)	0·0367
O(1)	0·4407 (1)	0·3731 (2)	0·5120 (3)	0·0466
O(2)	0·2566 (2)	0·1040 (2)	0·3707 (4)	0·0678
N(1)	0·4511 (1)	0·3160 (1)	−0·0398 (4)	0·0226
N(2)	0·5992 (2)	0·0960 (2)	−0·0609 (4)	0·0384
N(3)	0·4966 (1)	0·0279 (1)	−0·2315 (3)	0·0331
N(4)	0·3902 (1)	0·1065 (1)	−0·3806 (3)	0·0292
C(1)	0·3684 (2)	0·4169 (2)	0·4413 (4)	0·0434
C(2)	0·3196 (2)	0·3646 (2)	0·2988 (3)	0·0399
C(3)	0·3626 (2)	0·3561 (2)	0·1451 (3)	0·0277
C(4)	0·4172 (1)	0·2949 (2)	0·1084 (3)	0·0247
C(5)	0·4451 (2)	0·2162 (2)	0·2092 (4)	0·0406
C(6)	0·4252 (2)	0·3904 (2)	−0·1105 (3)	0·0304
C(7)	0·5168 (1)	0·2666 (2)	−0·1044 (4)	0·0292
C(8)	0·4861 (1)	0·1829 (2)	−0·1889 (3)	0·0228
C(9)	0·5279 (2)	0·1030 (2)	−0·1593 (3)	0·0263
C(10)	0·4284 (2)	0·0317 (2)	−0·3383 (3)	0·0289
C(11)	0·3906 (2)	−0·0492 (2)	−0·4153 (4)	0·0467
C(12)	0·4175 (2)	0·1815 (2)	−0·3047 (4)	0·0285
H(O1)	0·473 (2)	0·374 (2)	0·446 (5)	0·05
H(O2*A*)	0·267 (2)	0·109 (2)	0·278 (5)	0·05
H(O2*B*)	0·228 (2)	0·145 (2)	0·350 (5)	0·05
H(N2*B*)	0·629 (2)	0·142 (2)	−0·019 (4)	0·05
H(N2*A*)	0·622 (2)	0·052 (2)	−0·051 (4)	0·05

Table 2. *Distances* (Å) *and angles* (°) *in* $HThiCoCl_4$, *with estimated standard deviations in parentheses*

Co–Cl(1)	2·2835 (8)	S–C(3)	1·731 (3)
Co–Cl(2)	2·2725 (8)	N(1)–C(7)	1·472 (3)
Co–Cl(3)	2·2563 (8)	C(7)–C(8)	1·511 (3)
Co–Cl(4)	2·2934 (8)	C(8)–C(9)	1·419 (3)
O(1)–C(1)	1·421 (4)	C(9)–N(2)	1·327 (3)
C(1)–C(2)	1·525 (4)	C(9)–N(3)	1·364 (3)
C(2)–C(3)	1·489 (4)	N(3)–C(10)	1·317 (3)
C(3)–C(4)	1·364 (4)	C(10)–C(11)	1·489 (4)
C(4)–C(5)	1·492 (4)	C(10)–N(4)	1·338 (3)
C(4)–N(1)	1·399 (3)	N(4)–C(12)	1·354 (3)
N(1)–C(6)	1·324 (3)	C(12)–C(8)	1·358 (3)
C(6)–S	1·668 (3)		
Cl(1)–Co–Cl(2)	108·74 (3)	C(6)–N(1)–C(7)	121·1 (2)
Cl(1)–Co–Cl(3)	108·93 (3)	N(1)–C(6)–S	112·3 (2)
Cl(1)–Co–Cl(4)	111·05 (3)	C(6)–S–C(3)	91·8 (1)
Cl(2)–Co–Cl(3)	108·69 (3)	N(1)–C(7)–C(8)	112·0 (2)
Cl(2)–Co–Cl(4)	108·10 (3)	C(7)–C(8)–C(9)	122·9 (2)
Cl(3)–Co–Cl(4)	111·26 (3)	C(7)–C(8)–C(12)	120·8 (2)
O(1)–C(1)–C(2)	111·9 (3)	C(9)–C(8)–C(12)	116·2 (2)
C(1)–C(2)–C(3)	112·5 (2)	C(8)–C(9)–N(2)	122·9 (2)
C(2)–C(3)–C(4)	129·3 (2)	C(8)–C(9)–N(3)	121·4 (2)
C(2)–C(3)–S	120·0 (2)	N(2)–C(9)–N(3)	115·7 (2)
C(4)–C(3)–S	110·2 (2)	C(9)–N(3)–C(10)	118·3 (2)
C(3)–C(4)–N(1)	111·3 (2)	N(3)–C(10)–C(11)	120·1 (2)
C(3)–C(4)–C(5)	128·2 (3)	N(3)–C(10)–N(4)	122·3 (2)
C(5)–C(4)–N(1)	120·4 (2)	C(11)–C(10)–N(4)	117·7 (2)
C(4)–N(1)–C(7)	124·2 (2)	C(10)–N(4)–C(12)	120·7 (2)
C(4)–N(1)–C(6)	114·3 (2)	N(4)–C(12)–C(8)	120·8 (2)

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* Lists of structure factors, anisotropic thermal parameters, calculated hydrogen-atom positions, least-squares planes, and hydrogen bonds have been deposited with the British Library Lending Division, as Supplementary Publication No. SUP 38466 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

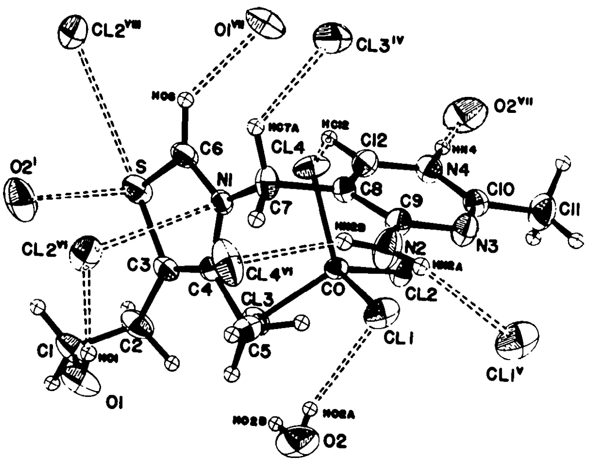

Fig. 1. The $HThi^{2+}$ and $CoCl_4{}^{2-}$ ions, showing the numbering scheme and thermal ellipsoids. The view is down the x axis. Short contacts other than hydrogen bonds are: $N(1)\cdots Cl(2^{vi})$ 3·265 (3), $S\cdots Cl(2^{viii})$ 3·350 (1), $S\cdots O(2^{i})$ 3·413 (3) Å. Symmetry superscripts (chosen to correspond to $HThiCdCl_4.H_2O$): (i) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; (iv) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$; (v) $1-x$, $-y$, $-z$; (vi) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$; (vii) x, y, $-1+z$; (viii) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $-\frac{1}{2}-z$.

$HThiCoCl_4.H_2O$ is isostructural with $HThiCdCl_4.H_2O$ (Richardson, Franklin & Thompson, 1975). The main difference between the two structures lies in the locations of the metal and chlorine atoms, since cobalt has a smaller radius than cadmium. The Co—Cl distances range from 2·2563 (8) to 2·2934 (8) Å, compared to Cd—Cl 2·432–2·465 Å in $HThiCdCl_4.H_2O$. Nonetheless, the tetrachlorocobaltate anion is a nearly regular tetrahedron, as is the tetrachlorocadmate anion. Distances and angles other than those involving cobalt and chlorine are essentially the same as in $HThiCdCl_4.H_2O$.

The smaller tetrachlorocobaltate anion has an essentially negligible effect on the thiamine conformation. The C(8)—C(7)—N(1)—C(6) and N(1)—C(7)—C(8)—C(9) torsion angles are 111·6 (2) and 135·6 (2)° respectively, nearly the same as observed for $HThiCdCl_4.H_2O$ (110·4 and 137·3°, respectively). Thus, the extent to which a large anion stabilizes the *S* conformation, and the mechanism by which it effects this stabilization are still uncertain.

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Acta Cryst. (1983). C**39**, 856–858

Structural Characterization of 3-η-Cyclopentadienyl-1,2-dimethyl-1,2-dicarba-3-cobalta-*closo*-octaborane, $1,2\text{-}(CH_3)_2\text{-}3,1,2\text{-}(\eta\text{-}C_5H_5)CoC_2B_5H_5$

By George J. Zimmerman and Larry G. Sneddon*

Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104, *USA*

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Abstract. $M_r = 237{\cdot}22$, monoclinic, $P2_1/n$, $a = 11{\cdot}534$ (5), $b = 13{\cdot}618$ (8), $c = 7{\cdot}754$ (4) Å, $\beta = 103{\cdot}11$ (1)°, $V = 1187$ (2) Å^3, $Z = 4$, $F(000) = 488$, $D_x = 1{\cdot}327$ g cm^{-3}, D_m not measured, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 14{\cdot}549$ cm^{-1}, 298 K. The structure was refined by the full-matrix least-squares method to a final R of 0·040 and R_w of 0·056 for the 1775 reflections with $F_o{}^2 > 3\sigma(F_o{}^2)$. In agreement with the structure previously proposed based on the spectroscopic data, the compound is shown to be a cyclopentadienyl substituted cobaltacarborane cage complex in which the

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* To whom correspondence should be addressed.

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