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Neutron Diffraction Study of $[H_4Co_4(C_5Me_4Et)_4]$, a Tetrahedral Metal Cluster Complex with Four Face-Bridging Hydride Ligands

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A single-crystal neutron diffraction analysis of the cluster complex $[H_4Co_4(C_5Me_4Et)_4]$ was carried out on the new quasi-Laue diffractometer VIVALDI at the Institut Laue-Langevin. The structure consists of four face-bridging hydrides attached to a tetrahedral cobalt metal core. Average distances and angles in the core of the molecule are as follows: Co–Co = 2.571(8), Co–C = 2.158(6), Co–H = 1.749(7), H···H = 2.366(9) Å; Co–H–Co = 94.6(3), H–Co–H = 85.1(3)°. The hydride ligands are located off the Co–Co–Co planes by an average distance of 0.923(8) Å. It is suggested that the dimensions of the HCo_3 fragments found in this molecule provide reasonable estimates for analogous distances and angles associated with chemisorbed H atoms situated on the 3-fold hollows of a cobalt surface. Crystallographic details: space group $P2_1/a$ (monoclinic); $a = 21.979(2)$, $b = 10.924(1)$, $c = 34.406(2)$ Å; $\beta = 90.81(1)°$; $Z = 8$. Final agreement factor: $R(F) = 0.099$ for 3779 reflections $[I > 2\sigma(I)]$ collected at 20 K.

Introduction

Face-bridging (μ_3-H) hydrides in metal cluster complexes are quite rare. The ability of a hydrogen atom to coordinate to three other atoms simultaneously is a phenomenon unique to metal hydrides and is unknown in organic or biological compounds. Although such triply bridging hydride ligands have received some attention, they are more difficult to locate with X-rays than terminal M−H ligands.[1] Some time ago, Huttner and Lorenz reported the X-ray structure of $H_4Co_4(C_5H_5)_4$, in which face-bridging H atoms were found.[2] To obtain more precise bonding distances and angles associated with these types of triply bridging hydride ligands, we report here the neutron diffraction analysis of a closely related derivative, $[H_4Co_4(C_5Me_4Et)_4]$, which represents the first neutron diffraction study of a H_4Co_4 compound.

Experimental Section

The title complex, $[H_4Co_4(C_5Me_4Et)_4]$, was prepared by letting cobalt metal vapor condense into a solution of $EtMe_4CpH$ in methylcyclohexane.[3] Crystals were obtained after purification of the reaction mixture by chromatography and crystallization of the eluant from ethanol and diethyl ether at −30 °C. In an inert-atmosphere chamber, a small dark-blue (almost black) crystal with dimensions of approximately $0.4 \times 1.0 \times 1.5$ mm^3 was placed into a quartz capillary. This sample, which is small by usual neutron data-collection standards (∼0.6 mm^3), was mounted on the new very-intense vertical-axis Laue diffractometer (VIVALDI) at the Institut Laue-Langevin, which uses an unconventional quasi-Laue geometry for data collection.[4] In this technique, the crystal is irradiated with a broad wave band of neutrons, in contrast to the usual mode of data collection which uses a monochromatic neutron beam. This procedure allows the flux of neutrons at the sample position to be increased by nearly 2 orders of magnitude. The diffraction data were recorded using a cylindrical area detector made from Gd_2O_3-doped BAFBR:Eu^{2+} image plates and which subtends 8 sterad at the sample position.[5a] A total of 10 Laue diffraction

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patterns, each accumulated over 7.5 h, were collected at 20° intervals in rotation of the crystal perpendicular to the incident beam. The patterns were indexed using the program LAUEGEN of the Daresbury Laboratory Laue Suite,[5b,c] and the reflections were integrated and the background subtracted using the local program INTEGRATE+, which uses a two-dimensional version of the $\sigma(I)/I$ algorithm.[5d] The reflections were normalized for the incident wavelength, using a curve derived by comparing equivalent reflections and multiple observations, via the program LAUENORM.[5e] This normalization would also have corrected for most of the (small) absorption variation in this sample. Reflections were observed with wavelengths between 1.0 and 3.5 Å, but only reflections with wavelengths between 1.1 and 2.5 Å were accepted for scaling, as those outside this range were too weak or had too few equivalents to be able to determine the normalization curve with confidence. In all 45 114 reflections were observed, of which 24 837 were single reflections with wavelengths between 1.1 and 2.5 Å, to yield 5323 unique reflections, 71% of the unique data for *d* spacing > 1.05 Å, the minimum d observed in this experiment. The merged reflections were phased with the non-hydrogen positions from the earlier X-ray analysis.[3]

The title complex, $[H_4Co_4(C_5Me_4Et)_4]$, crystallizes in space group $P2_1/a$ with two independent molecules in the asymmetric unit cell and the following unit cell parameters: $a = 21.979(2)$, $b = 10.924(1)$, $c = 34.406(2)$ Å; $\beta = 90.81(1)°$. The positions of the hydride ligands were not determined in the earlier X-ray structure determination.[3] In the present neutron analysis they appeared as negative peaks in the difference Fourier maps and were found to be on the cluster surfaces at the four face-bridging sites. All the other H atoms in the structure (the 136 hydrogen atoms of the C−H groups) were also unambiguously located in this manner. The positional and isotropic thermal displacement parameters for all atoms in each of the two independent molecules in the asymmetric unit were refined by a full-matrix least-squares procedure.[6] Despite a fairly small crystal volume with a relatively large number of parameters, the refinement successfully converged to give the following agreement factors: $R(F) = 9.9\%$ for 3779 nonzero reflections $[I > 2\sigma(I)]$ and $R(F) = 14.3\%$ for all data (5323 reflections). In particular, the H_4Co_4 cores of both molecules were well-behaved, with average thermal parameter values of $U(\text{iso}) = 0.026$ and 0.035 Å^2 for the cobalt and hydrogen atoms, respectively. A summary of crystal data and refinement parameters is given in Table 1. The title complex is a saturated 60-electron tetrahedral cluster, with two independent molecules in the unit cell that are essentially identical to each other. The overall structure of the molecule is shown in Figure 1.

Table 1. Crystal Data and Refinement Details for $[H_4Co_4(C_5Me_4Et)_4]$

empirical formula	$C_{44}H_{72}Co_4$
fw	1672.00
temp	20(2) K
wavelength range accepted	1.1−2.5 Å
cryst system	monoclinic
space group	$P2_1/a$
unit cell dimens[a]	$a = 21.979(2)$ Å; $\alpha = 90°$
	$b = 10.924(1)$ Å; $\beta = 90.81(1)°$
	$c = 34.406(2)$ Å; $\gamma = 90°$
unit cell vol[a]	8260.0(12) Å^3
Z	8
D(calcd)	1.345 g/cm^3
cryst size	1.5 × 1.0 × 0.4 mm^3
min *d* spacing obsd	1.05 Å
θ range for data collcn	2.0−72.0°
no. of reflcns (all data)	5323
no. of reflcns $[I > 2\sigma(I)$ data]	3779
no. of params refined	962
refinement method	full-matrix, least-squares on F^2
final R indices $[I > 2\sigma(I)$ data]	R1 = 0.0994, wR2 = 0.233
R indices (all data)	R1 = 0.143, wR2 = 0.257

[a] Based on the X-ray structure determination carried out at 100 K.[3]

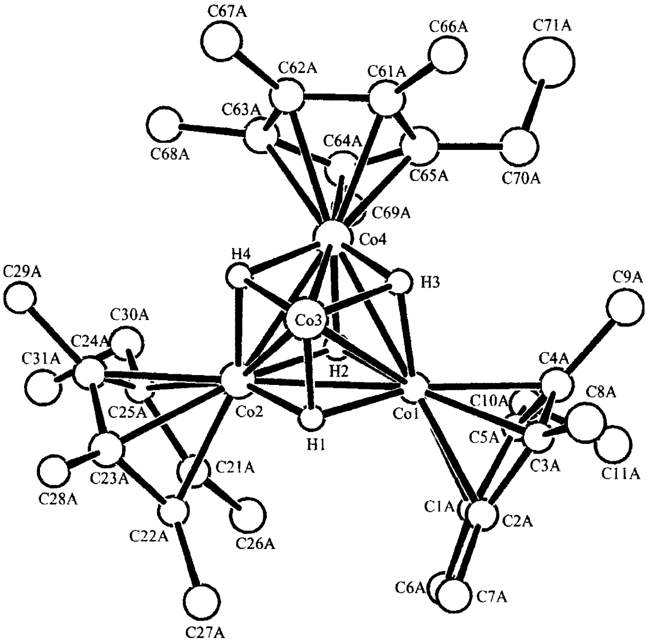

Figure 1. Molecular structure of $[H_4Co_4(C_5Me_4Et)_4]$ by neutron diffraction analysis at 20 K. The C_5Me_4Et moiety in the foreground and the hydrogen atoms of the C_5Me_4Et ligands have been removed for clarity.

Results and Discussion

As mentioned in the Introduction, the structural analysis of the unsubstituted parent compound, $H_4Co_4(C_5H_5)_4$, was carried out many years ago.[2] Although the H atoms were located in that early X-ray study, their positions were apparently not refined, and part of the rationale for carrying out the present neutron study was to provide precise measurements of the H_4Co_4 cores of such complexes. As expected, the overall geometry of the title complex, $H_4Co_4(C_5Me_4Et)_4$ (such as Co−Co distances, Co−C distances, etc.), very closely matches that of $H_4Co_4(C_5H_5)_4$.[2] In the present neutron analysis of $H_4Co_4(C_5Me_4Et)_4$, we find the relevant distances and angles of the central core of the molecule to be as follows: Co−H = 1.749(7) (Table 2), Co−Co = 2.571(8) Å (Table 3); Co−H−Co = 94.6(3), H−Co−H = 85.1(3)°; H···H = 2.366(9), Co−C = 2.158(6) Å. It is indeed surprising that we were able to produce such low estimated standard deviations from a relatively small (by neutron diffraction standards) crystalline sample. Although the measurements of the *individual* distances and angles in the title compound may not be as accurate as in a more typical neutron structure determination (that is, of a larger crystal or of a smaller unit cell), the fact that each molecular parameter occurs a large number of times (for example, there are 12 individual Co−H distances in each molecule), coupled with the fact that there are two independent molecules in the asymmetric unit, allowed us to compute *average* geometrical parameters with high precision.

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Table 2. M−H Bond Lengths (Å) in [$H_4Co_4(C_5Me_4Et)_4$][a]

cluster no. 1		cluster no. 2	
Co(1)−H(1)	1.781(24)	Co(5)−H(6)	1.674(21)
Co(1)−H(2)	1.736(20)	Co(5)−H(5)	1.753(24)
Co(1)−H(3)	1.735(21)	Co(5)−H(8)	1.739(20)
Co(2)−H(1)	1.739(22)	Co(6)−H(6)	1.817(19)
Co(2)−H(2)	1.709(25)	Co(6)−H(7)	1.755(23)
Co(2)−H(4)	1.729(23)	Co(6)−H(8)	1.805(22)
Co(3)−H(1)	1.726(26)	Co(7)−H(5)	1.779(22)
Co(3)−H(3)	1.786(26)	Co(7)−H(6)	1.732(23)
Co(3)−H(4)	1.785(23)	Co(7)−H(7)	1.700(19)
Co(4)−H(2)	1.738(24)	Co(8)−H(5)	1.768(21)
Co(4)−H(3)	1.706(21)	Co(8)−H(7)	1.780(23)
Co(4)−H(4)	1.735(25)	Co(8)−H(8)	1.763(25)
av	1.742(8)	av	1.755(12)

[a] Overall average Co−H distance = 1.749(7) Å.

Table 3. M−M Bond Lengths (Å) in [$H_4Co_4(C_5Me_4Et)_4$][a]

cluster no. 1		cluster no. 2	
Co(1)−Co(4)	2.560(26)	Co(5)−Co(6)	2.599(23)
Co(1)−Co(3)	2.574(25)	Co(5)−Co(7)	2.555(23)
Co(1)−Co(2)	2.595(24)	Co(5)−Co(8)	2.576(26)
Co(2)−Co(4)	2.518(31)	Co(6)−Co(7)	2.563(25)
Co(2)−Co(3)	2.545(26)	Co(6)−Co(8)	2.595(30)
Co(3)−Co(4)	2.604(29)	Co(7)−Co(8)	2.566(25)
av	2.566(13)	av	2.576(7)

[a] Overall average Co−Co distance = 2.571(8) Å.

Table 4. (μ_3-H)M_3-Bridged Compounds Analyzed by Neutron Diffraction

complex	M−H (Å)[a]	M−H−M (deg)[a]	M−M (Å)[a]	ref
$H_3Ni_4(C_5H_5)_4$[b]	1.691(8)	93.9(3)	2.469(6)	7
[$H_4Co_4(C_5Me_4Et)_4$][c]	1.749(7)	94.6(3)	2.571(8)	this work
$HFeCo_3(CO)_9(P(OMe)_3)_3$	1.734(4)	91.8(2)	2.489(7)	9
$H_6Cu_6[P(p\text{-tolyl})_3]_6$	1.77(3)	94(4)	2.60(3)	10
$[HOs_6(CO)_{18}]^-[N(^nBu)_4]^+$	1.93(3)	100(1)	2.97(1)	11
$[H_4Os_{10}(CO)_{24}]^{2-}[PPN^+]_2$	1.87(1)	102(1)	2.885(8)	12
$[H_4Rh_4Cp^*_4]^{2+}[BF_4^-]_2$	1.859(6)	95.7(2)	2.720(5)	8
$H_4Re_4(CO)_{12}$[d]	1.99(2)	94(1)	2.924(2)	13

[a] Average values. [b] For $H_3Ni_4(C_5H_5)_4$, H···H = 2.316(6) Å and H−M−H = 86.1(6)°. [c] For $H_4Co_4(C_5Me_4Et)_4$, H···H = 2.366(9) Å and H−M−H = 85.1(3)°. [d] For $H_4Re_4(CO)_{12}$, H···H = 2.69(2) Å and H−M−H = 85(1)°.

Table 5. Out-of-Plane Hydride Distances in (μ_3-H)M_3 Compounds Determined by Neutron Diffraction Analysis

complex	out-of-plane dist (Å)[a]	ref
$H_3Ni_4(C_5H_5)_4$	0.907(6)	7
[$H_4Co_4(C_5Me_4Et)_4$]	0.923(8)	this work
$HFeCo_3(CO)_9(P(OMe)_3)_3$	0.978(3)	9
$H_6Cu_6[P(p\text{-tolyl})_3]_6$	1.0(1)	10
$[HOs_6(CO)_{18}]^-[N(^nBu)_4]^+$	0.89(2)	11
$[H_4Rh_4Cp^*_4]^{2+}[BF_4^-]_2$	0.957(6)	8
$H_4Re_4(CO)_{12}$	1.06(2)	13

The overall geometry of $H_4Co_4(C_5Me_4Et)_4$, a 60-electron diamagnetic cluster, is also very similar to that of the closely related molecule $H_3Ni_4(C_5H_5)_4$,[7] despite the fact that the latter compound is a 63-electron paramagnetic cluster. The dimensions of the H_4Co_4 and H_3Ni_4 cores are rather similar (Table 4), with the main difference being that the triply bridging H atoms of the H_3Ni_4 cluster are very slightly asymmetric, presumably because of its lower symmetry (from an approximate T_d symmetry of the H_4Co_4 core to C_{3v} symmetry in the H_3Ni_4 case). In contrast, the 58-electron $[H_4Rh_4(C_5Me_5)_4]^{2+}$ cluster, analyzed by neutron diffraction by Ricci, Koetzle, and co-workers,[8] shows a much more distorted core (four long and two short Rh−Rh distances) because of strong Jahn−Teller effects arising from the absence of two electrons. Interestingly, in all three cases, $H_3Ni_4(C_5H_5)_4$, $H_4Co_4(C_5Me_4Et)_4$, and $[H_4Rh_4(C_5Me_5)_4]^{2+}$ (as well as in $H_4Re_4(CO)_{12}$[13]), the nonbonding H···H distances are actually shorter than the bonding metal−metal distances.

The average dimension of each HCo_3 face of the title compound can also be compared with the HCo_3 face of the compound $HCo_3Fe(CO)_9[P(OCH_3)_3]_3$ which was analyzed by neutrons many years ago.[9] These distances and angles are compared in Table 4, and it is significant to note that the dimensions of the two HCo_3 fragments are remarkably similar, despite the fact that the surrounding ligands in $HCo_3Fe(CO)_9[P(OCH_3)_3]_3$ and $H_4Co_4(C_5Me_4Et)_4$ are totally different. This could suggest that the geometry of the HCo_3 moiety is fairly robust and constant and is not strongly affected by the nature of surrounding ligands.

Along with other types of H bridges, the existence of triply bridging H atoms is often encountered in metal surfaces that contain chemisorbed hydrogen.[14] Thus, one rationale for studying the molecular dimensions of covalent metal hydride clusters is to provide reasonable estimates for corresponding distances and angles involving H atoms adsorbed on a metallic surface. Even though cobalt is active in Fischer−Tropsch catalysis,[15] there have been relatively few investigations of the interaction of hydrogen with Co surfaces,[16] in contrast to H/Ni systems which have been thoroughly investigated.[14] Nevertheless, the few studies on H/Co surfaces that have been carried out all seem to support the existence of H atoms on 3-fold hollow sites,[16] analogous to the triply bridging H bonding mode we find in the title compound.

Finally, we point out that, from the data gathered thus far from single-crystal neutron diffraction studies, there seems to be accumulation of evidence suggesting that triply bridging H atoms are displaced from their respective trimetallic surfaces by an approximately constant amount. In Table 5 we tabulate the out-of-plane displacements from a number of such studies, almost all of which show that the distances between three-coordinate H atoms and the M_3 planes fall in the range 0.9−1.0 Å. We suggest that these might be useful

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results for investigators engaged in surface studies of chemisorbed hydrogen.

The results from this study demonstrate an essential role for neutron diffraction in the full and precise geometrical characterization of large hydrido metal clusters. In particular, it also demonstrates the ability of the new Laue diffractometer (VIVALDI)[4] at the Institut Laue-Langevin to handle smaller-than-usual crystalline samples by using neutrons with a broad range of wavelengths and a detector with a large solid angle to increase greatly the total diffracted intensity. This enabled data collection to be completed in about 3 days, a rate that represents a 3-fold or 4-fold improvement over conventional (i.e., non-Laue) diffractometers. This study of the title complex, $[H_4Co_4(C_5Me_4Et)_4]$, is the first H_4Co_4 compound that has been fully characterized by the neutron diffraction technique.

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Supporting Information Available: Tables of the individual molecular parameters including M−H−M bond angles (Table S-1), H−M−H bond angles (Table S-2), H···H nonbonding distances (Table S-3), and H/Co_3 out-of-plane distances (Table S-4) as well as neutron crystallographic files for the neutron structural analysis of the title compound $H_4Co_4(C_5Me_4Et)_4$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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