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(31) In going from $[FeS(SC_6H_5)]_4{}^{2-}$ to its trianion,[7c] the Fe_4S_4 core (of idealized D_{2d} symmetry in both cases) changes from a slightly compressed cubane-like structure (with eight long and four short Fe–S bonds of 2.296 (av) and 2.267 (av) Å, respectively) to a somewhat elongated configuration (with four long and eight short Fe–S bonds of 2.351 (av) and 2.288 (av) Å, respectively). This can be described in terms of an axial expansion along the $\bar{4}$ axis resulting in the elongation of the four short Fe–S bonds in the dianion by 0.08 Å to the four long ones in the trianion. On the other hand, the increases in average Fe–S and Fe–Fe distances, in going from the dianion to the trianion, amount to only 0.025 and 0.007 Å, respectively.

Neutron Diffraction Analysis of the Structure of $H_3Ni_4(C_5H_5)_4$

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Abstract: The structure of $H_3Ni_4Cp_4$ ($Cp = \eta^5\text{-}C_5H_5$), an unusual paramagnetic metal cluster complex, has been analyzed by single-crystal neutron diffraction techniques at low temperature (81 K). As predicted from an earlier X-ray diffraction study, the hydrogen atoms bridge three faces of the Ni_4 tetrahedral core. Although the Ni_4 cluster itself is an essentially undistorted tetrahedron [with Ni-Ni edges of 2.469 (6) Å], the individual Ni_3H linkages are unsymmetrical. The H atoms are slightly displaced away from the unique apical Ni atom: Ni-H distances involving the apical Ni atom average to 1.716 (3) Å, while those involving the basal Ni atoms average to 1.678 (6) Å. The overall mean Ni-H distance is 1.691 (8) Å, and the H atoms are situated an average of 0.907 (6) Å above the Ni_3 faces. Other average distances and angles in the molecule follow: H···H = 2.316 (6) Å, Ni-C = 2.132 (5) Å, Ni-H-Ni = 93.9 (3)°, H-Ni-H = 86.1 (6)°. The title compound crystallizes in space group $C2/c$ with the following cell parameters at 81 K: $a = 28.312$ (13) Å, $b = 9.234$ (5) Å, $c = 14.783$ (7) Å, $\beta = 103.35$ (2)°, $V = 3760$ (3) Å^3, $Z = 8$. The structure has been refined to yield final agreement factors of $R_F = 0.107$ and $R_{wF} = 0.067$ for 2616 reflections having $I > 1.5\ \sigma(I)$.

Introduction

Tetrakis(η^5-cyclopentadienyl)tetranickel trihydride is one of the few known examples of polynuclear organometallic complexes not containing carbonyl ligands. The compound was isolated from the reaction of CpNi(NO) ($Cp = \eta^5$-cyclopentadienyl) with $AlCl_3$ and $LiAlH_4$.[2] The presence of the three hydride ligands was inferred from the mass spectrum of the complex which showed ions resulting from the loss of one, two, and three H atoms. A particularly interesting aspect of $H_3Ni_4Cp_4$ is its electronic configuration. The unknown species Ni_4Cp_4 would have the expected "closed-shell" 60-electron configuration[3] and would be diamagnetic. Such a 60-electron species is in fact known as $H_4Co_4Cp_4$.[4] However, $H_3Ni_4Cp_4$ has three additional electrons which are all unpaired,[2] making the compound a rare example of a paramagnetic metal cluster complex. Spectral data give no indication of the presence of the hydride ligands,[2] but IR spectra frequently do not show absorptions due to stretching frequencies from bridging hy-

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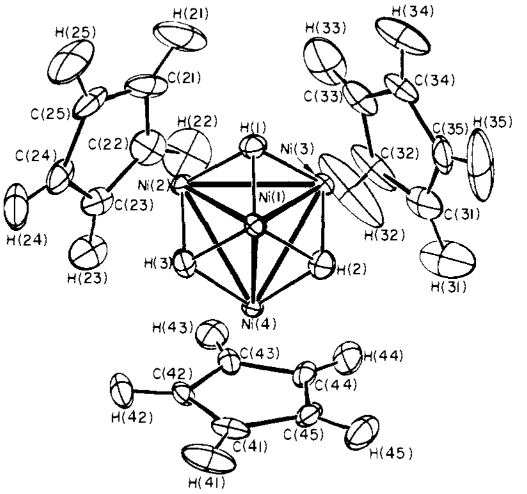

Figure 1. A molecular plot[43] of $H_3Ni_4Cp_4$, viewed along the approximate threefold axis of the molecule. One of the Cp rings has been removed for clarity. In this and all other plots, 50% probability ellipsoids are shown.

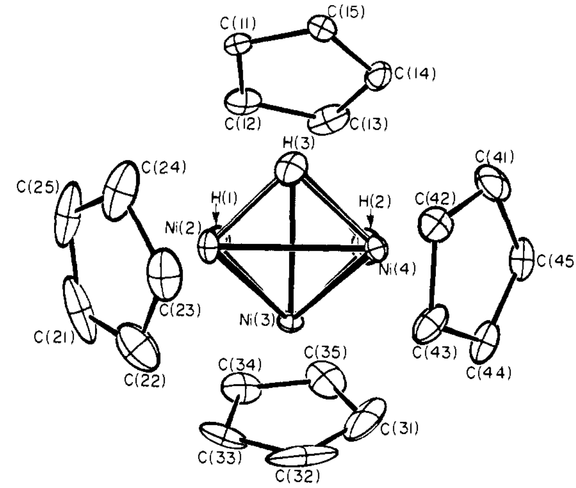

Figure 2. An alternative view of the $H_3Ni_4Cp_4$ molecule, showing all four Cp rings. Ni(1) is completely hidden behind H(3). The H atoms on the Cp rings have been removed for clarity.

Table I. Experimental Quantities and Refinement Parameters

empirical formula	$H_3Ni_4(C_5H_5)_4$	
mol wt	498.2	
space group	$C2/c$ ($Z = 8$)	
unit cell parameters	room temp[a]	81 (1) K[b]
a	28.32(2) Å	28.312(13) Å
b	9.23(1)°	9.234(5)°
c	15.03(1)°	14.783(7)°
β	102.77(8)°	103.35(2)°
unit cell volume	3832(6) $Å^3$	3760(3) $Å^3$
wavelength		1.0183(1) Å
sample volume		12.5 mm^3
calc density		1.76 g cm^{-3}
data collection limit ($\sin \theta/\lambda$)		0.68 $Å^{-1}$
absorption coefficient (μ)[c]		1.94 cm^{-1}
max and min transmission coefficients		0.83, 0.57
total no. of reflections measured		10 840
no. of symmetry-independent reflections		5236
agreement factor for data averaging[d]		0.12
N_0 (no. of reflections used in structure analysis)		2616
N_v (no. of variable parameters)		425
$R_F = \Sigma\|F_o - \|F_c\|\|/\Sigma F_o$		0.107
$R_{wF} = \{\Sigma w(F_o - \|F_c\|)^2/\Sigma w F_o^2\}^{1/2}$		0.067
$S = \{\Sigma w(F_o - \|F_c\|)^2/(N_o - N_v)\}^{1/2}$		1.84
g' (extinction parameter)		0.64(8)

[a] Reference 2b. [b] Refinement based on the setting angles of 32 carefully centered reflections. [c] Calculated assuming an incoherent scattering cross section for hydrogen of 40 b. [d] ($R_c = \Sigma_{hkl}[\Sigma_{i=1}^{n}|F_{oi}^2 - \langle F_o^2\rangle|]/\Sigma_{hkl}n|\langle F_o^2\rangle|$).

drides. Moreover, the paramagnetic properties of $H_3Ni_4Cp_4$ prevent the hydride ligands from being detected in the NMR spectrum.

An X-ray investigation of $H_3Ni_4Cp_4$ was conducted by Müller, Huttner, and co-workers in 1973.[2] Although the H atoms were not located directly, the authors were able to assign them to face-bridging positions, based on the observation that three of the Cp rings are tilted away from the fourth. Curiously enough, no distortion of the Ni_4 cluster itself was observed. In order to confirm the proposed structure, and to obtain accurate distances and angles associated with the triply bridging hydride ligands, we undertook the neutron diffraction analysis described in this paper.

Experimental Section

Single crystals of $H_3Ni_4Cp_4$ suitable for neutron diffraction work were grown by very slow evaporation (7 days) of a benzene solution at room temperature. The solvent was removed by absorption of the vapor on silica gel in a closed system. Measurements were made at the Brookhaven high flux beam reactor, with an automated four-circle diffractometer operating under the Reactor Experimental Control Facility,[5] and a neutron wavelength of 1.0183 (1) Å (based on KBr, $a = 6.6000$ Å). A platelike specimen of $H_3Ni_4Cp_4$ with a volume of 12.5 mm^3 was mounted on an aluminum pin oriented approximately along the crystallographic (010) direction, and placed in a liquid-nitrogen cooled cryostat. The temperature of a copper block in direct contact with the aluminum pin was monitored periodically and found to be 81 ± 1 K. Some tendency toward split peaks was observed for certain reflections, indicating that the crystal may have developed a slight crack upon cooling. Crystal data,[6] together with other experimental quantities of interest and parameters describing the subsequent least-squares refinements, are given in Table I.

Intensities of Bragg reflections were measured with a $\theta/2\theta$ step-scan technique. For $0 < d^* < 0.65$ $Å^{-1}$, the scan range was given by $\Delta(2\theta) = 2.6°$, with a step size of 0.04°. For $0.65 \leqslant d^* \leqslant 1.39$ $Å^{-1}$, the scan range was varied according to $\Delta(2\theta) = 2.15\ (1 + 1.13 \tan \theta)°$, and the step size varied to give approximately 65 points in each scan. Background corrections were determined by summing the counts for four steps on either end of each scan. Squared observed structure factors were obtained as $F_o^2 = I \sin 2\theta$ and corrected for absorption by a modification of the analytical method of de Meulenaer and Tompa.[7,8] A total of 10 840 measured F_o^2 values were reduced to 5236 unique observations by averaging over the $2/m$ Laue symmetry (13 individual measurements, for which F_o^2 varied by more than 10σ from the mean, were discarded).

Initial atomic positions for the Ni and C atoms were taken from the X-ray results.[2] The H atoms on the Cp rings were placed in calculated positions assuming $d(C-H) = 1.08$ Å, and the three hydride ligands were located in a (neutron) difference-Fourier synthesis. Least-squares refinements were carried out using a modified version of the program by Busing, Martin, and Levy,[9] minimizing the quantity $\sum w(F_o - k|F_c|)^2$. Weights were chosen as $w = 1/\sigma^2(F_o)$, where $\sigma^2(F_o) = [\sigma_{count}^2(F_o^2) + (0.02F_o^2)^2]/4F_o^2$. In the later stages of refinement, all reflections with $F_o^2 > 1.5\sigma_{count}(F_o^2)$ were included in the analysis. The total of 425 variable parameters included positional and anisotropic thermal parameters for all atoms, a scale factor (k), and an extinction correction parameter, g'.[10] The effects of extinction were moderate, and the most significant correction factor was 0.82 (on F) for the $(6\ 0\ \bar{2})$ reflection. Parameters were blocked into groups of

Table II. Fractional Atomic Positional and Thermal Parameters[a] for $H_3Ni_4Cp_4$

atom	10^4x	10^4y	10^4z	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Ni(1)	1390(1)	4836(2)	0247(1)	32(1)	24(1)	26(1)	0(1)	6(1)	−3(1)
Ni(2)	0820(1)	3170(3)	0787(1)	26(1)	41(1)	32(1)	6(1)	11(1)	14(1)
Ni(3)	1118(1)	2579(3)	−0604(1)	34(1)	26(1)	23(1)	−2(1)	3(1)	−1(1)
Ni(4)	1671(1)	2464(3)	0955(1)	26(1)	33(1)	26(1)	1(1)	3(1)	3(1)
H(1)	0848(3)	3986(9)	−0218(5)	39(4)	47(5)	46(4)	8(4)	9(3)	8(3)
H(2)	1648(3)	3284(10)	−0063(5)	49(4)	66(6)	52(4)	0(5)	18(4)	5(4)
H(3)	1362(3)	3914(9)	1238(4)	56(5)	59(6)	33(3)	8(5)	13(3)	−1(3)
C(11)	1278(2)	7088(4)	0486(3)	44(2)	33(3)	55(2)	1(2)	6(2)	−16(2)
C(12)	1211(2)	6827(5)	−0483(3)	79(3)	32(3)	46(2)	−1(3)	4(2)	9(2)
C(13)	1668(2)	6282(5)	−0621(3)	115(5)	40(3)	71(3)	−15(3)	64(4)	2(2)
C(14)	1999(2)	6203(5)	0264(4)	43(3)	41(3)	113(4)	−5(3)	37(3)	−15(3)
C(15)	1756(2)	6691(5)	0943(3)	39(2)	46(3)	66(3)	−6(2)	3(2)	−18(2)
H(11)	1017(3)	7451(12)	0848(7)	63(6)	80(8)	95(7)	22(7)	20(5)	−17(6)
H(12)	0884(5)	7009(11)	−1005(6)	142(11)	52(7)	69(6)	9(7)	−34(6)	15(5)
H(13)	1729(6)	5976(12)	−1288(8)	248(17)	70(8)	111(9)	−22(10)	141(11)	−13(7)
H(14)	2364(4)	5830(17)	0381(11)	45(6)	122(12)	250(15)	−3(8)	69(8)	−29(11)
H(15)	1911(4)	6734(13)	1647(7)	79(7)	86(8)	88(7)	4(6)	−24(5)	−43(6)
C(21)	0070(2)	2705(11)	0508(4)	30(3)	199(10)	100(5)	−14(5)	8(3)	74(6)
C(22)	0337(2)	1543(8)	0991(4)	72(4)	105(6)	104(5)	−44(5)	36(4)	19(5)
C(23)	0591(2)	2018(6)	1867(3)	54(3)	80(4)	76(4)	5(3)	30(3)	47(3)
C(24)	0490(2)	3485(7)	1948(4)	88(4)	107(6)	72(4)	44(4)	58(3)	50(4)
C(25)	0162(2)	3928(8)	1115(4)	67(4)	121(6)	107(5)	58(5)	59(4)	72(5)
H(21)	−0155(4)	2688(26)	−0185(9)	54(7)	345(30)	117(10)	−55(13)	−21(7)	90(15)
H(22)	0365(7)	0374(15)	0699(13)	202(21)	59(10)	218(18)	−37(12)	73(15)	22(11)
H(23)	0823(4)	1367(15)	2383(8)	99(8)	126(11)	101(7)	25(8)	43(7)	80(8)
H(24)	0634(5)	4169(14)	2529(7)	162(14)	110(11)	69(7)	54(10)	65(8)	13(7)
H(25)	−0013(6)	4979(19)	0952(11)	171(16)	184(18)	179(14)	139(15)	101(13)	126(13)
C(31)	1365(3)	1103(10)	−1452(4)	139(8)	133(9)	71(5)	78(7)	−21(5)	−68(5)
C(32)	0966(4)	0526(6)	−1182(3)	268(13)	24(3)	49(4)	−12(5)	−35(5)	−5(2)
C(33)	0571(2)	1384(6)	−1549(3)	102(4)	65(4)	46(2)	−51(4)	−8(3)	−9(3)
C(34)	0723(2)	2487(6)	−2036(3)	91(4)	62(4)	34(2)	−3(4)	−16(2)	5(2)
C(35)	1214(2)	2297(8)	−1976(3)	86(4)	134(6)	41(2)	−26(5)	30(3)	−35(3)
H(31)	1732(8)	0668(30)	−1277(13)	242(25)	410(44)	181(18)	255(31)	−79(17)	−199(24)
H(32)	0963(12)	−0475(16)	−0753(9)	666(51)	48(11)	82(9)	−87(18)	−39(15)	3(7)
H(33)	0220(6)	1182(24)	−1459(9)	127(12)	271(25)	105(10)	−122(16)	17(9)	−27(12)
H(34)	0500(6)	3358(15)	−2403(8)	179(14)	99(11)	86(7)	4(10)	−51(8)	36(7)
H(35)	1435(7)	3091(24)	−2268(10)	244(20)	303(25)	127(11)	−177(19)	143(14)	−88(14)
C(41)	2338(2)	2405(6)	1990(3)	50(3)	66(4)	62(3)	−2(3)	−23(2)	1(3)
C(42)	1970(2)	1645(5)	2318(2)	51(2)	52(3)	25(2)	7(2)	3(2)	5(2)
C(43)	1806(2)	0472(5)	1722(2)	69(3)	50(3)	34(2)	29(3)	11(2)	8(2)
C(44)	2072(2)	0462(6)	1016(3)	52(3)	59(4)	53(3)	27(3)	21(2)	17(2)
C(45)	2396(1)	1630(6)	1170(3)	35(2)	72(4)	54(2)	17(3)	16(2)	15(2)
H(41)	2520(5)	3377(15)	2319(8)	87(8)	98(10)	109(8)	−44(8)	−44(6)	10(7)
H(42)	1821(4)	1916(11)	2915(5)	113(8)	77(7)	38(4)	40(6)	21(4)	6(4)
H(43)	1541(4)	−0212(12)	1771(6)	77(8)	73(8)	79(7)	18(7)	16(6)	24(6)
H(44)	2033(4)	−0286(12)	0494(7)	98(8)	82(8)	78(6)	50(7)	28(6)	8(6)
H(45)	2644(4)	1895(13)	0737(7)	60(6)	115(9)	100(7)	14(6)	41(6)	35(7)

[a] Thermal parameters are in units of Å^2 and have the form exp $[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] The numbering of Ni(2) and Ni(4), as well as their attached Cp rings, has been interchanged compared to that given in ref 2b. This has been done to ensure that atom numbers increase upon clockwise rotation when viewed along the threefold axis with Ni(1) pointing up.

approximately 100 variables, in order to reduce the expense of the computations, and these blocks refined alternately to convergence. Neutron scattering lengths used are $b_H = -0.374$, $b_C = 0.6648$, and $b_{Ni} = 1.03$ (all $\times 10^{-12}$ cm).[11] Lists of observed and calculated structure factors are available (see paragraph at end of paper regarding supplementary material). Final agreement factors and the mean quadratic error ("goodness of fit") are given in Table I. A final difference synthesis was essentially featureless.

Discussion

Final atomic positional and thermal parameters are listed in Table II, and selected interatomic distances and angles given in Table III.[12] The overall molecular geometry is shown in Figures 1 and 2. In agreement with the results predicted from the earlier X-ray structure determination,[2] the three hydride ligands are situated on three of the four faces of the Ni_4 tetrahedron to give the H_3Ni_4 core approximate C_{3v} symmetry. The geometry of the H_3Ni_4 cluster (Figure 3) may also be

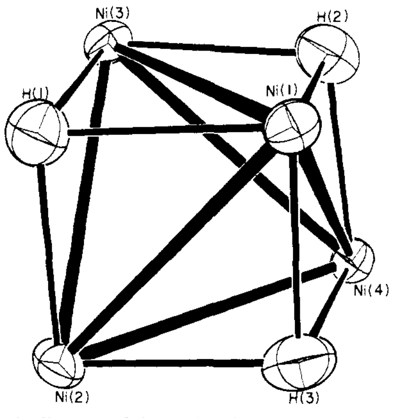

Figure 3. The H_3Ni_4 core of the molecule, in a view emphasizing its resemblance to a cube with one corner vacant.

Table III. Selected Interactomic Distances (Å) and Angles[a] (deg)

Ni(1)-Ni(2)	2.490(3)	Ni(2)-Ni(3)	2.458(3)
Ni(1)-Ni(3)	2.464(3)	Ni(2)-Ni(4)	2.454(3)
Ni(1)-Ni(4)	2.478(3)	Ni(3)-Ni(4)	2.471(3)
	mean 2.477(8)		mean 2.461(5)
Ni(1)-H(1)	1.720(8)	H(1)···H(2)	2.317(11)
Ni(1)-H(2)	1.718(9)	H(1)···H(3)	2.305(10)
Ni(1)-H(3)	1.711(7)	H(2)···H(3)	2.326(9)
	mean 1.716(3)		mean 2.316(6)
Ni(2)-H(1)	1.684(7)	Ni(1)-H(1)-Ni(2)	94.0(4)
Ni(2)-H(3)	1.674(8)	Ni(1)-H(1)-Ni(3)	93.1(4)
Ni(3)-H(1)	1.674(8)	Ni(1)-H(2)-Ni(3)	93.6(4)
Ni(3)-H(2)	1.661(9)	Ni(1)-H(2)-Ni(4)	93.9(4)
Ni(4)-H(2)	1.672(8)	Ni(1)-H(3)-Ni(2)	94.7(3)
Ni(4)-H(3)	1.704(8)	Ni(1)-H(3)-Ni(4)	93.0(3)
	mean 1.678(6)		mean 93.7(3)
Ni(2)-Ni(1)-Ni(3)	59.5(1)	Ni(1)-Ni(2)-Ni(3)	59.7(1)
Ni(2)-Ni(1)-Ni(4)	59.2(1)	Ni(1)-Ni(2)-Ni(4)	60.2(1)
Ni(3)-Ni(1)-Ni(4)	60.0(1)	Ni(1)-Ni(3)-Ni(2)	60.8(1)
	mean 59.6(2)	Ni(1)-Ni(3)-Ni(4)	60.3(1)
		Ni(1)-Ni(4)-Ni(2)	60.7(1)
Ni(3)-Ni(2)-Ni(4)	60.4(1)	Ni(1)-Ni(4)-Ni(3)	59.7(1)
Ni(2)-Ni(3)-Ni(4)	59.7(1)		mean 60.2(2)
Ni(2)-Ni(4)-Ni(3)	59.9(1)		
	mean 60.0(2)		
H(1)-Ni(1)-H(2)	84.7(4)	Ni(2)-H(1)-Ni(3)	94.1(4)
H(1)-Ni(1)-H(3)	84.4(4)	Ni(3)-H(2)-Ni(4)	95.7(4)
H(2)-Ni(1)-H(3)	85.4(4)	Ni(2)-H(3)-Ni(4)	93.1(4)
	mean 84.8(3)		mean 94.3(8)
H(1)-Ni(2)-H(3)	86.7(4)		
H(1)-Ni(3)-H(2)	88.0(4)		
H(2)-Ni(4)-H(3)	87.1(4)		
	mean 87.3(4)		
Cp(1)-X-Cp(2)[b]	117.5(2)	Cp(2)-X-Cp(3)[b]	105.0(2)
Cp(1)-X-Cp(3)[b]	112.3(2)	Cp(2)-X-Cp(4)[b]	103.6(2)
Cp(1)-X-Cp(4)[b]	112.3(2)	Cp(3)-X-Cp(4)[b]	105.1(2)
	mean 114.0(17)		mean 104.6(5)

	n = 1	*n* = 2	*n* = 3	*n* = 4
C(*ni*)-C(*nj*)				
i = 1 *j* = 2	1.423(5)	1.408(10)	1.389(11)	1.431(6)
2 3	1.445(7)	1.399(8)	1.377(10)	1.405(6)
3 4	1.426(7)	1.396(8)	1.373(7)	1.421(5)
4 5	1.415(6)	1.420(7)	1.383(7)	1.400(7)
5 1	1.415(6)	1.428(11)	1.358(9)	1.450(6)
C(*ni*)-H(*ni*)				
i = 1	1.062(10)	1.075(15)	1.088(21)	1.091(14)
2	1.073(12)	1.172(20)	1.122(17)	1.092(9)
3	1.078(10)	1.069(12)	1.050(18)	0.996(14)
4	1.065(12)	1.069(17)	1.088(14)	1.022(13)
5	1.032(11)	1.091(15)	1.114(16)	1.081(10)
Ni(*n*)-C(*ni*)				
i = 1	2.145(5)	2.112(6)	2.080(5)	2.139(5)
2	2.134(5)	2.098(6)	2.083(6)	2.136(4)
3	2.125(5)	2.139(4)	2.138(5)	2.148(5)
4	2.134(5)	2.155(5)	2.156(4)	2.160(5)
5	2.140(5)	2.147(5)	2.123(4)	2.145(6)
∠C-C-C				
at C(*n*1)	109.1(4)	106.6(5)	107.8(6)	105.8(4)
C(*n*2)	106.6(4)	109.4(7)	107.9(5)	109.0(4)
C(*n*3)	108.0(4)	108.1(5)	108.0(6)	108.2(5)
C(*n*4)	108.1(4)	108.1(6)	107.7(6)	108.3(4)
C(*n*5)	108.2(4)	107.8(6)	108.7(6)	108.7(4)
∠H-C-Ni				
at C(*n*1)	122.4(7)	122.5(7)	122.3(8)	123.0(8)
C(*n*2)	124.3(6)	120.4(8)	123.1(7)	122.7(6)
C(*n*3)	123.3(7)	124.8(6)	124.9(8)	122.4(6)
C(*n*4)	124.2(9)	124.5(7)	124.8(8)	125.6(6)
C(*n*5)	124.1(7)	127.9(8)	119.8(8)	124.1(6)
H-C-C				
H(*n*1)-C(*n*1)-C(*n*2)	127.9(6)	127.1(16)	125.8(20)	123.9(8)
H(*n*1)-C(*n*1)-C(*n*5)	122.9(6)	126.4(15)	126.4(20)	130.3(8)
H(*n*2)-C(*n*2)-C(*n*1)	128.1(8)	126.1(11)	126.4(20)	127.5(7)
H(*n*2)-C(*n*2)-C(*n*3)	127.3(7)	124.5(10)	125.7(20)	123.4(7)
H(*n*3)-C(*n*3)-C(*n*2)	124.0(11)	125.8(10)	123.7(13)	126.0(6)
H(*n*3)-C(*n*3)-C(*n*4)	128.0(11)	126.0(10)	128.3(13)	125.8(7)

Table III (*Continued*)

	$n = 1$	$n = 2$	$n = 3$	$n = 4$
H-C-C				
H(n4)-C(n4)-C(n3)	125.0(9)	126.5(8)	126.4(10)	125.0(8)
H(n4)-C(n4)-C(n5)	126.9(9)	125.4(8)	125.9(10)	126.7(7)
H(n5)-C(n5)-C(n1)	127.4(7)	123.9(12)	128.5(15)	126.7(8)
H(n5)-C(n5)-C(n4)	124.4(7)	128.3(12)	122.6(14)	124.7(8)

Overall Mean Values

C-C	1.408(5)	C-C-C	108.0(2)
C-H	1.076(8)	Ni-C-H	123.6(4)
Ni-C	2.132(5)	H-C-C	126.0(3)
Ni-Ni	2.469(6)	Ni-Ni-Ni	60.0(2)
Ni-H	1.691(8)	Ni-H-Ni	93.9(3)
H···H	2.316(6)	H-Ni-H	86.1(6)
Ni-Cp[b,c]	1.763(3)		

[a] Standard deviations of mean values have been calculated as $[\Sigma(x_i - \bar{x})^2/n(n-1)]^{1/2}$, where n is the number of observations. The resulting deviations are to be regarded as rough estimates of uncertainty, in cases where $n = 3$. [b] Cp = center of cyclopentadienyl ring; X = centroid of Ni_4 tetrahedron. [c] Computed from the perpendicular distances from the Ni atoms to the Cp ring planes.

envisaged as a cube with one corner vacant. No indication of disorder of the hydride ligands was found. The substantial elongation of the thermal ellipsoids of the cyclopentadienyl atoms suggests that there is considerable ring motion in the solid state (and possibly also limited disorder of the rings), even at the low temperature of data collection.

In this structure, the apical Ni(1) is unique in that it is bonded to all three H atoms. On this basis, one might predict that those Ni-Ni bonds involving Ni(1) would be somewhat different from the others. However, the two groups of Ni-Ni bonds have mean distances that are almost indistinguishable [2.477 (8) vs. 2.461 (5) Å, see Table III], although the difference is in the expected direction, with bonds involving Ni(1) being very slightly longer on the average. The uniqueness of Ni(1) is manifested more clearly in the Ni-H distances. The average Ni(1)-H distance is 1.716 (3) Å while the average Ni-H distance involving Ni(2), Ni(3), and Ni(4) is 1.678 (6) Å. The H atoms are situated closer to the three basal Ni atoms, perhaps so that the M-H bonding may be equally distributed among all four Ni atoms in the cluster. Another departure of $H_3Ni_4Cp_4$ from tetrahedral symmetry is seen in the positions of the Cp ring centroids, as was first observed in the X-ray structure.[2] If X designates the centroid of the Ni_4 cluster, the average Cp(1)-X-Cp(n)[13] angle is 114 (2)° (n = 2, 3, 4) while the average Cp-X-Cp angle not involving Cp(1) is 105 (1)°. Thus, rings 2, 3, and 4 are bent toward the vacant Ni(2)-Ni(3)-Ni(4) face of the cluster.

The average metal-metal distance in $H_3Ni_4Cp_4$ [2.469 (6) Å] is 0.026 Å shorter than that found at room temperature in nickel metal (2.492 Å).[14] It is, however, considerably longer than the Ni-Ni single bonds in the ligand-bridged molecules $Ni_2Cp_2(PhC{\equiv}CPh)$ (2.33 Å)[15] and $Ni_3Cp_3(CO)_2$ (2.39 Å),[16] and the unbridged Ni-Ni bonds in $K_4[Ni_2(CN)_6]$ (2.32 Å)[17] and $Rb_4[Ni_2(CN)_6]$ (2.29 Å).[18] The length of the Ni-Ni bonds in $H_3Ni_4Cp_4$ may reflect the delocalization of the three excess electrons into low-lying antibonding Ni-centered orbitals. Hoffmann and co-workers have recently carried out extended Hückel calculations on $H_3Ni_4Cp_4$ and related tetrahedral clusters.[19] They have shown that, for the 60-electron Ni_4Cp_4 cluster, the lowest unoccupied molecular orbital is a degenerate set of three low-lying antibonding orbitals of t_1 symmetry, which in $H_3Ni_4Cp_4$ become occupied by the electrons from the H atoms. This bonding picture rationalizes why a fourth H atom may not be added to $H_3Ni_4Cp_4$, and also explains the rather long Ni-Ni distances in the cluster.[20] In fact, the Ni-Ni bond lengths are longer than the nonbonding H···H contact distances, which average 2.316 (6) Å.

It is interesting to speculate where the unpaired electron density may be in $H_3Ni_4Cp_4$. According to Hoffmann's calculations,[19] it should be more or less equally distributed among the four metal atoms. With neutron diffraction, it is possible to study spin densities in paramagnetic systems under the influence of an external aligning field. However, in the present experiment, with no external field, the only effect of the paramagnetic scattering is to increase slightly the incoherent background.

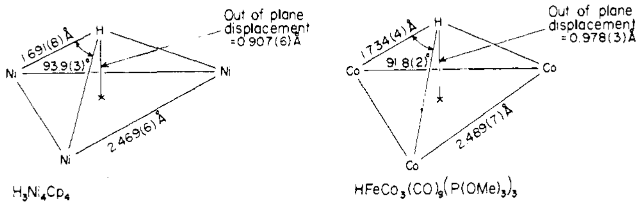

Figure 4. A schematic comparison between the HM_3 fragments of $H_3Ni_4Cp_4$ and $HFeCo_3(CO)_9(P(OMe)_3)_3$ (ref 21). It is suggested that the distances and angles found in these covalent molecules are reliable estimates for those associated with H atoms chemisorbed on metallic surfaces.

The H atoms on $H_3Ni_4Cp_4$ are situated an average of 0.907 (6) Å from the Ni_3 planes (Figure 4). Individual H···Ni_3 distances are 0.911, 0.894, and 0.915 Å for H(1), H(2), and H(3), respectively. Similar bonding situations are found in $HFeCo_3(CO)_9[P(OMe)_3]_3$[21] and $H_4Co_4Cp_4$.[4] In $HFeCo_3(CO)_9[P(OMe)_3]_3$ neutron diffraction measurements show the H atom to be 0.978 (3) Å above the Co_3 face of the cluster (Figure 4), while in $H_4Co_4Cp_4$ the H atoms are found from an X-ray difference-Fourier map to be displaced by an average of 0.8 Å from the faces of the tetrahedron. This difference of ~0.2 Å is consistent with the usual situation in which H atom positions derived from X-ray data yield bond lengths that are found to be systematically short. This effect is generally attributed to the fact that the centroid of electron density associated with a bonded H atom is not located at the nucleus but is displaced somewhat toward the atom(s) to which it is covalently linked.

The average Ni-C distance in $H_3Ni_4Cp_4$ [2.132 (5) Å] falls in the range 2.11-2.14 Å found in other cyclopentadienylnickel complexes (Table IV). The four cyclopentadienyl rings show no systematic deviations from planarity (Table V). The average out-of-plane deviation of the C atoms is only 0.003 Å, while that for the H atoms is 0.025 Å. It has been found that in several π-cyclopentadienyl complexes the ring H atom are systematically distorted toward the metal (as in $FeCp_2$,[22,23] $Fe(C_5H_4COOH)_2$,[24] and $CrCp_2$[22]). However, examples are also known where the distortion is away from the metal [as in

Table IV. Molecular Dimensions (Å) of Various Ni-Cp Complexes

compd	Ni-Cp	Ni-C	ref
$Cp_4Ni_4H_3$	1.763	2.132	present work
Cp_2Ni	1.828	2.196	40
$Cp_4Ni_5S_4$	1.76	2.14	41
$Cp_3Ni_3S_2$	1.75	2.13	42
$Cp_2Ni_2(PhC{\equiv}CPh)$	1.74	2.11	15
$Cp_3Ni_3(CO)_2$	1.74	2.12	16

$HMo_2Cp_2(CO)_4(PMe_2)$[25]]. In some cases, the out-of-plane distortion of the H atoms is apparently governed by packing considerations (as in H_3TaCp_2[26]). In $H_3Ni_4Cp_4$, a combination of effects may be important. H atoms on Cp(1) are systematically bent toward Ni(1), but no trend is apparent for the other three rings, except for the fact that the *average* out-of-plane deviation is always toward the Ni atoms.

The structure of $H_3Ni_4Cp_4$ can serve as a model for hydrogen adsorption on nickel metal. Because the Ni-Ni distances are not very different between $H_3Ni_4Cp_4$ and Ni metal, it is reasonable to suppose that the absorption of hydrogen gas on some metal surfaces (such as the {111} face of a ccp metal or the {001} face of a hcp metal) may lead to a configuration very similar to that found in the compound studied here.

Existing evidence pertaining to the geometry of hydrogen chemisorption on Ni surfaces is somewhat contradictory, but is becoming increasingly supportive of multiply bonding H atoms. Early neutron inelastic scattering studies of hydrogen chemisorbed on Raney nickel suggested that the H atoms are terminally bound, based on the observation that peaks found at lower energy transfers (<320 cm^{-1}) are nearly identical with the spectrum of lattice frequencies of the pure metal.[27] This conclusion was supported by extended Hückel calculations on nickel/hydrogen clusters, which indicated that the stability of hydrogen adsorption decreases in the order terminal > bridging > multiply bridging.[28] However, more recent experimental and theoretical studies suggest otherwise. A reinvestigation of the neutron inelastic scattering spectra from hydrogen/Raney nickel, by the original workers[29] and by others,[30] indicate that most of the H atoms are nonterminally bound. These investigators found peaks at 950 and 1130 cm^{-1} (120 and 140 meV, respectively), frequencies which are normally associated with bridging or triply bridging hydride ligands in covalent metal hydride complexes.[31] One of these groups[30] also found a weak peak at 624 cm^{-1} (78 meV), which was assigned to hydrogen at a fourfold coordination site. Semiempirical[32] and CNDO[33] calculations on H/Ni(111) revealed the threefold coordination site as most favored, and low-energy electron diffraction (LEED) measurements on the H/Ni(111) system indicated the presence of triply bridging H atoms.[34,35] The LEED analysis showed the H atoms to be situated in threefold positions 1.15 ± 0.10 Å above the Ni surface, yielding a Ni-H bond length of 1.84 ± 0.06 Å. This distance is within 3σ of the value of 1.691 (8) Å determined in the present study for $H_3Ni_4Cp_4$.

Hartree-Fock calculations for binding of a H atom at high-symmetry sites on Ni_{20} clusters also indicate that the triply bridging geometry is the most stable arrangement.[36] In these calculations it was predicted that chemisorption energies would increase with the coordination number of the binding site, with bond energies of 1.6, 2.8, 3.2, and 3.0 eV for one-, two-, three-, and fourfold coordinated sites, respectively. It was also predicted that Ni-H bond distances would increase in the same order (Ni-H = 1.50, 1.59, 1.63, and 1.78 Å for coordination numbers of 1, 2, 3, and 4). These distances are in quite good agreement with our present results, and also with the terminal Ni-H distances of 1.47 Å found in diatomic NiH.[37,38]

Table V. Least-Squares Planes[a] through Cyclopentadienyl Rings

A. Normal Equations

Cp(1) $9.621x + 8.617y - 2.848z - 7.192 = \delta$
Cp(2) $25.190x + 2.272y - 8.569z - 0.352 = \delta$
Cp(3) $0.445x + 5.214y + 11.815z + 1.081 = \delta$
Cp(4) $16.434x - 5.380y + 6.199z - 3.785 = \delta$

B. Out-of-Plane Deviations

	$n = 1$	$n = 2$	$n = 3$	$n = 4$
C(n1)	−0.007	0.003	0.000	0.003
C(n2)	0.006	0.000	0.002	−0.004
C(n3)	−0.003	−0.003	−0.003	0.003
C(n4)	−0.001	0.005	0.003	−0.001
C(n5)	0.005	−0.005	−0.002	−0.001
H(n1)	0.035	0.026	−0.002	0.023
H(n2)	0.015	0.054	−0.014	0.017
H(n3)	0.012	−0.010	−0.017	0.040
H(n4)	0.002	0.024	0.015	−0.016
H(n5)	0.021	−0.069	0.077	0.003
Ni(n)	1.758	1.760	1.761	1.772

mean δ_C = 0.003 Å
mean δ_H = 0.025 Å
mean Ni-Cp = 1.763 (3) Å

[a] The out-of-plane deviation of an atom, δ, is in ångstroms and x, y, and z are in fractional coordinates. The normal equations were calculated using only the carbon atom positions.

Based upon the results accumulated thus far, it appears that the triply bridging arrangement is indeed the most stable for the H/Ni(111) system. Thus, we believe that the metal-hydrogen distances and angles found in metal hydride cluster complexes, such as the present H_3Ni_4 system, are reasonable estimates for those in binary metal hydrides. We anticipate that, as more examples of bridging, triply bridging, and interstitial metal-hydrogen bonds become accurately characterized in covalent clusters,[39] we will have a better idea of the distances and angles associated with H atoms on a metallic surface or in bulk metals.

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Supplementary Material Available: A listing of the observed and calculated structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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Analysis of the Oscillations in "Beating Mercury Heart" Systems

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Abstract: A column of mercury whose top surface is covered with aqueous acid or base undergoes periodic changes in height when the surface is brought into contact with a corroding metal electrode. The voltage between the mercury and the corroding electrode also undergoes periodic changes which we have followed on an oscilloscope. We present here a thorough analysis of a mechanism for these oscillations which is based on the effect of voltage and adsorption on the surface tension of mercury. Oscillations in sulfuric acid solutions of strong oxidants, such as $Cr_2O_7^{2-}$(aq), apparently are associated with a film of Hg_2SO_4 on the mercury. The reduction of this film by the corroding electrode—or, in the absence of strong oxidants, the reduction of electron acceptors such as O_2(aq)—modifies the surface tension of mercury. For an appropriate placement of the corroding electrode and the mercury, the altered surface tension switches the direction in which the surface moves. This effect breaks electrical contact between the mercury and the corroding electrode, so that the voltage of the mercury is free to rise as the oxidation or reduction process proceeds. The increasing voltage, in turn, modifies the surface tension in such a manner as to bring the mercury and electrode back into contact, completing the oscillation. We support this mechanism with quantitative measurements of the oscillations under a variety of conditions. Finally we show that the limit-cycle oscillations which occur in a simple mathematical model of this mechanism are in close correspondence to the observed oscillations.

I. Introduction

Oscillations in electrochemical systems have been known for many years,[2,3] although they have often been treated as curiosities of little consequence. Recently, however, it has been recognized that oscillations are among the novel kinds of phenomena that can occur in systems which are far from equilibrium.[4-6] For these sort of systems it is apparent that the kinetic point of view is more fundamental than the thermodynamic. In fact, the kinetic point of view is more fundamental than the thermodynamic, quite generally, if one takes cognizance of the molecular mechanisms which underlie the kinetics.[7] In chemical investigations this molecular perspective is mandatory, and we adopt it here.

It is our purpose in this communication to describe work

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