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Structures of Metallocarboranes. 9. Crystal and Molecular Structure of the 10-Vertex Heterobimetallocarborane 2,3-Di-η-cyclopentadienyl-10-carba-(2,3)-(nickelacobalta)decaborane(8), 2,3-(η-C_5H_5)$_2$-(2,3)-NiCo-10-CB_7H_8[1]

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A complete three-dimensional crystal structure determination of the title compound was carried out. Crystal data: space group *C*2/*c*, $a = 15.794$ (4) Å, $b = 7.955$ (2) Å, $c = 24.273$ (7) Å, $\beta = 104.12$ (2)°, $Z = 8$, $d_{\text{obsd}} = 1.55$ (2) g cm^{-3}, $d_{\text{calcd}} = 1.54$ g cm^{-3}. Diffraction data to $2\theta_{\max} = 50°$ were obtained with a Syntex $P\bar{1}$ automated diffractometer (Mo Kα radiation), and the structure was solved by conventional Patterson, Fourier and full-matrix least-squares techniques to a conventional $R = 0.047$ for 2048 independent nonzero reflections. The molecule has the bicapped square-antiprismal geometry expected for a closo ten-vertex polyhedron. The two metal atoms are indistinguishable and occupy adjacent sites in the same equatorial belt. The carbon atom resides in the four-coordinate site nonadjacent to the two metal atoms.

Introduction

Polyhedral expansion of the monocarbacobaltacarborane anion[2,3] $[C_5H_5CoCB_7H_8]^-$ with $NiBr_2 \cdot 2$glyme in the presence of $C_5H_5^-$ affords several neutral isomeric complexes of the formula $(C_5H_5)_2NiCoCB_7H_8$ which contain formal Ni(IV) and Co(III) vertices[4,5] and which are isoelectronic with $(C_5H_5)_2Co_2C_2B_6H_8$. The structure of one isomer of the latter has previously been reported;[6] the mixed cobalt–nickel compounds exist in more numerous isomeric forms. An x-ray structural investigation of one isomer of this complex is reported herein.

Unit Cell and Space Group

A sample of the compound was furnished by Dr. C. G. Salentine. It was found to be stable to both air and x rays. Preliminary x-ray diffraction photographs of the black crystals indicated monoclinic symmetry with systematic absences indicative of space group *C*2/*c* or *Cc*. The density, measured by flotation, was 1.55 (2) g cm^{-3}, in good agreement with the calculated density of 1.54 ($Z = 8$).

Collection and Refinement of X-Ray Data

Intensity data were collected on a Syntex $P\bar{1}$ automated diffractometer equipped with scintillation counter and pulse height analyzer. A graphite crystal was used to produce monochromatic Mo Kα radiation (λ 0.71069 Å). Fifteen automatically centered reflections were used in the determination of the lattice parameters: $a = 15.794$ (4) Å, $b = 7.955$ (2) Å, $c = 24.273$ (7) Å, $\beta = 104.12$ (2)°. Intensity data were collected on a small crystal of irregular shape (average diameter about 0.1 mm) with a θ–2θ scan technique to a limit of $2\theta = 50°$. Reflections were scanned at a constant rate of 2.0°/min from 1° below the Kα_1 reflection to 1.0° above the Kα_2 reflection. Background was measured at each end of the scan. The total time counting background was equal to the scan time for each reflection. The intensities of three standard reflections were measured after every 97 reflections. No significant change in the intensities of these reflections was observed in the course of the data collection.

The reflections were corrected for Lorentz and polarization effects. The intensity of a reflection, $I(hkl)$, and $\sigma[I(hkl)]$, its estimated standard deviation, were calculated according to the equations $I = \text{CT} - (t_c/t_b)(B_1 + B_2)/2$ and $\sigma = \{\sigma_s^2 + [(0.04I)^2]\}^{1/2}$, where I is the net integrated intensity, CT is the total integrated count, t_c and t_b are the times employed for counting the scan and background, respectively, B_1 and B_2 are the background counts on the low and high sides of the reflection, and σ_s is the standard deviation in the intensity due to counting statistics. Reflections having intensities less than 3 times their standard deviations were defined as unobserved and not included in subsequent calculations. Because of the small and irregular shape of the crystal, no absorption correction was applied.

Table I. Final Atomic Parameters[a]

Atom	*x*	*y*	*z*
M2	0.21175 (4)	0.61403 (10)	0.36659 (3)
M3	0.36816 (4)	0.61233 (10)	0.37044 (3)
B1	0.2730 (5)	0.4860 (9)	0.3172 (3)
B4	0.3455 (6)	0.3492 (9)	0.3619 (3)
B5	0.2289 (5)	0.3506 (9)	0.3579 (4)
B6	0.3133 (4)	0.5962 (0)	0.4404 (3)
B7	0.3931 (5)	0.4177 (9)	0.4308 (3)
B8	0.3051 (6)	0.2697 (10)	0.4187 (4)
B9	0.2243 (5)	0.4215 (9)	0.4277 (3)
C10	0.3208 (4)	0.4129 (8)	0.4664 (3)
Cp1	0.1722 (6)	0.8495 (11)	0.3364 (8)
Cp2	0.1257 (9)	0.7368 (22)	0.3024 (4)
Cp3	0.0813 (7)	0.6434 (13)	0.3329 (9)
Cp4	0.1046 (7)	0.7121 (22)	0.3873 (8)
Cp5	0.1588 (10)	0.8352 (19)	0.3871 (5)
Cp6	0.4948 (7)	0.6750 (23)	0.3805 (11)
Cp7	0.4573 (15)	0.7959 (29)	0.4011 (6)
Cp8	0.3984 (9)	0.8544 (12)	0.3577 (13)
Cp9	0.3995 (11)	0.7682 (31)	0.3113 (6)
Cp10	0.4608 (14)	0.6562 (18)	0.3272 (11)
CpH1	0.211 (4)	0.921 (7)	0.334 (3)
CpH2	0.129 (4)	0.735 (8)	0.271 (3)
CpH3	0.049 (4)	0.561 (7)	0.328 (3)
CpH4	0.085 (4)	0.679 (8)	0.412 (3)
CpH5	0.174 (4)	0.880 (9)	0.413 (3)
CpH6	0.523 (4)	0.618 (8)	0.399 (3)
CpH7	0.473 (4)	0.820 (8)	0.429 (3)
CpH8	0.365 (4)	0.917 (7)	0.352 (3)
CpH9	0.368 (4)	0.771 (7)	0.277 (3)
CpH10	0.473 (4)	0.594 (7)	0.309 (3)
B1H	0.259 (3)	0.494 (7)	0.272 (2)
B4H	0.375 (4)	0.293 (7)	0.335 (2)
B5H	0.181 (3)	0.275 (7)	0.337 (2)
B6H	0.320 (3)	0.690 (7)	0.468 (2)
B7H	0.454 (4)	0.412 (7)	0.449 (2)
B8H	0.306 (3)	0.137 (6)	0.432 (2)
B9H	0.164 (4)	0.390 (7)	0.444 (2)
C10H	0.334 (4)	0.387 (7)	0.506 (2)

[a] Values in parentheses are estimated standard deviations and refer to the last digit of the preceding number.

Solution and Refinement of the Structure

The coordinates of the two metal atoms were determined by the solution of a three-dimensional Patterson map, and a Fourier map based on these positions revealed the positions of all the nonhydrogen cage atoms. Successive Fourier maps were used to identify the positions of the cyclopentadienyl carbon atoms. Full-matrix least-squares refinement of these parameters was followed by a Fourier difference map in which all the cage hydrogen atoms except H9 were

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Table II. Anisotropic Thermal Parameters $\times 10^4$ [a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
M2	27.2 (4)	117.2 (15)	12.8 (2)	−4.3 (6)	5.6 (2)	5.1 (4)
M3	27.5 (4)	113.7 (15)	14.9 (2)	3.0 (6)	5.9 (2)	5.4 (5)
B1	46 (4)	149 (13)	12.1 (13)	−20 (6)	3.6 (17)	−11 (4)
B4	69 (5)	101 (14)	21 (2)	16 (6)	15 (2)	−11 (4)
B5	57 (4)	114 (15)	21 (2)	−31 (6)	6 (2)	−8 (4)
B6	50 (4)	155 (14)	9.6 (12)	4 (6)	3.7 (16)	−6 (4)
B7	45 (4)	131 (15)	17.2 (16)	13 (6)	4.7 (19)	6 (4)
B8	66 (5)	125 (14)	23 (2)	−5 (6)	12 (2)	12 (4)
B9	58 (4)	127 (15)	19 (2)	−13 (6)	8 (2)	16 (4)
C10	64 (4)	171 (14)	15.1 (13)	9 (5)	7.7 (17)	12 (4)
Cp1	37 (4)	169 (17)	64 (5)	31 (6)	20 (4)	53 (7)
Cp2	84 (7)	485 (36)	17 (2)	118 (13)	5 (3)	45 (8)
Cp3	42 (5)	215 (23)	65 (5)	−25 (8)	−23 (5)	9 (9)
Cp4	48 (6)	459 (38)	57 (6)	92 (12)	42 (5)	102 (13)
Cp5	92 (10)	301 (37)	33 (3)	107 (16)	7 (4)	−25 (7)
Cp6	32 (4)	493 (45)	78 (7)	1 (11)	−4 (5)	129 (14)
Cp7	125 (11)	540 (42)	38 (3)	−207 (18)	35 (5)	−62 (11)
Cp8	51 (6)	112 (18)	115 (9)	11 (7)	43 (6)	55 (10)
Cp9	82 (9)	588 (51)	30 (3)	130 (18)	−8 (4)	89 (10)
Cp10	116 (11)	333 (36)	74 (6)	−52 (16)	79 (7)	−44 (12)

[a] See footnote *a* of Table I. The anisotropic temperature factor *T* is defined as $T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. Thermal ellipsoids are depicted in the figure.

Table III. Interatomic Distances[a]

Atoms	Distance, Å	Atoms	Distance, Å
I. Distances around Metal Atoms			
M2–M3	2.4492 (11)	M3–Cp6	2.018 (10)
M2–Cp1	2.052 (8)	M3–Cp7	2.040 (9)
M2–Cp2	2.049 (7)	M3–Cp8	2.027 (8)
M2–Cp3	2.037 (9)	M3–Cp9	2.048 (10)
M2–Cp4	2.034 (10)	M3–Cp10	2.028 (10)
M2–Cp5	2.060 (9)	M3–B1	1.998 (6)
M2–B1	1.993 (8)	M3–B4	2.126 (7)
M2–B5	2.129 (7)	M3–B6	2.090 (8)
M2–B6	2.097 (6)	M3–B7	2.102 (7)
M2–B9	2.109 (7)		
II. Distances in Cyclopentadienyl Rings			
Cp1–Cp2	1.315 (15)	Cp6–Cp7	1.293 (19)
Cp1–Cp5	1.304 (15)	Cp6–Cp10	1.281 (19)
Cp2–Cp3	1.360 (17)	Cp7–Cp8	1.310 (18)
Cp3–Cp4	1.393 (18)	Cp8–Cp9	1.322 (20)
Cp4–Cp5	1.302 (17)	Cp9–Cp10	1.303 (18)
III. Boron–Boron Distances			
B1–B4	1.750 (10)	B5–B9	1.803 (13)
B1–B5	1.720 (11)	B6–B7	1.949 (10)
B4–B5	1.820 (12)	B6–B9	1.947 (10)
B4–B7	1.745 (11)	B7–B8	1.790 (11)
B4–B8	1.771 (13)	B8–B9	1.808 (12)
B5–B8	1.781 (11)		
IV. Boron–Carbon Distances			
B6–C10	1.582 (9)	B8–C10	1.600 (11)
B7–C10	1.591 (11)	B9–C10	1.584 (9)
V. Carbon–Hydrogen Distances			
C10–CH10	0.95 (5)	Cp6–CpH6	0.71 (6)
Cp1–CpH1	0.85 (6)	Cp7–CpH7	0.70 (6)
Cp2–CpH2	0.79 (6)	Cp8–CpH8	0.72 (6)
Cp3–CpH3	0.82 (6)	Cp9–CpH9	0.86 (5)
Cp4–CpH4	0.78 (7)	Cp10–CpH10	0.73 (6)
Cp5–CpH5	0.71 (6)		
VI. Boron–Hydrogen Distances			
B1–BH1	1.06 (5)	B7–BH7	0.96 (5)
B4–BH4	0.99 (6)	B8–BH8	1.10 (5)
B5–BH5	1.00 (5)	B9–BH9	1.15 (6)
B6–BH6	1.00 (5)		

[a] See footnote *a* of Table I.

Table IV. Average Bond Lengths

Atoms	No.	Range,[a] Å	Average,[b] Å
M–C	10	2.018 (10)–2.060 (9)	2.039 (13)
M–B	8	1.993 (8)–2.129 (7)	2.08 (5)
C–C	10	1.281 (19)–1.393 (18)	1.32 (3)
B–B	11	1.720 (11)–1.949 (10)	1.81 (8)
B–C	4	1.582 (9)–1.600 (11)	1.589 (8)
C–H	11	0.70 (6)–0.95 (5)	0.78 (8)
B–H	7	0.96 (5)–1.15 (6)	1.04 (7)

[a] See footnote *a* of Table I. [b] Esd's for average bond lengths were calculated using the internal routine of an HP-45 calculator.

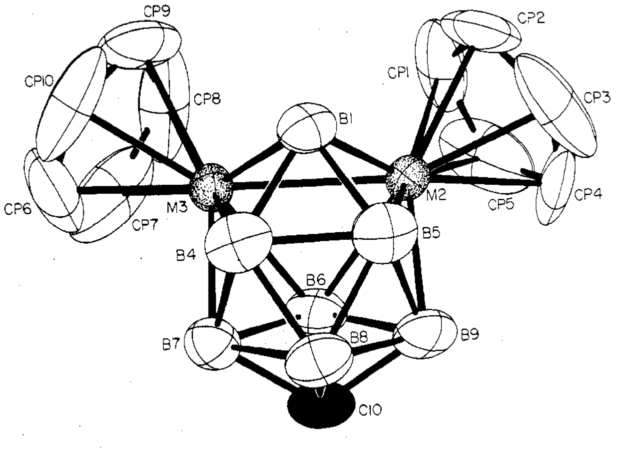

Figure 1.

located. Idealized positions for the cyclopentadienyl hydrogen atoms and for H9 were calculated, and the positions of all hydrogen atoms were refined in subsequent least-squares cycles. The position of the carbon atom was identified by short bond distances to its neighbors and its small temperature factor when refined as a boron atom. No distinction could be made between the two metal sites and therefore they were both assigned scattering factors which corresponded to the average of the nickel and cobalt scattering factors. In the final refinement, the positions of all atoms and anisotropic thermal parameters for all nonhydrogen atoms were refined. The temperature factors for the hydrogen atoms were set at 2.0. This refinement converged to $R = 4.7\%$.

The programs used in this structure determination, the scattering factors, and the refinement techniques were the same as those used in the preceding paper.[1]

The final observed atomic fractional coordinates are collected in Table I. Anisotropic thermal parameters are presented in Table II. The final observed calculated structure factors are available.[7]

Table V. Interatomic Angles[a]

Atoms 1,2,3	Angle, deg	Atoms 1,2,3	Angle, deg
I. Angles around Metals			
A. C_5H_5-M-C_5H_5			
Cp1-M2-Cp2	37.4 (4)	Cp6-M3-Cp7	37.2 (5)
Cp2-M2-Cp3	38.9 (5)	Cp7-M3-Cp8	37.6 (5)
Cp3-M2-Cp4	40.0 (5)	Cp8-M3-Cp9	37.9 (6)
Cp4-M2-Cp5	37.1 (5)	Cp9-M3-Cp10	37.3 (5)
Cp5-M2-Cp1	37.0 (4)	Cp10-M3-Cp6	36.9 (6)
Cp1-M2-Cp3	64.0 (4)	Cp6-M3-Cp8	61.3 (5)
Cp3-M2-Cp5	64.5 (5)	Cp8-M3-Cp10	62.0 (5)
Cp2-M2-Cp4	64.4 (5)	Cp7-M3-Cp9	63.8 (5)
Cp2-M2-Cp5	62.9 (4)	Cp6-M3-Cp9	62.1 (5)
Cp4-M2-Cp1	62.6 (4)	Cp7-M3-Cp10	62.9 (5)
B. C_5H_5-M-CB_7H_8			
Cp1-M2-B1	113.7 (5)	Cp6-M3-B1	140.3 (9)
Cp1-M2-B5	153.9 (6)	Cp6-M3-B4	113.2 (6)
Cp1-M2-B6	118.0 (5)	Cp6-M3-B6	120.8 (8)
Cp1-M2-B9	152.0 (6)	Cp6-M3-B7	95.0 (4)
Cp2-M2-B1	96.6 (4)	Cp7-M3-B1	160.1 (7)
Cp2-M2-B5	118.1 (5)	Cp7-M3-B4	145.7 (9)
Cp2-M2-B6	155.4 (6)	Cp7-M3-B6	97.7 (4)
Cp2-M2-B9	144.4 (6)	Cp7-M3-B7	106.2 (7)
Cp3-M2-B1	114.1 (6)	Cp8-M3-B1	123.2 (8)
Cp3-M2-B5	102.3 (3)	Cp8-M3-B4	164.1 (8)
Cp3-M2-B6	147.0 (7)	Cp8-M3-B6	110.1 (8)
Cp3-M2-B9	106.1 (6)	Cp8-M3-B7	142.7 (9)
Cp4-M2-B1	154.0 (7)	Cp9-M3-B1	97.1 (4)
Cp4-M2-B6	108.9 (6)	Cp9-M3-B6	145.7 (9)
Cp4-M2-B9	92.6 (4)	Cp9-M3-B7	154.0 (7)
Cp5-M2-B1	150.0 (6)	Cp10-M3-B1	106.1 (7)
Cp5-M2-B5	158.9 (7)	Cp10-M3-B4	104.2 (4)
Cp5-M2-B6	97.0 (3)	Cp10-M3-B6	157.7 (8)
Cp5-M2-B9	115.1 (6)	Cp10-M3-B7	116.9 (8)
C. Boron-Metal-Boron			
B1-M2-B5	49.2 (3)	B1-M3-B4	50.1 (3)
B1-M2-B6	95.5 (3)	B1-M3-B6	95.6 (3)
B1-M2-B9	94.4 (3)	B1-M3-B7	93.6 (3)
B5-M2-B6	85.9 (3)	B4-M3-B6	85.7 (3)
B5-M2-B9	50.4 (3)	B4-M3-B7	48.7 (3)
B6-M2-B9	55.1 (3)	B6-M3-B7	55.4 (3)

Atoms 1,2,3	Angle, deg	Atoms 1,2,3	Angle, deg
D. Boron-Metal-Metal			
B1-M2-M3	52.2 (2)	B6-M2-M3	54.1 (2)
B5-M2-M3	81.2 (2)	B9-M2-M3	92.8 (2)
E. Carbon-Metal-Metal			
Cp1-M2-M3	103.5 (3)	Cp4-M2-M3	152.2 (6)
Cp2-M2-M3	120.5 (4)	Cp5-M2-M3	117.4 (5)
Cp3-M2-M3	158.2 (7)		
II. B-B-B Angles			
B4-B1-B5	63.3 (8)	B7-B6-B9	85.6 (5)
B1-B4-B5	57.6 (4)	B4-B7-B6	101.6 (5)
B1-B4-B7	117.6 (5)	B4-B7-B8	60.1 (5)
B1-B4-B8	113.5 (6)	B6-B7-B8	90.0 (5)
B5-B4-B7	104.1 (6)	B4-B8-B5	61.7 (4)
B5-B4-B8	59.5 (8)	B4-B8-B7	58.7 (5)
B7-B4-B8	61.2 (5)	B4-B8-B9	104.7 (5)
B1-B5-B4	59.2 (4)	B5-B8-B7	103.8 (5)
B1-B5-B8	114.5 (6)	B5-B8-B9	60.3 (5)
B1-B5-B9	117.3 (5)	B7-B8-B9	94.8 (5)
B4-B5-B8	58.9 (5)	B5-B9-B8	59.1 (5)
B8-B5-B9	60.6 (5)	B6-B9-B8	89.6 (5)
III. C-B-B Angles			
C10-B6-B7	52.3 (4)	C10-B8-B5	107.2 (6)
C10-B6-B9	52.1 (4)	C10-B8-B7	55.6 (4)
C10-B7-B4	108.3 (6)	C10-B8-B9	55.0 (4)
C10-B7-B6	51.9 (4)	C10-B9-B5	106.9 (7)
C10-B7-B8	56.1 (5)	C10-B9-B6	52.0 (4)
C10-B8-B4	106.7 (6)	C10-B9-B8	55.8 (4)
IV. B-C-B Angles			
B6-C10-B7	75.8 (5)	B7-C10-B8	68.3 (5)
B6-C10-B8	112.6 (5)	B7-C10-B9	113.0 (6)
B6-C10-B9	75.9 (4)	B8-C10-B9	69.2 (5)
V. Cyclopentadienyl Ring Angles			
Cp2-Cp1-Cp5	109.8 (12)	Cp7-Cp6-Cp10	111.0 (13)
Cp1-Cp2-Cp3	108.3 (10)	Cp6-Cp7-Cp8	104.8 (13)
Cp2-Cp3-Cp4	104.4 (9)	Cp7-Cp8-Cp9	110.3 (13)
Cp3-Cp4-Cp5	108.3 (13)	Cp8-Cp9-Cp10	105.3 (12)
Cp4-Cp5-Cp1	109.1 (12)	Cp9-Cp10-Cp6	108.6 (14)

[a] See footnote *a* of Table I.

Molecular Structure and Discussion

Intramolecular distances and their estimated standard deviations (esd's) are listed in Table III. Average bond distances, with their root-mean-square deviations, are collected in Table IV. The individual bond angles and their associated esd's are presented in Table V. The structure of $(C_5H_5)_2NiCoCB_7H_8$ is shown in Figure 1, which also illustrates the numbering system employed.[8]

The structure of the complex may be described as a distorted bicapped square antiprism, a 10-vertex closed polyhedron comprised of seven boron, one carbon, one cobalt, and one nickel atom vertices. The carbon and boron atoms are further bonded to terminal hydrogen atoms, while the metal vertices are attached to η-cyclopentadienyl ligands. The metals occupy adjacent equatorial positions on the polyhedral framework, 2.4492 (11) Å apart, while the apical positions are occupied by one boron atom and the carbon atom. The metals reside in the same equatorial belt, the belt closest to the apical boron atom and furthest removed from the apical carbon atom. The positions occupied by the metals are totally equivalent in the polyhedron, and there is consequent random orientation of the two metals such that specification of the unique positions of the cobalt or nickel vertices is impossible. Instead, an averaged "half-nickel, half-cobalt" atom is seen at those two sites. The polyhedron exhibits mirror symmetry; the mirror plane, which includes atoms B1, B6, B8, and C10, is not crystallographically required but related bond distances are equal within three standard deviations.

This compound is a close analogue of the bimetallocarborane $(C_5H_5)_2Co_2C_2B_6H_8$, whose structure has been previously reported.[6] This latter species has the same overall geometry, with the two cobalt atoms occupying different equatorial belts (still in adjacent polyhedral positions at a distance of 2.489 (1) Å) and the two carbon atoms at the two low-coordinate apical positions. Rationalizations of the energetic relationship between these two geometries are complicated by the observation that while $(C_5H_5)Co_2C_2B_6H_8$ thermally rearranges to give an isomer with nonadjacent metal vertices, the isomer of $(C_5H_5)CoNiCB_7H_8$ studied here is stable to thermal rearrangement at 450 °C. Both $(C_5H_5)_2Co_2C_2B_6H_8$ and $(C_5H_5)_2NiCoCB_7H_8$ fit the theoretical models of *closo*-metallocarboranes[9] in that they are constituted of $n = 10$ polyhedral atoms and $2n + 2$ or 22 framework electrons. Another 10-vertex complex $(C_5H_5)_2Fe_2C_2B_6H_8$, whose structure was recently reported,[10] is two electrons short of the $2n + 2$ rule and exhibits major distortion from the idealized closo structure of a bicapped square antiprism. The symmetrical structure and lack of distortion (other than that produced by the presence of heteroatoms) found for $(C_5H_5)_2NiCoCB_7H_8$ is good evidence for the validity of the electron-counting scheme and lends further justification to the idea previously put forth[9,11] that $\{C_5H_5Co\}$ is electronically equivalent to $\{BH\}$ and that $\{C_5H_5Ni\}$ is equivalent to a polyhedral {CH} group, for similar geometries are observed in the electronically similar complexes $(C_5H_5)_2NiCoCB_7H_8$, $(C_5H_5)_2Co_2C_2B_6H_8$,[6] $(CoC_2B_7H_9)_2^-$,[12] $C_2B_8H_{10}$,[13] and $B_{10}H_{10}^{2-}$.[14] Within experimental errors, all equivalent bond distances are the same in this series of compounds.[15]

Although it is impossible to discern between the cobalt and nickel atoms, it is interesting that the metal–metal distance is significantly shorter than is the Co–Co distance in $(C_5H_5)_2Co_2C_2B_6H_8$. It should be noted that "tropical"[12] bond distances in bicapped square antiprisms are generally found to be longer than "equatorial" bond distances, thus diminishing the significance of this observation.

The cyclopentadienyl rings, while exhibiting the large librational motion typical in compounds of this type studied at room temperature, exhibit D_{5h} symmetry, as expected. The metal–carbon distances to the cyclopentadienyl rings are again equal within experimental error, further establishing the positional disorder of the metals.

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Registry No. 2,3-(η-C_5H_5)$_2$-(2,3)-NiCo-10-CB_7H_8, 57483-40-6.

Supplementary Material Available: A listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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Notes

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$[(C_6H_5)_4As]_2[Ni(Se_2C{=}C(CN)_2)_3]$, a New Ni(IV) Chelate with an Unsaturated 1,1-Diselenolate Ligand

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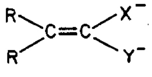
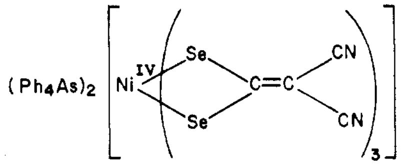
Usually chelates with selenium donor atoms are more difficult to prepare than the analogous sulfur compounds.[1] We report the preparation of the Ni(IV) tris chelate of isomaleonitrilediselenolate which was isolated as the tetraphenylarsonium salt. Curiously, the corresponding sulfur chelate could not be prepared applying the same conditions. Considerable work has been devoted to the stabilization of high formal oxidation states of transition-metal ions by unsaturated sulfur or selenium donor ligands like 1,2-dichalcogenolenes[2] or dichalcogenocarbamates.[3] It is noteworthy, however, that only two examples are known up to now with a 1,1-disubstituted ethylene dichalcogenolate (**1**). Coucouvanis and co-workers prepared the Cu(III) bis chelate $[Cu(ded)_2]^-$ and the Fe(IV) tris chelate $[Fe(ded)_3]^{2-}$ ($R = COOC_2H_5$; $X = Y = S$).[4,5] However, the isolation of Ni species with high formal oxidation states was unsuccessful. Obviously, substitution of the sulfur donor atoms by selenium facilitates the oxidation and enables the isolation of the Ni(IV) complex $(Ph_4As)_2[Ni(i\text{-mns})_3]$[6] (**2**) with R = CN and X = Y = Se.



1

X = Y = S; Se
X = S; Y = Se



2

Experimental Section

Physical Measurements. Electronic spectra were recorded on a Specord spectrophotometer (VEB Carl Zeiss, Jena). Infrared spectra from 400 to 3500 cm^{-1} in KBr were recorded using a UR 20 spectrometer (VEB Carl Zeiss, Jena). Molar conductivities were measured at 10^{-4} M in CH_3NO_2 (20 °C) using a conductivity bridge Type LM 301 (VEB Hydromat Bannewitz).

The X-band ESR spectra were recorded on a Varian E 112 spectrometer.

Voltammetric measurements were made in acetonitrile solution on a Radiometer (Copenhagen) PO 4 instrument. The concentration of the supporting electrolyte ($NaClO_4$) was 10^{-1} M. A rotating Pt electrode (1500 rpm) was used.

Preparation of the Complexes. $(n\text{-}Bu_4N)_2[Ni(i\text{-mns})_2]$.[6] $K_2Se_2C{=}C(CN)_2$,[7] 3.12 g (0.01 mol), was dissolved in 30 mL of methanol. Dropwise addition of a solution of $NiCl_2 \cdot 6H_2O$, 1.188 g (0.005 mol), in 20 mL of methanol, yields a red-brown complex solution to which tetra-*n*-butylammonium bromide, 3.3 g (0.01 mol), dissolved in 20 mL of methanol, was added. A red precipitate was obtained and filtered. The complex salt could be recrystallized by dissolving in acetone, adding 2-propanol, and reducing the volume by evaporation. Yield 60%; mp 198 °C; Λ_M 189 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd: C, 47.49; H, 7.17; N, 8.31; Se, 31.22. Found: C, 48.31; H, 7.07; N, 8.02; Se, 31.30. Electronic spectrum in acetonitrile solution (ν_{max} in cm^{-1} × 10^3, log ϵ in parentheses): 16.3 (2.96), 20.1 (4.14), 21.7 (3.89 sh), 26.9 (4.57), 31.9 (4.39), 33.5 (4.42).

$(Ph_4As)_2[Ni(i\text{-mns})_2]$. This compound was prepared according to above using tetraphenylarsonium chloride. It could be recrystallized from acetonitrile/2-propanol in about 50% yield; mp 220–222 °C;

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