

not differ significantly. It can be assumed that formamidine disulphide exists as a diprotonated cation, and not in the monoprotated form, and that the crystals contain water of crystallization and not H₃O⁺ ions, as was reported earlier (Lis, 1978).

The structure is held together by weak hydrogen bonds; their lengths and angles are given in Table 4.

In the present and earlier investigations (Lis, 1976, 1977, 1978) it was found that in the system ReO₄⁻ + (NH₂)₂CS + HCl there is a redox reaction between ReO₄⁻ ions and thiourea molecules. It was observed that, depending on the thiourea concentrations, quite different Re complexes may be obtained. The reaction is postulated to proceed stepwise. At first, if the HCl concentration is relatively small, the octahedral yellow-brown complex of Re^{VII} is formed. Next, as the HCl concentration increases, the Re⁷⁺ ions are reduced by thiourea to Re⁵⁺ ions and thiourea is transformed into dithiobisformamidinium dichloride. At this stage, some coloured Re complexes may be easily isolated in the crystalline state, depending on the HCl and thiourea concentrations. Further, at an extreme concentration of HCl and with excess thiourea the reduction most probably stops at the Re⁴⁺ complexes.

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Tetramethylammonium 2-(η -Cyclopentadienyl)-1-carba-2-cobalta-closo-undecahydro-dodecaborate(1-)

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Abstract. [N(CH₃)₄][(η -C₅H₅)CoCB₁₀H₁₁], C₄H₁₂N⁺.C₆H₁₆B₁₀Co⁻, *M_r* = 329.48, orthorhombic, *Pbcm*, *a* = 8.891 (1), *b* = 15.934 (6), *c* = 12.808 (1) Å, *V* = 1814.5 (7) Å³, *Z* = 4, *D_x* = 1.206, *D_m* = 1.204 Mg m⁻³ (by flotation), μ (Mo *K*α) = 0.93 mm⁻¹. The

structure was refined to *R* = 0.045 for 1568 counter reflections. The anion can be described as an icosahedron with one Co, one C and ten B atoms at its vertices. The anion and cation exhibit crystallographic symmetry *m* and 2 respectively.

Introduction. The present study reports the X-ray investigation of [N(CH₃)₄][(η -C₅H₅)CoCB₁₀H₁₁], previously described by Rietz, Dustin & Hawthorne (1974). The sample was prepared by treating 7-NMe₃CB₁₀H₁₂ with cyclopentadiene and CoCl₂·6H₂O in an alkaline methanolic solution, at the Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences in Řež near Praha (J. Dolanský & B. Štibr, unpublished). The present study represents the first example of a mixed cyclopentadienyl complex involving a monocarbaborane icosahedral cage.

The yellow-brown crystals are stable to air and X-rays. Preliminary lattice constants and space group (*Pbcm* or *Pbc2*₁) were obtained from photographs (Cu K α radiation). Refined cell parameters were obtained from the orientation matrix calculated by least squares (Shoemaker, 1970) from 30 reflections centered on the diffractometer. A crystal 0.6 × 0.3 × 0.2 mm was used for intensity measurements on a Hilger & Watts four-circle diffractometer with Mo K α radiation (λ = 0.71073 Å). The ω -2 θ scan technique was used with a constant scan speed of 2° min⁻¹ over a range of 2° to measure 2293 independent reflections with 2 θ ≤ 56°. 725 of these were classified as unobserved on the criterion $I < 2\sigma_1(I)$, where $I = TC - B_1 - B_2$ and $\sigma_1(I) = (TC + B_1 + B_2)^{1/2}$ (TC = total count, B_1 and B_2 =

backgrounds measured at the scan limits for half the scan time). Only observed reflections were used in the refinement. The intensities of one standard measured after every ten reflections showed no significant variation. The data were corrected for Lorentz and polarization effects, but not for absorption or extinction.

The structure was solved by the heavy-atom method. The x and y coordinates of Co were determined from a Patterson map and z was chosen as $\frac{1}{4}$. At this stage we chose space group *Pbc2*₁. A Fourier synthesis based on these input parameters provided the positions of all the remaining non-hydrogen atoms and showed the most likely space group to be *Pbcm*. Refinement was carried out with a local version of the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962). The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$ {derived from $\sigma_2(I) = [\sigma_1(I) + (0.015I)^2]^{1/2}$ }. The scale and overall temperature factor were estimated from a Wilson plot. Refinement with isotropic temperature factors converged to $R = 0.092$ and with anisotropic to $R = 0.070$ (for observed reflections). A subsequent difference synthesis revealed the positions of all H atoms. Final refinement was carried out in two blocks: the first consisted of parameters of non-hydrogen atoms, the second of parameters of H atoms. The final R was 0.045 for the observed reflections. The maximum residual electron density in the final difference synthesis was 0.31 e Å⁻³. Final coordinates are given in Table 1.* Scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). The calculations were carried out on a TESLA 200 computer.

Table 1. Fractional atomic coordinates

E.s.d.'s (in parentheses) refer to the last decimal place.

	x	y	z
Co(2)	0.54391 (6)	0.52395 (3)	0.25
BC(1)	0.4245 (3)	0.4572 (2)	0.1407 (2)
B(3)	0.4835 (5)	0.3989 (3)	0.25
B(4)	0.3167 (4)	0.3720 (2)	0.1812 (3)
B(5)	0.2310 (4)	0.4657 (2)	0.1383 (3)
B(6)	0.3434 (4)	0.5511 (2)	0.1788 (3)
B(9)	0.1620 (6)	0.4125 (3)	0.25
B(10)	0.1777 (5)	0.5238 (4)	0.25
C(1)	0.6400 (5)	0.6404 (3)	0.25
C(2)	0.6844 (4)	0.5973 (2)	0.3379 (3)
C(3)	0.7617 (3)	0.5256 (2)	0.3038 (3)
C(6)	0.0030 (5)	0.6901 (2)	0.4428 (3)
C(7)	0.1992 (5)	0.7056 (2)	0.5755 (3)
N	0.1009 (4)	0.75	0.5
H(BC1)	0.482 (3)	0.447 (1)	0.065 (2)
H(B3)	0.576 (4)	0.357 (2)	0.25
H(B4)	0.311 (3)	0.310 (1)	0.133 (2)
H(B5)	0.166 (3)	0.468 (2)	0.065 (2)
H(B6)	0.343 (2)	0.611 (1)	0.132 (2)
H(B9)	0.061 (4)	0.382 (2)	0.25
H(B10)	0.091 (5)	0.564 (2)	0.25
H(C1)	0.592 (4)	0.689 (2)	0.25
H(C2)	0.663 (3)	0.609 (2)	0.413 (2)
H(C3)	0.780 (3)	0.496 (2)	0.345 (2)
H(C6 ₁)	0.921 (5)	0.723 (3)	0.386 (4)
H(C6 ₂)	0.939 (4)	0.662 (2)	0.495 (3)
H(C6 ₃)	0.065 (4)	0.657 (2)	0.412 (3)
H(C7 ₁)	0.256 (5)	0.745 (3)	0.619 (4)
H(C7 ₂)	0.147 (5)	0.676 (2)	0.623 (3)
H(C7 ₃)	0.269 (5)	0.672 (2)	0.542 (3)

Discussion. The cage C atom was distinguished from B atoms by lower temperature factors and shorter bond distances. This analysis led to the surprising result that the C atom was not located on the crystallographic mirror plane. This fact is not consistent with results of the chemical and NMR study of this compound which shows the anion to have only one C atom. We refined two possibilities. The first was that the suspect atom was a C atom, the second that this atom was composed of C and B atoms with half weight. The second possibility was significantly better by a Hamilton test. A possible explanation is that the crystallographic symmetry is only the average symmetry over all the crystal and that the C atom is distributed uniformly between two possible positions. It should lead to the space group *Pbc2*₁ but it is not possible to refine this

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34682 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances (Å) and bond angles (°)*

E.s.d.'s (in parentheses) refer to the last decimal place.

(I) Cobalt–icosahedral-cage distances

Co(2)–BC(1)	2.054 (3)	Co(2)–B(6)	2.049 (3)
Co(2)–B(3)	2.064 (4)		

(II) Icosahedral-cage distances

BC(1)–B(3)	1.760 (4)	BC(1)–B(5)	1.723 (4)
BC(1)–B(4)	1.741 (4)	BC(1)–B(6)	1.732 (4)
B(3)–B(4)	1.777 (6)	B(5)–B(9)	1.772 (5)
B(4)–B(5)	1.764 (5)	B(5)–B(10)	1.768 (5)
B(4)–B(8)	1.763 (5)	B(6)–B(10)	1.789 (5)
B(4)–B(9)	1.756 (6)	B(6)–B(11)	1.824 (5)
B(5)–B(6)	1.766 (5)	B(9)–B(10)	1.778 (8)

(III) Cobalt–cyclopentadienyl distances

Co(2)–C(1)	2.043 (5)	Co(2)–C(3)	2.055 (3)
Co(2)–C(2)	2.048 (4)		

(IV) Cyclopentadienyl-ring distances

C(1)–C(2)	1.377 (5)	C(3)–C(4)	1.377 (5)
C(2)–C(3)	1.403 (5)		

(V) N–C distances in the $[N(CH_3)_4]^+$ cation

N–C(6)	1.485 (5)	N–C(7)	1.484 (5)
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(VI) BC–H and B–H icosahedral-cage distances

BC(1)–H(BC1)	1.11 (3)	B(6)–H(B6)	1.14 (2)
B(3)–H(B3)	1.06 (3)	B(9)–H(B9)	1.02 (4)
B(4)–H(B4)	1.16 (2)	B(10)–H(B10)	1.00 (4)
B(5)–H(B5)	1.10 (3)		

(VII) C–H cyclopentadienyl-ring distances

C(1)–H(C1)	0.88 (4)	C(3)–H(C3)	0.73 (3)
C(2)–H(C2)	0.99 (3)		

(VIII) C–H methyl distances

C(6)–H(C6 ₁)	1.15 (5)	C(7)–H(C7 ₁)	0.98 (5)
C(6)–H(C6 ₂)	0.99 (4)	C(7)–H(C7 ₂)	0.90 (4)
C(6)–H(C6 ₃)	0.86 (4)	C(7)–H(C7 ₃)	0.92 (4)

(IX) Cobalt–icosahedral-cage angles

BC(1)–Co–BC(7)	85.97 (11)	Co–BC(1)–B(4)	119.03 (17)
BC(1)–Co–B(3)	50.62 (10)	Co–BC(1)–B(5)	119.10 (17)
BC(1)–Co–B(6)	49.93 (12)	Co–B(3)–BC(1)	64.40 (17)
BC(1)–Co–B(11)	87.89 (13)	Co–B(6)–BC(1)	65.18 (18)
B(6)–Co–B(11)	52.86 (15)	Co–B(6)–B(11)	63.57 (18)
B(3)–Co–B(6)	88.71 (15)	Co–B(3)–B(4)	116.74 (21)
Co–BC(1)–B(3)	64.98 (18)	Co–B(6)–B(5)	117.40 (18)
Co–BC(1)–B(6)	64.89 (17)	Co–B(6)–B(10)	116.03 (18)

(X) Icosahedral-cage angles

B(3)–BC(1)–B(4)	61.02 (23)	B(4)–B(9)–B(5)	59.97 (27)
B(4)–BC(1)–B(5)	61.15 (22)	B(4)–B(9)–B(8)	60.25 (21)
B(5)–BC(1)–B(6)	61.43 (21)	B(5)–B(4)–B(9)	60.47 (24)
B(3)–BC(1)–B(5)	110.62 (23)	B(5)–B(6)–B(10)	59.68 (24)
B(3)–BC(1)–B(6)	110.84 (21)	B(5)–B(9)–B(10)	59.73 (21)
B(4)–BC(1)–B(6)	111.11 (21)	B(5)–B(10)–B(6)	59.58 (27)
BC(1)–B(3)–BC(7)	105.41 (21)	B(5)–B(10)–B(9)	59.98 (22)
BC(1)–B(3)–B(4)	58.96 (24)	B(6)–B(5)–B(10)	60.74 (25)
BC(1)–B(4)–B(3)	60.02 (22)	B(6)–B(10)–B(11)	61.37 (20)
BC(1)–B(4)–B(5)	59.03 (23)	B(9)–B(5)–B(10)	60.29 (28)
BC(1)–B(5)–B(4)	59.83 (22)	B(10)–B(6)–B(11)	59.31 (20)
BC(1)–B(5)–B(6)	59.43 (22)	B(3)–B(4)–B(5)	108.11 (24)
BC(1)–B(6)–B(5)	59.15 (21)	B(3)–B(4)–B(9)	108.41 (24)
BC(1)–B(3)–B(8)	105.87 (24)	B(4)–B(5)–B(6)	108.44 (23)
BC(1)–B(4)–B(8)	107.33 (22)	B(4)–B(5)–B(10)	107.86 (25)
BC(1)–B(4)–B(9)	107.13 (25)	B(4)–B(9)–B(10)	107.74 (28)
BC(1)–B(5)–B(9)	107.05 (25)	B(5)–B(4)–B(8)	108.13 (23)
BC(1)–B(5)–B(10)	107.10 (23)	B(5)–B(6)–B(11)	107.08 (22)
BC(1)–B(6)–B(10)	106.06 (25)	B(5)–B(9)–B(8)	108.04 (26)
BC(1)–B(6)–B(11)	106.38 (21)	B(5)–B(9)–B(12)	107.62 (25)
B(3)–B(4)–B(8)	60.26 (22)	B(5)–B(10)–B(11)	108.63 (24)
B(4)–B(3)–B(8)	59.47 (20)	B(5)–B(10)–B(12)	108.01 (26)
B(4)–B(5)–B(9)	59.56 (26)	B(6)–B(5)–B(9)	109.11 (24)
B(4)–B(8)–B(9)	59.87 (23)	B(6)–B(10)–B(9)	107.94 (28)

Table 2 (cont.)

(XI) Cobalt–cyclopentadienyl-ring angles

C(1)–Co–C(2)	39.34 (13)	Co–C(1)–C(2)	70.54 (25)
C(2)–Co–C(3)	39.98 (15)	Co–C(2)–C(1)	70.12 (26)
C(3)–Co–C(4)	39.16 (14)	Co–C(2)–C(3)	70.28 (22)
C(1)–Co–C(3)	66.07 (16)	Co–C(3)–C(2)	69.74 (22)
C(2)–Co–C(4)	66.56 (14)	Co–C(3)–C(4)	70.42 (20)
C(2)–Co–C(5)	66.71 (14)		

(XII) Cyclopentadienyl-ring angles

C(1)–C(2)–C(3)	106.96 (30)	C(2)–C(1)–C(5)	109.73 (31)
C(2)–C(3)–C(4)	108.16 (30)		

(XIII) Angles in the $[N(CH_3)_4]^+$ cation

C(6)–N–C(7)	111.12 (13)	C(6)–N–C(9)	109.28 (24)
C(6)–N–C(8)	108.27 (27)	C(7)–N–C(9)	107.78 (27)

(XIV) Angles involving H atoms

Co–BC(1)–H(BC1)	115.9 (13)	B(6)–B(11)–H(B11)	122.2 (12)
Co–B(3)–H(B3)	113.9 (18)	B(9)–B(4)–H(B4)	122.9 (13)
Co–B(6)–H(B6)	114.9 (11)	B(9)–B(5)–H(B5)	121.5 (13)
Co–C(1)–H(C1)	126.2 (25)	B(9)–B(10)–H(B10)	125.5 (22)
Co–C(2)–H(C2)	121.3 (17)	B(10)–B(5)–H(B5)	122.0 (13)
Co–C(3)–H(C3)	116.7 (22)	B(10)–B(6)–H(B6)	118.3 (11)
B(3)–BC(1)–H(BC1)	119.0 (13)	B(10)–B(9)–H(B9)	122.8 (20)
B(4)–BC(1)–H(BC1)	113.5 (12)	C(1)–C(2)–H(C2)	130.1 (17)
B(5)–BC(1)–H(BC1)	116.9 (14)	C(2)–C(1)–H(C1)	125.1 (2)
B(6)–BC(1)–H(BC1)	124.4 (12)	C(2)–C(3)–H(C3)	113.9 (23)
BC(1)–B(3)–H(B3)	124.3 (5)	C(3)–C(2)–H(C2)	122.8 (17)
BC(1)–B(4)–H(B4)	121.9 (13)	C(3)–C(4)–H(C4)	137.1 (23)
BC(1)–B(5)–H(B5)	122.7 (13)	N–C(6)–H(C6 ₁)	112.7 (23)
BC(1)–B(6)–H(B6)	125.7 (12)	N–C(6)–H(C6 ₂)	107.4 (23)
B(3)–B(4)–H(B4)	120.1 (13)	N–C(6)–H(C6 ₃)	104.0 (24)
B(4)–B(3)–H(B3)	119.8 (15)	N–C(7)–H(C7 ₁)	111.6 (28)
B(4)–B(5)–H(B5)	121.3 (13)	N–C(7)–H(C7 ₂)	112.8 (27)
B(4)–B(8)–H(B8)	121.8 (13)	N–C(7)–H(C7 ₃)	111.5 (26)
B(4)–B(9)–H(B9)	121.1 (16)	H(C6 ₁)–C(6)–H(C6 ₂)	105.5 (33)
B(5)–B(4)–H(B4)	122.4 (13)	H(C6 ₂)–C(6)–H(C6 ₃)	113.2 (35)
B(5)–B(6)–H(B6)	119.5 (11)	H(C6 ₃)–C(6)–H(C6 ₁)	114.1 (31)
B(5)–B(9)–H(B9)	122.1 (6)	H(C7 ₁)–C(7)–H(C7 ₂)	102.7 (39)
B(5)–B(10)–H(B10)	122.8 (6)	H(C7 ₂)–C(7)–H(C7 ₃)	106.9 (37)
B(6)–B(5)–H(B5)	121.3 (13)	H(C7 ₃)–C(7)–H(C7 ₁)	110.8 (36)
B(6)–B(10)–H(B10)	118.4 (18)		

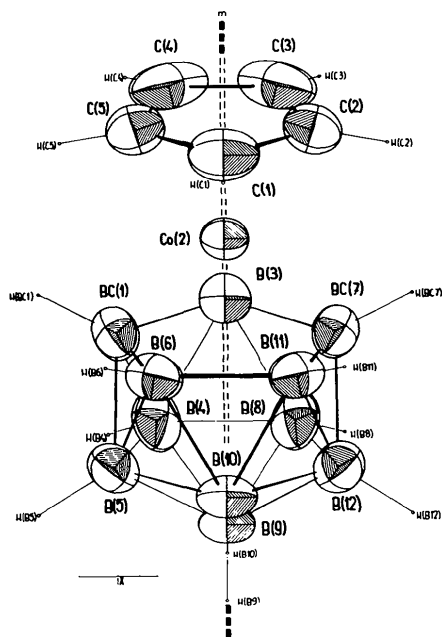


Fig. 1. View of the anion.

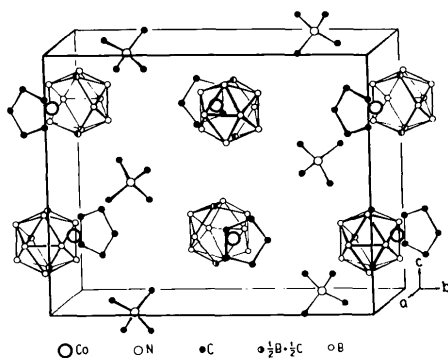


Fig. 2. Contents of the unit cell.

structure because the normal equations are nearly singular.

The structure is built up of [(C₅H₅)CoCB₁₀H₁₁]⁻ anions and [N(CH₃)₄]⁺ cations. The anion and cation exhibit crystallographic symmetry *m* and 2 respectively. The anion can be described as an icosahedron with one Co, one C, and ten B atoms at its vertices. Within one anion, atom pairs C(2) and C(5), C(3) and C(4), BC(1) and BC(7), B(4) and B(8), B(5) and B(12), and B(6) and B(11) are related by the mirror plane. Co(2), C(1), B(3), B(9) and B(10) are on the mirror plane. Fig. 1 shows the anion viewed down the vector [1̄50] with the numbering of the borane skeleton following the IUPAC system (Adams, 1972). Bond

lengths and angles are given in Table 2. The Co atom is coordinated to the pentagonal face containing BC(1), B(3), BC(7), B(11) and B(6). The mean value for Co—B and Co—BC distances is 2.054 Å which is close to the average in cobaltamonocarbaborate [(C₅H₅)Co₂CB₉H₁₀]⁻ (Šubrtová, Línek, Novák, Petříček & Ječný, 1977). The mean Co—C = 2.050 Å agrees with the average found for mixed cyclopentadienylcobaltcarbaborane complexes. The mean values for the cage distances are B—B = 1.773 and BC—B = 1.739 Å, close to the average found in the same monocarbaborane ligand (Carroll, Green, Stone & Welch, 1975). The mean value of N—C in the [N(CH₃)₄]⁺ cation is 1.484 Å. For terminal H atoms the average B—H = 1.10 and C—H = 0.94 Å. The packing of the molecules within the unit cell is shown in Fig. 2.

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Structure of Tetrakis[1-methyl-2(3*H*)-imidazolinethione]zinc(II) Nitrate Monohydrate

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Abstract. [Zn(C₄H₆N₂S)₄](NO₃)₂·H₂O, C₁₆H₂₄N₈S₄Zn²⁺·2NO₃⁻·H₂O, *M_r* = 664.09, orthorhombic, *Pbca*, *a* = 20.756 (8), *b* = 12.410 (5), *c* = 22.059 (8) Å, *U* = 5682.0 Å³, Mo *K*α, λ = 0.71069 Å, *Z* = 8, *D_m* = 1.53 (2), *D_c* = 1.55 Mg m⁻³, μ = 1.14 mm⁻¹, *F*(000) = 2736; final *R* = 0.046 for 2941 counter reflections. All four ligands are S-bonded to the metal (mean Zn—S 2.339 Å) to give a distorted tetrahedral ZnS₄ unit with S—Zn—S angles varying from

103.3 (1) to 121.5 (1)°. The complex cations are linked together by H bonding involving the amido H atoms of the ligand and the nitrate O atoms.

Introduction. Reaction of 1-methyl-2(3*H*)-imidazolinethione (mimt) with hydrated Zn^{II} nitrate in anhydrous ethanol gives a colourless crystalline material analysing as [Zn(mimt)₄(NO₃)₂].H₂O. The presence of the water molecule has been demonstrated by means of thermal