

Vibrational Study and Crystal Structure of (μ_4 - η^2 -Acetylene)decacarbonyltetracobalt, (μ_4 - η^2 -C₂H₂)Co₄(CO)₈(μ -CO)₂

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The title compound and its deuterium and ¹³C isotopic derivatives have been prepared by the reactions of Co₄(CO)₁₂ and C₂H₂, C₂D₂, and ¹³C₂H₂, respectively. Infrared data on the acetylene ligand vibrational modes were collected and assigned on the basis of the frequency shifts by isotopic labeling and of comparison with appropriate models. The very low value of the C-C stretching frequency suggests a large π -back-bonding donation from the Co₄ unit, which lowers considerably the C-C bond order. Comparison of the acetylene frequencies with those of the acetylene adsorbed on some transition-metal surfaces shows good correspondence. The molecule structurally consists of a butterfly arrangement of cobalt atoms, which coordinate the C₂H₂ ligand in such a way that the C-C axis is nearly parallel to the hinge of the butterfly. The C-C bond length (1.399 (7) Å) and the great back-bending angle (53°) of the acetylene confirm the strong decrease of the "acetylenic" character of the ligand. Each Co atom bears two terminal CO groups, whereas two asymmetric CO's bridge two opposite edges of the butterfly. The Co-Co distances are 2.559 Å (hinge), 2.464 Å (average) (unbridged edge), and 2.450 Å (average) (bridged edge); the dihedral angle of the butterfly is 116°. The entire molecule possesses approximate C₂ symmetry. The complex crystallizes in the monoclinic P2₁/c space group with *a* = 11.228 (2) Å, *b* = 8.514 (2) Å, *c* = 17.793 (3) Å, β = 94.35 (2)°, and *Z* = 4. The hydrogen atoms were located, and the final indexes are *R* = 0.044 and *R*_w = 0.039 using 2750 observed reflections.

Introduction

The interaction of alkynes with transition metals¹ has always been of great importance for a variety of chemical reactions, including several homogeneous and heterogeneous catalytic processes. As the homogeneous reactions have been increasingly used as models for heterogeneous reactions,² a ligand bonded to a metal cluster can simulate the adsorption of the same species on a metal surface.³ In view of this, the comparison of the vibrational data of a species as a ligand on a well-characterized complex and as a chemisorbate on a surface seems one of the more promising ways to test the cluster-surface analogy.⁴ The acetylene molecule, because of its structural simplicity and of its chemical importance, is a good candidate for this study. The title complex represents an especially suitable model because of the presence of only the CO ligands and of the typical μ_4 - η^2 interaction of the acetylene with an M₄ cluster. From the structural point of view, the complex is one of the few examples with a butterfly-shaped tetrametal core coordinating the acetylene and the first member of a well-known series of Co₄(CO)₁₀(alkyne) complexes,⁵ whose structure is reported in detail, except for the old undetailed data about the structure of Co₄(CO)₁₀C₂-(C₂H₅)₂.⁶

Experimental Section

(a) Preparation of the Complexes. Solvents and common chemical products were reagent grade and were used without further purification. Other reagents were purchased as follows: Co₂(CO)₈ (Strem), D₂O (MSD Isotope), [¹³C]acetylene (Stolher Isotope Chemicals).

Co₄(CO)₁₀HCCH (I). In a typical preparation 1 g of dicobalt octacarbonyl (ca. 2.9 mmol), dissolved in 100 mL of *n*-heptane, was warmed at ca. 60 °C under a continuous slow stream of nitrogen in a glass vessel equipped with a reflux condenser; the formation of Co₄(CO)₁₂ was complete in ca. 5 h. The solution was filtered and transferred in a 300-mL glass vial provided with a serum cap and connected to a vacuum line. After the solution was cooled with liquid nitrogen and degassed, ca. 20 mmol of gaseous acetylene was introduced. The vial was sealed and allowed to warm to room temperature. The formation of the complex was demonstrated by a clear color change from dark brown to deep blue and monitored by infrared spectroscopy. The reaction was complete in ca. 2 days; no carbonyl-containing side products were observed. The solution was filtered, concentrated in a stream of nitrogen, and cooled to -20 °C, whereupon large, blue crystals of Co₄(CO)₁₀HCCH were obtained (approximate yield 0.63 g, ca. 80% with respect to the starting Co₂(CO)₈). The reaction is very clean so further purification is usually not necessary. If required, it can be performed by subsequent crystallization from a concentrated hydrocarbon solution. Column chromatography or TLC should be avoided, owing to the sensitivity of the compound to air.

Co₄(CO)₁₀H¹³C¹³CH (Ia). By the same procedure, from 0.20 g of Co₂(CO)₈ and 120 mL of [¹³C]acetylene, 130 mg of Ia were obtained: the sample contained ca. 20% of Co₄(CO)₁₀H¹²C¹³CH (Ib).

Co₄(CO)₁₀DCCD (Ic). The deuterated acetylene was prepared by reacting finely divided CaC₂ with deuterated water. In a glass vial, similar to the reaction vessel, containing CaC₂ and carefully degassed, small aliquots of D₂O were introduced by syringe through a serum cap. Measured quantities of deuterated acetylene were transferred to the Co₄(CO)₁₂ solution by freezing with liquid nitrogen. Surprisingly, the deuterium content of the coordinated acetylene in the final product was lower than that of the deuterated water (40% vs. 98%), probably because of the H/D exchange during the reaction with traces of water present in the solvent and/or with the walls of the reaction vessel and/or with the filter paper. To minimize the exchange, some precautions were used: before the reaction, samples of deuterated acetylene were stored at 60 °C in the reaction vial for several hours; *n*-heptane was carefully dried on molecular sieves; a drop of D₂O was added to reaction mixture, which was finally centrifugated. The final deuterium content was thereby raised to ca. 90%.

(b) Infrared Spectra. The preparation of the samples was carried out in a glovebox filled with dry nitrogen. The spectra

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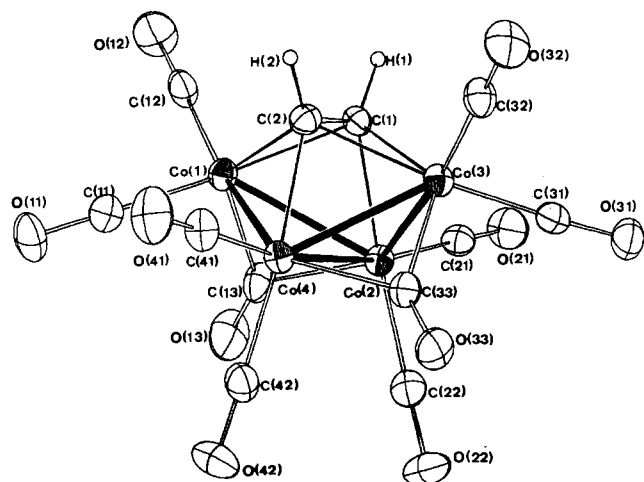


Figure 1. Molecular structure of $\text{Co}_4(\text{CO})_{10}\text{C}_2\text{H}_2$ with the atom labeling scheme.

Table I. Experimental and Crystal Data for X-ray Analysis^a

space group	$P2_1/c$
a , Å	11.228 (2)
b , Å	8.514 (2)
c , Å	17.793 (3)
β , deg	94.35 (2)
V , Å ³	1695.9
mol wt	541.87
Z	4
ρ (calcd), g cm ⁻³	2.12
μ (Mo $K\alpha$), cm ⁻¹	37.5
approx cryst dimens, mm	0.10 × 0.20 × 0.40
rel transmission factor	0.720–0.996
diffractometer	Nicolet R3
radiation	Mo $K\alpha$ graphite monochromatized
scan technique	ω
scan width, deg	1.3
scan speed, deg min ⁻¹	1.5–15.0
scan range (2θ), deg	2–56
collected reflectns	3881
reflectns with $F > 4\sigma(F)$	2750
final R	0.044
final R_w	0.039

^a Here and in the subsequent table the esd's are in parentheses.

were recorded by a Perkin-Elmer (Model 580 B) IR grating spectrophotometer; all the spectral manipulations (background subtraction, difference spectra, etc.) were performed by using the CDS data station (Model 3500) with the PE580 software provided.

(c) **Collection and Reduction of X-ray Data.** The crystal data and the experimental details for the structure determination are collected in Table I. The lattice parameters were obtained from the refinement of 25θ angles. No decrease in the intensity of a standard reflection (102), measured every 50 reflections, occurred. A secondary extinction correction was not made. The absorption correction was applied according to the method in ref 7.

(d) **Solution and Refinement of the Structure.** The space group $P2_1/c$ was assumed on the basis of extinctions and confirmed by the subsequent refinement. The four heavy atoms were located by using the automatic centrosymmetric "direct methods", program SHELX 76,⁸ and the carbon and oxygen atoms were revealed by subsequent difference Fourier analyses. In the final least-squares cycle all the atoms were refined anisotropically. At this stage the difference Fourier maps showed peaks interpretable as hydrogen atoms of the acetylene molecule and they were introduced in the refinement with a constant thermal factor. They reached satisfactory values for distances and angles and in the

Table II. Fractional Atomic Coordinates Referred to One Molecule for $\text{Co}_4(\text{CO})_{10}(\text{C}_2\text{H}_2)$

atom	x/a	y/b	z/c
Co(1)	0.25751 (6)	0.27383 (8)	0.75245 (4)
Co(2)	0.36858 (6)	0.21134 (8)	0.87231 (4)
Co(3)	0.24013 (6)	0.37796 (8)	0.94499 (4)
Co(4)	0.14074 (6)	0.18845 (8)	0.85726 (4)
C(1)	0.3064 (4)	0.4205 (6)	0.8399 (3)
H(1)	0.3587	0.5195	0.8268
C(2)	0.1817 (5)	0.4091 (6)	0.8347 (3)
H(2)	0.1203	0.5011	0.8264
C(11)	0.1490 (5)	0.1656 (7)	0.6969 (3)
O(11)	0.0822 (4)	0.0970 (6)	0.6585 (2)
C(12)	0.3213 (5)	0.3773	0.6771 (3)
O(12)	0.3594 (4)	0.4422(6)	0.6288 (2)
C(13)	0.3733 (5)	0.1138 (7)	0.7710 (3)
O(13)	0.4221 (4)	0.0133 (6)	0.7432 (2)
C(21)	0.5254 (5)	0.2662 (6)	0.8852 (3)
O(21)	0.6225 (3)	0.2999 (5)	0.8939 (3)
C(22)	0.3823 (5)	0.0278 (7)	0.9230 (3)
O(22)	0.3889 (4)	-0.0861 (5)	0.9561 (3)
C(31)	0.3635 (5)	0.3670 (6)	1.0131 (3)
O(31)	0.4423 (4)	0.3659 (5)	1.0579 (2)
C(32)	0.1590 (5)	0.5343 (7)	0.9868 (3)
O(32)	0.1114 (4)	0.6340 (6)	0.0128 (3)
C(33)	0.1502 (5)	0.2023 (7)	0.9710 (3)
O(33)	0.1173 (4)	0.1308 (5)	0.0207 (2)
C(41)	-0.0198 (5)	0.2071 (7)	0.8359 (3)
O(41)	-0.1185 (4)	0.2142 (7)	0.8218 (3)
C(42)	0.1394 (5)	-0.0232 (8)	0.8556 (3)
O(42)	0.1372 (5)	-0.1557 (5)	0.8524 (3)

last cycle were kept fixed. Only the reflections with $F > 4\sigma(F)$ were taken into account and used for refinement. The weighting scheme was $w = 1/(\sigma(F)^2 + aF^2)$ where a was varied, in order to maintain $\sum w\Delta^2$ sufficiently constant for the amplitudes batched in various ranges of F_0 .

All the calculations were performed by using SHELX 76.⁸ The best planes passing through the atoms were calculated by the method of ref 9. Listing of observed and calculated structure factors and thermal anisotropic parameters is available.¹⁰ Final fractional coordinates and values of bond distances and angles are listed in Tables II and III, respectively.

Discussion

(1) **Description of the Molecular Structure.** The tetracobalt core of the complex has a butterfly structure. The acetylene molecule is coordinated to the concave side such that the C–C bond is nearly parallel to the hinge of the butterfly. From another point of view the complex can be seen as a dicarbottetrametal cluster with a nearly octahedral arrangement. The Co–Co distances are not very different; the hinge bond is longer (2.559 Å) than the bridged wing bonds (2.450 Å (average)). Each is close to the Co–Co distance of the metal lattice (2.50 Å), and the dihedral angle between the wings of the butterfly is only slightly opened with respect to the angle between two octahedral faces (116° vs. 109°). Therefore the cluster framework may simulate a metal fragment in which one molecule of acetylene is adsorbed.

The coordination of the acetylene can be formally described, according to the well-known Dewar–Chatt–Duncanson model,¹¹ as consisting of two σ bonds (C(1)–Co(2) and C(2)–Co(4)) and a delocalized four-center π -bonding system between C(1), Co(1), C(2), and Co(3). In agreement with this scheme, the former carbon–cobalt distances are significantly shorter than those implied in the π bond (1.98

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Table III. Interatomic Distances (Å) and Angles (deg) of $\text{Co}_4(\text{CO})_{10}(\text{C}_2\text{H}_2)$

Bond Distances					
Co(1)-Co(2)	2.446 (1)	Co(2)-C(21)	1.819 (5)	C(1)-C(2)	1.399 (7)
Co(1)-Co(3)	3.558 (1)	Co(2)-C(22)	1.804 (6)	C(1)-H(1)	1.063 (5)
Co(1)-Co(4)	2.469 (1)	Co(3)-Co(4)	2.454 (1)	C(2)-H(2)	1.047 (5)
Co(1)-C(1)	2.038 (5)	Co(3)-C(1)	2.095 (5)	C(11)-O(11)	1.137 (6)
Co(1)-C(2)	2.094 (5)	Co(3)-C(2)	2.038 (5)	C(12)-O(12)	1.132 (6)
Co(1)-C(11)	1.769 (6)	Co(3)-C(31)	1.773 (6)	C(13)-O(13)	1.148 (6)
Co(1)-C(12)	1.798 (6)	Co(3)-C(32)	1.805 (6)	C(21)-O(21)	1.127 (6)
Co(1)-C(13)	1.895 (6)	Co(3)-C(33)	1.882 (6)	C(22)-O(22)	1.135 (6)
Co(2)-Co(3)	1.459 (1)	Co(4)-C(2)	1.982 (5)	C(31)-O(31)	1.145 (6)
Co(2)-Co(4)	2.559 (1)	Co(4)-C(33)	2.022 (5)	C(32)-O(32)	1.121 (6)
Co(2)-C(1)	1.982 (5)	Co(4)-C(41)	1.821 (5)	C(33)-O(33)	1.157 (6)
Co(2)-C(13)	1.988 (5)	Co(4)-C(42)	1.802 (7)	C(41)-O(41)	1.119 (6)
				C(42)-O(42)	1.130 (7)
Bond Angles					
Co(2)-Co(1)-Co(4)	62.8 (0)	Co(2)-Co(3)-C(1)	50.8 (1)	C(33)-Co(4)-C(41)	100.3 (2)
Co(2)-Co(1)-C(1)	51.5 (1)	Co(2)-Co(3)-C(2)	74.2 (1)	C(33)-Co(4)-C(42)	94.3 (2)
Co(2)-Co(1)-C(2)	73.6 (1)	Co(2)-Co(3)-C(31)	82.5 (2)	C(41)-Co(4)-C(42)	94.4 (3)
Co(2)-Co(1)-C(11)	131.1 (2)	Co(2)-Co(3)-C(32)	167.6 (2)	Co(1)-C(1)-Co(2)	74.9 (2)
Co(2)-Co(1)-C(12)	123.4 (2)	Co(2)-Co(3)-C(33)	91.0 (2)	Co(1)-C(1)-Co(3)	118.8 (2)
Co(2)-Co(1)-C(13)	52.7 (2)	Co(4)-Co(3)-C(1)	73.8 (1)	Co(1)-C(1)-Co(4)	60.0 (1)
Co(4)-Co(1)-C(1)	74.4 (1)	Co(4)-Co(3)-C(2)	51.4 (1)	Co(1)-C(1)-C(2)	72.4 (3)
Co(4)-Co(1)-C(2)	50.7 (1)	Co(4)-Co(3)-C(31)	134.0 (2)	Co(1)-C(1)-H(1)	116.1 (3)
Co(4)-Co(1)-C(11)	83.4 (2)	Co(4)-Co(3)-C(32)	121.9 (2)	Co(2)-C(1)-Co(3)	74.1 (2)
Co(4)-Co(1)-C(12)	166.4 (2)	Co(4)-Co(3)-C(33)	53.7 (2)	Co(2)-C(1)-Co(4)	63.1 (1)
Co(4)-Co(1)-C(13)	93.0 (2)	C(1)-Co(3)-C(31)	107.9 (2)	Co(2)-C(1)-C(2)	106.6 (3)
C(1)-Co(1)-C(2)	39.6 (2)	C(1)-Co(3)-C(32)	117.7 (2)	Co(2)-C(1)-H(1)	126.0 (4)
C(1)-Co(1)-C(11)	151.7 (2)	C(1)-Co(3)-C(33)	126.2 (2)	Co(3)-C(1)-Co(4)	5.91 (1)
C(1)-Co(1)-C(12)	99.8 (2)	C(2)-Co(3)-C(31)	147.4 (2)	Co(3)-C(1)-C(2)	68.0 (3)
C(2)-Co(1)-C(13)	125.7 (2)	C(2)-Co(3)-C(32)	99.5 (2)	Co(3)-C(1)-H(1)	124.9 (3)
C(11)-Co(1)-C(12)	97.8 (2)	C(2)-Co(3)-C(33)	101.6 (2)	Co(4)-C(1)-C(2)	43.5 (2)
C(11)-Co(1)-C(13)	99.1 (3)	C(31)-Co(3)-C(32)	98.6 (2)	Co(4)-C(1)-H(1)	70.0 (4)
C(12)-Co(1)-C(13)	100.1 (3)	C(31)-Co(3)-C(33)	101.3 (2)	C(2)-C(1)-H(1)	127.3 (4)
Co(1)-Co(2)-Co(3)	93.0 (0)	C(32)-Co(3)-C(33)	100.8 (2)	Co(1)-C(2)-Co(3)	118.9 (2)
Co(1)-Co(2)-Co(4)	59.1 (0)	Co(1)-Co(4)-Co(2)	58.2 (0)	Co(1)-C(2)-Co(4)	74.5 (2)
Co(1)-Co(2)-C(1)	53.6 (1)	Co(1)-Co(4)-Co(3)	92.6 (0)	Co(1)-C(2)-C(1)	68.1 (3)
Co(1)-Co(2)-C(13)	49.3 (2)	Co(1)-Co(4)-C(2)	54.8 (1)	Co(1)-C(2)-H(2)	127.7 (4)
Co(1)-Co(2)-C(21)	118.6 (2)	Co(1)-Co(4)-C(33)	138.4 (2)	Co(3)-C(2)-Co(4)	75.2 (2)
Co(1)-Co(2)-C(22)	130.0 (2)	Co(1)-Co(4)-C(41)	113.0 (2)	Co(3)-C(2)-C(1)	72.4 (3)
Co(3)-Co(2)-Co(4)	58.5 (0)	Co(1)-Co(4)-C(42)	106.6 (2)	Co(3)-C(2)-H(2)	113.2 (3)
Co(3)-Co(2)-C(1)	55.0 (1)	Co(2)-Co(4)-Co(3)	58.7 (0)	Co(4)-C(2)-C(1)	107.4 (3)
Co(3)-Co(2)-C(13)	140.8 (2)	Co(2)-Co(4)-C(2)	72.8 (1)	Co(4)-C(2)-H(2)	125.2 (4)
Co(3)-Co(2)-C(22)	105.5 (2)	Co(2)-Co(4)-C(33)	85.1 (2)	C(1)-C(2)-H(2)	127.1 (5)
Co(4)-Co(2)-C(1)	73.2 (1)	Co(2)-Co(4)-C(41)	168.9 (2)	Co(1)-C(11)-O(11)	176.9 (5)
Co(4)-Co(2)-C(13)	88.2 (2)	Co(2)-Co(4)-C(42)	94.9 (2)	Co(1)-C(12)-O(12)	178.7 (5)
Co(4)-Co(2)-C(21)	169.4 (2)	Co(3)-Co(4)-C(2)	53.4 (1)	Co(1)-C(13)-O(13)	143.5 (5)
Co(4)-Co(2)-C(22)	91.9 (2)	Co(3)-Co(4)-C(33)	48.5 (2)	Co(2)-C(13)-O(13)	138.5 (5)
C(1)-Co(2)-C(13)	98.3 (2)	Co(3)-Co(4)-C(41)	118.1 (2)	Co(2)-C(21)-O(21)	179.4 (5)
C(1)-Co(2)-C(21)	97.0 (2)	Co(3)-Co(4)-C(42)	132.1 (2)	Co(2)-C(22)-O(22)	178.2 (5)
C(1)-Co(2)-C(22)	159.7 (2)	C(2)-Co(4)-C(33)	98.7 (2)	Co(3)-C(31)-O(31)	177.3 (5)
C(13)-Co(2)-C(21)	97.4 (2)	C(2)-Co(4)-C(41)	96.7 (2)	Co(3)-C(32)-O(32)	178.1 (5)
C(13)-Co(2)-C(22)	194.8 (2)	C(2)-Co(4)-C(42)	161.1 (2)	Co(3)-C(33)-O(33)	144.6 (5)
C(21)-Co(2)-C(22)	96.5 (2)			Co(4)-C(33)-O(33)	137.6 (5)
Co(2)-Co(3)-Co(4)	62.8 (0)			Co(4)-C(41)-O(41)	178.0 (6)
				Co(4)-C(42)-O(42)	177.9 (6)

Å (average) vs. 2.07 Å (average)). The coordination should give rise to an unequal electronic distribution between the cobalt atoms, which should be partially balanced by the presence of the two asymmetrically bridging CO groups.¹² As a consequence, two bridged Co-Co bonds of the wings are shorter than the other two (2.450 Å (average) vs. 2.464 Å (average)), causing a small distortion of the entire metal core. The acetylene is slightly rotated with respect to the Co_4 framework around a C_2 axis, which passes through the midpoint of both the C(1)-C(2) and Co(2)-Co(4) bonds and is the only symmetry element of the complex (Figure 2). In agreement with the C_2 symmetry, the distance between the C atoms and the apical Co atoms are equal two-by-two and the acetylene carbon atoms and the hinge Co atoms do not lie in a plane. (A value of $\chi^2 = \sum(d/\sigma)^2$

= 21.5 corresponds to the Co(2)Co(4)C(1)C(2) plane of the equation $-1.33X + 2.14Y + 17.20Z = 14.97$ in fractional coordinates).

The position of the terminal CO ligands reflects the symmetry of the complex as a whole. Even if the Co-C and C-O distances fall within the usual ranges, within each pair of carbonyl ligands bonded to a cobalt atom one CO has a "long" and the other a "short" Co-C distance, similar bonds being related by the twofold axis. The difference is significant (ca. 5σ) for the carbonyl ligands bonded to the apical Co atoms, among which the "short" CO's are slightly inclined toward the cobalt atoms of the hinge.

The key to understanding the overall molecular distortion is likely to be found, as suggested above, in the inequality of the electron distribution through the metal framework. It does not seem to depend on crystal packing effects, as the $\text{Co}_4(\text{CO})_{10}(\text{C}_2\text{Et}_2)$ complex shows the same unsymmetric arrangement.⁶

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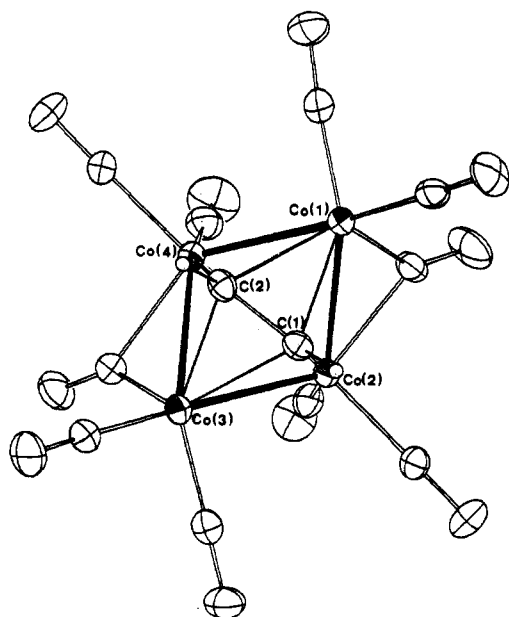


Figure 2. View of the molecule down the C_2 axis.

The coordination of the acetylene gives rise to the lengthening of the C-C bond and to the bending of the C-H bonds away from the metal cluster. Both effects depend mainly on the π -back-donation from metal orbitals to an antibonding MO of the acetylene and can be taken as measure of the reduction of the triple-bond character upon coordination. In order to test this assumption, we have collected the values of the C-C-R angles of coordinated alkynes vs. the length of the C-C bond for several complexes (Figure 3). The complexes are placed in different groups on the basis of the number of metal atoms to which the alkyne is bound. In principle, the comparison should be made only between complexes coordinating acetylene in order to avoid distortions due to steric hindrance of large R groups, but only four examples are reported. Anyway, as can be seen easily from the figure, the steric effect, together with the uncertainty in the values resulting from the presence of heavy-metal atoms, must be responsible for some scatter in the plots. However, the general trends are apparent.

Some conclusions can be drawn from the figure. (i) The values of the C-C distance correlate well with the bending angle and both appear to be a rough measure of the extent of the coordination of the alkyne. (ii) The plot appears to be divided into reasonably well separated sectors, which means that the number of metal atoms to which the alkyne is bonded is one of the most important factors. (iii) Neither the type of metal nor the geometry of the complex has a significant effect: for example, there is no significant difference between trinuclear complexes in which the alkyne is parallel or perpendicular to a M-M bond or between tetranuclear clusters with butterfly or planar structures.

The values of the C-C bond distance and angle of the title compound (1.399 Å and 127°) suggest that the coordinated acetylene has a nearly olefinic character. Comparison with the only reported cobalt compound containing acetylene, $\text{Co}(\text{CO})_4(\text{PMe}_3)_2(\mu\text{-}\eta^2\text{-C}_2\text{H}_2)$ ¹³ (1.327 Å and 138°), supports this contention.

(2) Infrared Spectra. (a) CO Stretching Region. Eight bands are expected in the terminal CO stretching region, corresponding to the eight fundamental modes (4A

+ 4B) allowed by the C_2 symmetry. The spectrum (Figure 4) shows only five medium-strong bands, the usual finding for metal carbonyl clusters.¹⁴ The solitary band at 1879 cm^{-1} , corresponding to the symmetric and antisymmetric stretching of the bridging CO's, indicates that coupling between the stretching of the two CO groups is practically absent.

(b) Acetylenic Modes. The "acetylenic" modes (i.e., modes implying the vibration of the acetylene moiety) have been assigned on the following bases: (a) low-temperature spectra, in which the H modes in particular have greater intensity than in the room-temperature spectra; (b) frequency shifts due to the isotopic labeling (D or ¹³C) of the coordinated acetylene; (c) comparison with appropriate models, i.e., the cis-disubstituted olefins. For the last point, we prefer to treat the $\text{H}_2\text{C}_2\text{Co}_4$ core, as belonging to the idealized C_{2v} symmetry (the xz plane is the plane containing approximately the $\text{H}_2\text{C}_2\text{Co}(2)\text{Co}(4)$ framework).

As most of these modes give rise to bands in a well-defined range (1200–600 cm^{-1}), the coupling between them can be quite large and the correspondence between a band and a vibrational mode is always approximate.

(i) C-H Stretching Modes. The two expected modes give rise to the very weak bands at 3020 and 2993 cm^{-1} , which are only slightly shifted by ¹³C labeling (Table IV), indicating that the bands are "pure" $\nu(\text{C-H})$ modes. The corresponding $\nu(\text{C-D})$ bands are expected at ca. 2100 cm^{-1} and are obscured by the strong $\nu(\text{CO})$ modes. The highest frequency is usually assigned to the symmetric stretch;¹⁵ anyway the difference between the two bands (27 cm^{-1}) suggests that the coupling is not great. The frequencies are significantly lower than those of the free acetylene (ca. 300 cm^{-1}), indicating that the ligand has lost its acetylenic character (vide infra).

(ii) C-C Stretching Mode. The medium-intensity band at 1199 cm^{-1} has been assigned to the C-C mode on the basis of the ¹³C isotopic shifts (Ia, calcd 1177 cm^{-1} , exptl 1178 cm^{-1} ; Ib, calcd 1155 cm^{-1} , exptl 1157 cm^{-1}) (Figure 5). The agreement between the experimental and calculated values suggests that coupling between the $\nu(\text{C-C})$ mode and other modes is small. The value of the frequency is the lowest reported for an acetylene molecule coordinated to metal atoms,¹⁶ and it is close to the frequency associated to the single C-C bond stretching in hydrocarbons.

As previously indicated, the C-C bond distance is only a little shorter than the average olefinic bond length, whereas the recently reported value of ¹J_{CC} for the coordinated acetylene in II is even lower than that of ethane.²⁰ It is questionable if either parameter can be considered a reliable measure of the C-C bond order; their values (Table V) roughly suggest a C-C bond order not much greater than 1.

(iii) C-H Deformation Modes. Four C-H deformation modes are expected, two CH bendings in the plane of the HCCH unit (in-phase A₁ and out-of-phase B₁ bending

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(16) Significant $\nu(\text{C-C})$ values for differently coordinated acetylene are 1682 cm^{-1} for $\text{Ir}(\text{SnCl}_3)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)(\eta^2\text{-C}_2\text{H}_2)$,¹⁷ 1403 cm^{-1} for $\text{Co}_2(\text{CO})_6(\mu\text{-}\eta^2\text{-C}_2\text{H}_2)$,¹⁸ and 1310 cm^{-1} for $\text{Os}_3(\text{CO})_{10}(\mu_3\text{-}\eta^2\text{-C}_2\text{H}_2)$.¹⁹

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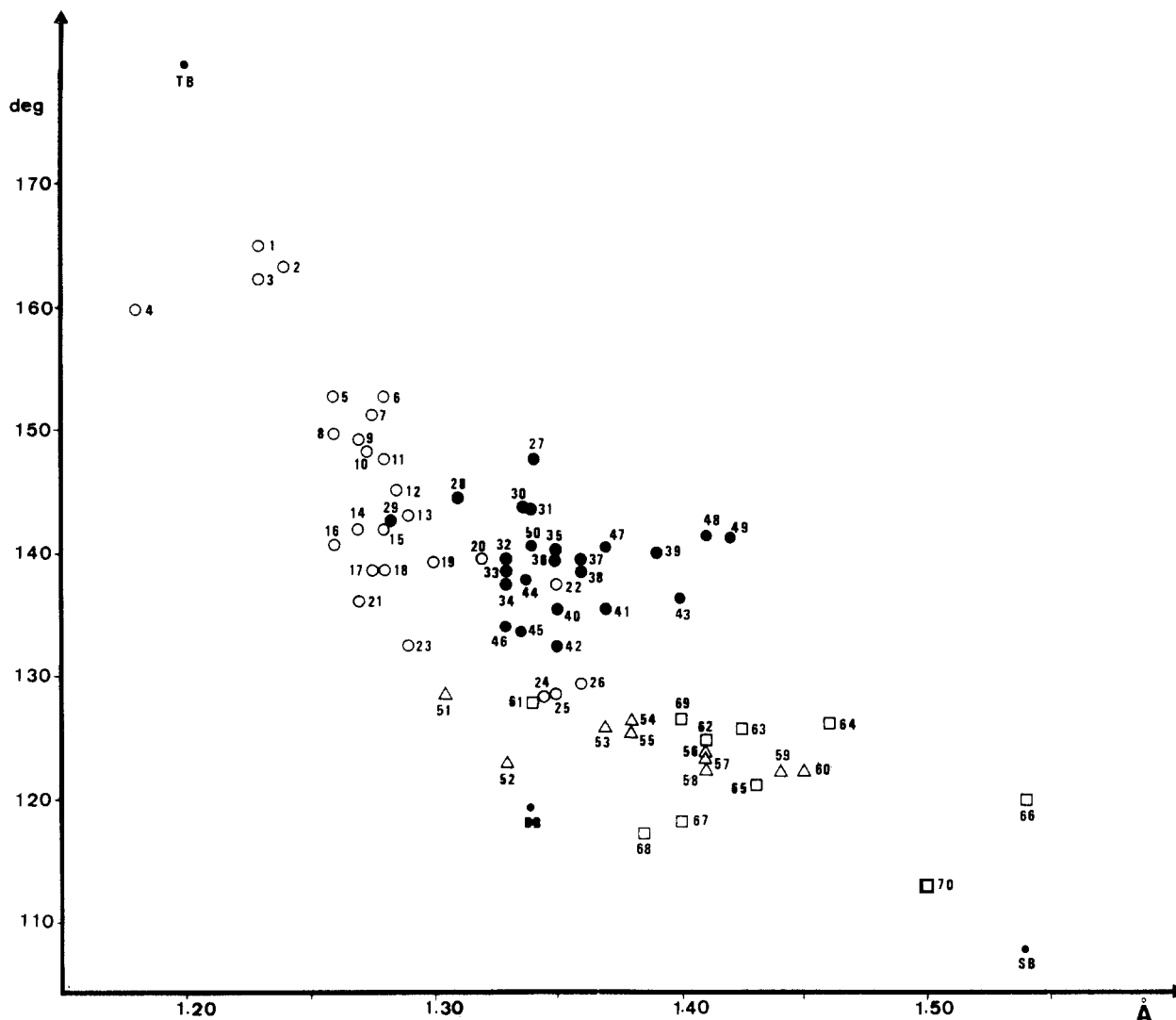


Figure 3. Plot of C-C-R angle value vs. C-C bond length of (alkyne)metal complexes: open circles, mononuclear complexes η^2 -type (1-26); closed circles, binuclear complexes μ_3 - η^2 -type (27-50); triangles, trinuclear complexes μ_3 - η^2 -type (51-60); squares, tetranuclear complexes μ_4 - η^2 -type (61-70). Letters SB, DB, and TB indicate the values of the ethane, ethylene, and acetylene, respectively. (1) Aleksandrov, G. G.; Gol'ding, I. R.; Sterlin, S. R.; Sladkov, A. M.; Struchov, Yu. T.; Garbuzova, I. A.; Aleksonyan, V. T. *Izv. Akad. Nauk SSSR, Ser. Fiz.* **1980**, *12*, 2679. (2) Gwyneth, R. D.; Hewertson, W.; Mais, R. H. B.; Owston, P. G.; Patel, C. G. *J. Chem. Soc. A* **1970**, 1873. (3) Clark, R.; Howard, J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1974**, 2027. (4) Beauchamp, A. L.; Rochon, F. D.; Teophanides, T. *Can. J. Chem.* **1973**, *51*, 126. (5) Green, M.; Grove, D. M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1976**, 759. (6) *Ibid.* (7) Carty, A. J.; Smith, W. F.; Taylor, N. J. *J. Organomet. Chem.* **1978**, *146*, C1. (8) Carty, A. J.; Paik, H. N.; Palenik, G. J. *Inorg. Chem.* **1977**, *16*, 300. (9) Newton, W. E.; McDonald, J. W.; Corbin, J. L.; Ricard, L.; Weiss, R. *Inorg. Chem.* **1980**, *19*, 1997. (10) Reference 8. (11) Dickson, R. S.; Ibers, J. A. *J. Organomet. Chem.* **1972**, *36*, 191. (12) Jacobson, S.; Carty, A. J.; Mathew, M.; Palenik, G. J. *J. Am. Chem. Soc.* **1974**, *96*, 4330. (13) Bokiy, N. G.; Gatilov, Yu. V.; Struchov, Yu. T.; Ustyniyuk, N. A. *J. Organomet. Chem.* **1973**, *54*, 213. (14) Foust, D. F.; Rausch, M. D.; Hunter, W. E.; Atwood, J. L.; Samuel, E. *J. Organomet. Chem.* **1980**, *197*, 217. (15) Fachinetti, G.; Floriani, C.; Marchetti, F.; Mellini, M. *J. Chem. Soc., Dalton Trans.* **1978**, 1398. (16) Nesmeyanov, A. N.; Gusev, A. I.; Pasynskii, A. A.; Anisimov, K. N.; Kolobova, N. E.; Struchov, Yu. T. *J. Chem. Soc., Chem. Commun.* **1969**, 739. (17) Davidson, J. L.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1976**, 738. (18) Davidson, J. L.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1977**, 287. (19) Kirillova, N. I.; Kolobova, N. E.; Gusev, A. I.; Antonova, A. B.; Struchov, Yu. T.; Anisimov, K. N.; Khitrova, Q. M. *Zh. Strukt. Khim.* **1974**, *15*, 651. Fischer, E. O.; Friedrich, P.; *Angew. Chem.* **1979**, *91*, 345. Laine, R. M.; Moriarty, R. E.; Bau, R. *J. Am. Chem. Soc.* **1972**, *94*, 1402. (20) Glanville, J. O.; Stewart, J. M.; Grim, S. O. *J. Organomet. Chem.* **1967**, *7*, P9. (21) Winston, P. B.; Burgmayer, S. J. N.; Templeton, J. L. *Organometallics* **1983**, *2*, 167. (22) Nesmeyanov, A. N.; Gusev, A. I.; Pasynskii, A.; Anisimov, K. N.; Kolobova, N. E.; Struchov, Yu. T. *J. Chem. Soc., Chem. Commun.* **1969**, 277. (23) Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G. J. J.; McDonald, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1318. (24) Corfield, P. W. R.; Baltusis, L. M.; Lippard, S. J. *Inorg. Chem.* **1981**, *20*, 922. (25) *Ibid.* (26) Wang, Y.; Coppens, P. *Inorg. Chem.* **1976**, *15*, 1122. (28) Cotton, F. A.; Jamerson, J. D.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 1774. (29) Nicholas, K.; Bray, L. S.; Davis, R. E.; Pettit, R. *J. Chem. Soc., Chem. Commun.* **1971**, 608. (30) Freeland, B. H.; Hux, J. E.; Payne, N. C.; Tyers, K. G. *Inorg. Chem.* **1980**, *19*, 693. (31) Gregson, D.; Howard, J. A. K. *Acta Crystallogr., Sect. C* **1983**, *39C*, 1024. (32) Bird, P. H.; Fraser, A. R.; Hall, D. N. *Inorg. Chem.* **1977**, *16*, 1923. (33) Reference 31. (34) Bonnet, J.; Mathieu, R. *Inorg. Chem.* **1978**, *17*, 1973. (35) Restivo, R. J.; Ferguson, G.; Ng, T. W.; Carty, A. J. *Inorg. Chem.* **1977**, *16*, 172. (36) Mills, O. S.; Shaw, B. W. *J. Organomet. Chem.* **1968**, *11*, 595. (37) Reference 31. (38) Bianchini, C.; Dapporto, P.; Meli, A. *J. Organomet. Chem.* **1979**, *174*, 205. (39) Day, V. W.; Abdel-Mequid, S. S.; Dabestani, S.; Thomas, M. G.; Pretzer, W. R.; Muettterties, E. L. *J. Am. Chem. Soc.* **1976**, *98*, 8289. (40) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1980**, *19*, 2354. (41) Bird, P. H.; Fraser, A. R.; Hall, D. N. *Inorg. Chem.* **1977**, *16*, 1923. (42) Fischer, E. O.; Ruhs, A.; Friedrich, P.; Huttner, G. *Angew. Chem.* **1977**, *89*, 481. (43) Potenza, J. A.; Johnson, R. J.; Chirico, R.; Efraty, A. *Inorg. Chem.* **1977**, *16*, 2354. (44) Bailey, W. I., Jr.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764. (45) *Ibid.* (46) *Ibid.* (47) Bennett, M. A.; Johnson, R. N.; Robertson, G. B.; Turney, T. W.; Whimp, P. O. *Inorg. Chem.* **1976**, *15*, 97. (48) Angoletta, M.; Bellon, P. L.; Demartin, F.; Sansoni, M. *J. Organomet. Chem.* **1981**, *208*, C12. (49) Boag, N. M.; Green, M.; Howard, J. A. K.; Stone, F. G. A.; Wadepohl, H. *J. Chem. Soc., Dalton Trans.* **1981**, 862. (50) Boag, N. M.; Green, M.; Howard,

Caption to Figure 3 continued

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Table IV. Frequency Values (cm^{-1}) of the Vibrational Modes of the Acetylene Coordinated in $\text{Co}_4(\text{CO})_{10}(\text{acetylene})$ Complexes^a

mode ^b	complexes ^c							
	I ^d		Ib ^d		Ic ^{d,e}		Id ^d	
	A	B	A	B	A	B	A	B
$\nu(\text{CH})$	3020 vw (a ₁) 2993 vw (b ₁)	not obsd not obsd	3012 vw (a ₁) 2985 vw (b ₁)	not obsd not obsd	2994 vw (a')	not obsd f	f f	f f
$\nu(\text{CC})$	1199 m (a ₁)	1205 m	1157 m (a ₁)	1165 m	not obsd	not obsd	1177 m (a ₁)	1185 m
$\delta(\text{CH})$	1120 m (a ₁) 983 ms (b ₁)	1125 w 990 m	1109 w (a ₁) 982 ms (b ₁)	1116 w 988 m	not obsd 793 (a')	not obsd 797	909 m (a ₁) 711 s (b ₁)	915 w 718 m
$\gamma(\text{CH})$	922 w (a ₂) 837 m (b ₂)	913 m 825 m	918 w (a ₂) 835 m (b ₂)	909 m 823 m	888 (a'') 666 (a'')	878 656	ca. 709 m, sh (a ₂) 636 (b ₂)	703 ms 630 w
$\nu(\text{CoC})$	619 m (b ₂)	619 m	603 m (b ₂)	603 m	ca. 598 (a'')	ca. 590	not obsd	not obsd

^aFor the complex Ia the only mode assigned with certainty is the $\nu(\text{CC})$ at 1178 cm^{-1} (CsI disk) and at 1184 cm^{-1} (CS_2 solution). ^b ν , δ , and γ denote bond stretching, in-plane angle bending and out-of-plane angle bending modes, respectively. ^cColumn A, CsI disk; column B, CS_2 solution. ^dIn parentheses, the symmetries of the modes, according to the formal C_{2v} or C_s symmetries of the Co_4C_2 core, respectively. ^eTentative assignments, observed as weak features in the spectra of Id. ^fObscured by the $\nu(\text{CO})$ modes.

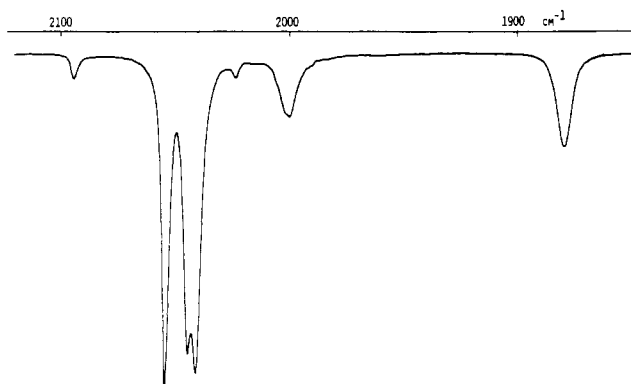
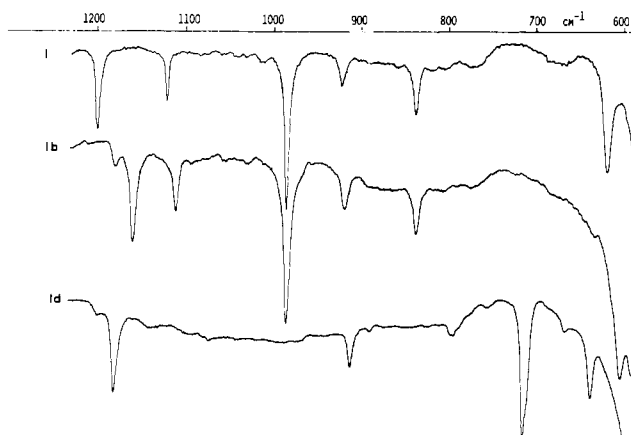
Figure 4. IR spectrum of $\text{Co}_4(\text{CO})_{10}\text{C}_2\text{H}_2$ in the CO stretching region (*n*-heptane solution; bands at 2093, 2053, 2043, 2040, 2023, 2000, and 1879 cm^{-1}).Figure 5. Middle-region IR spectra of $\text{Co}_4(\text{CO})_{10}\text{C}_2\text{H}_2$ (I), $\text{Co}_4(\text{CO})_{10}^{13}\text{C}_2\text{H}_2$ (Ib), and $\text{Co}_4(\text{CO})_{10}\text{C}_2\text{D}_2$ (Id) (CsI disk).

Table V

	ethane ^a	ethylene ^a	$\text{Co}_4(\text{CO})_{10}\text{C}_2\text{H}_2$
$d(\text{C}-\text{C}), \text{\AA}$	1.573	1.353	1.399
$\nu(\text{C}-\text{C}), \text{cm}^{-1}$	993	1623	1199
$^1J_{\text{CC}}, \text{Hz}$	34.6	67.6	21

^aFrom ref 15. ^bFrom ref 20.

motions) and two out-of-plane wagging motions (in-phase A_2 and out-of-phase B_2). The A_2 mode is not IR active in pure C_{2v} symmetry, but it is expected to gain some intensity, since the actual molecular geometry is C_2 . These modes have been unequivocally assigned^{15,21} for the cis-disubstituted olefins and give rise to bands at ca. 1400 cm^{-1} (B_1), ca. 1260 cm^{-1} (A_1), $970\text{--}900 \text{ cm}^{-1}$ (A_2), and $750\text{--}680 \text{ cm}^{-1}$ (B_2). Four bands are the obvious candidates for these modes in the spectrum of I at 1120 m, 983 ms, 922 w, and 837 m cm^{-1} (Figure 5) and can be assigned to the A_1 , B_1 , A_2 and B_2 modes, respectively. The reverse order of the in-plane bending motions with respect to the cis-disubstituted olefins is suggested on the basis of the relative intensity of the bands and of the value of the shifts in isotopically labeled acetylenes. The highest frequency band clearly shifts in the Ib spectrum (ca. 11 cm^{-1}) and the H/D isotopic ratio (1.23) is small: both effects probably can be ascribed to the coupling with the $\nu(\text{C}-\text{C})$ A_1 mode.

The CS_2 solution spectra (Figure 6 and Table IV) require a further comment. All bands in these spectra have frequencies very close to those of the corresponding bands in the spectra of the solid, but they also have different relative intensities and are significantly broader. Recognizing that CS_2 is not the best solvent for sharp infrared bands, we tentatively suggest that the broadness and in-

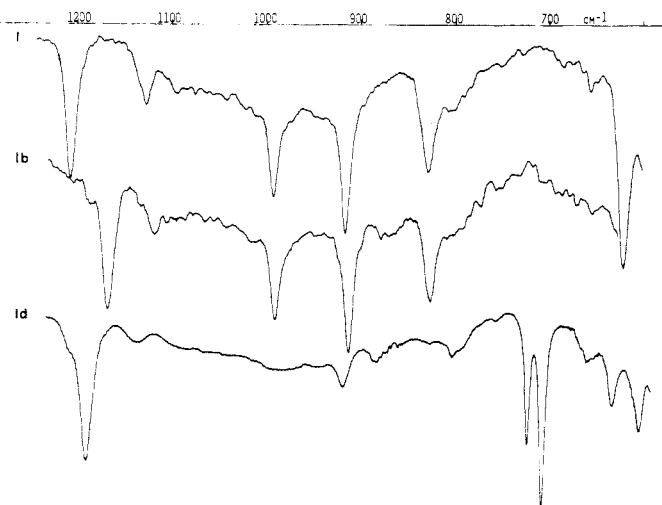


Figure 6. Middle-region IR spectra (CS_2 solution): see Figure 5 for captions.

tensity of the bands are due to a rather floppy geometry in solution, so that the effects arise from the coexistence of similar, but not identical, molecules.

(iv) Co-Acetylene Stretching Modes. The analysis of the cobalt-acetylene stretching vibrations is obviously very approximate, because the most part of the relevant absorptions are obscured by the strong bands belonging to the Co-CO stretching and deformation modes. To have some insight in this analysis, we used a very simplified model of the Co_4C_2 cluster with C_{2v} symmetry, taking the six Co-C bond stretchings as base and neglecting any coupling between the stretching modes and any other vibrational modes.

The Co-C stretchings span the $2A_1 + A_2 + 2B_1 + B_2$ modes and the relevant frequency values are expected to have approximately the order $\nu(B_2) > \nu(A_1(1)) > \nu(B_1(1)) \approx \nu(A_2) > \nu(A_1(2)) > \nu(B_1(2))$. Formally, these modes represent the vibration of the rigid C_2 unit along y (B_2), z ($A_1(1)$), and x ($B_1(1)$) axes and the rotation of the same unit around the z (A_2) and the y ($B_1(2)$) axes, respectively, whereas the $A_1(2)$ mode is mainly a deformation of the Co_4 framework. The only band clearly belonging to these modes is that at 619 cm^{-1} , shifted to 602 cm^{-1} in Ib, which can be tentatively assigned to the B_2 mode. Support for this assignment is provided by the observation that this band is greatly shifted in the Ic spectrum (to ca. 598 cm^{-1}), probably because of coupling to the mode with the band at 637 cm^{-1} (C-D wagging of the same symmetry). The value of the frequency agrees with the values reported for the vibration of a C_2 unit bonded to cobalt clusters, as in $\text{Co}_6\text{C}_2(\text{CO})_{14}\text{S}^{22}$ and $(\text{CO})_9\text{Co}_3\text{C}_2\text{Co}_3(\text{CO})_9$.²³

The bands belonging to the other modes fall in the region below 600 cm^{-1} and are obscured by the carbonyl bands. A careful comparison of the spectra of I and Ib in the $600\text{--}300\text{ cm}^{-1}$ region (Figure 7) suggests the presence of other Co-acetylene stretching modes at ca. 568 and ca. 545 cm^{-1} .

(3) Coordinated Acetylene and Acetylene Adsorbed on Metals. Very few complete vibrational studies have been reported for acetylenes coordinated to metal complexes. Ywashita et al.¹⁸ studied the vibrational behavior of the $\mu\text{-}\eta^2$ -acetylene coordinated to cobalt atoms in $\text{Co}_2(\text{CO})_6\text{C}_2\text{H}_2$ (II) and compared it with that of the free acetylene in the first electronically excited state. More

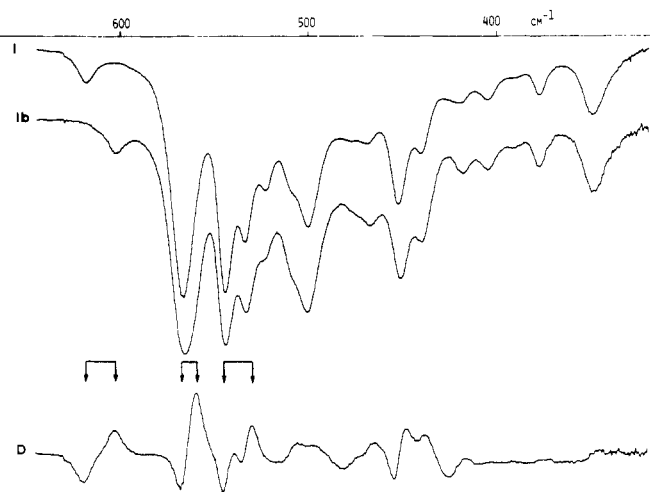


Figure 7. IR spectra in the CO deformation region of $\text{Co}_4(\text{CO})_{10}\text{C}_2\text{H}_2$ (I) and $\text{Co}_4(\text{CO})_{10}^{13}\text{C}_2\text{H}_2$ (Ib). Curve D is the difference between the above spectra; arrows indicate the presumed frequencies of the Co-acetylene stretching modes.

recently, Sheppard and co-workers reported the assignment of the vibrational modes of a $\mu_3\text{-}\eta^2$ -acetylene on $\text{Os}_3(\text{CO})_9(\mu\text{-CO})\text{C}_2\text{H}_2$ (III).¹⁹ In both studies the assignments are supported by isotopic labeling. It could be interesting to correlate the values of the frequencies of the main vibrational modes with the type of coordination of the acetylene but, unfortunately, the paucity of the examples makes such a correlation unreliable. Furthermore, structural data for III are, at the moment, unknown. We expect the acetylenic character of the ligand to decrease in the order $\text{II} > \text{III} > \text{I}$, taking into account the increasing electron donation from the metal orbitals to the antibonding orbitals of the acetylene owing to the increasing number of metal atoms coordinated to it. The best test is represented by the value of the C-C stretching frequency, which varies from 1402 cm^{-1} (II) to 1310 cm^{-1} (III) to 1199 cm^{-1} (I) and is also related to the value of the C-C distance (at least, for the Co complexes). The frequency values for the hydrogen modes are less clearly related, probably due to the greater effect that the crystal packing can have on the freedom of the hydrogen motions. In any event, whereas the C-H stretching frequencies indicate a decreasing acetylenic character in the order $\text{II} > \text{I} > \text{III}$, the C-H deformation frequencies increase in the expected order $\text{II} > \text{III} > \text{I}$, one which parallels the increasing average frequency of the same modes in the order alkyne $<$ olefins $<$ alkanes.²⁴

These relationships might also help identify species formed by chemisorption of an acetylene on a metal surface. It has been pointed out recently that the electron energy loss spectra of acetylene adsorbed on a range of transition-metal surfaces fall in two distinct groups.²⁵ Particularly significant in this classification are the features intensity and frequency of the loss assignable to the C-C stretching. Whereas the intensity depends on the metal surface selection rules for dipolar scattering,²⁶ the frequency value seems to be indicative of the kind of coordination between acetylene and metal surface and, in particular, of the number of the coordinating metal atoms. In one group the acetylene shows a $\nu(\text{C-C})$ value close to 1400 cm^{-1} and has been suggested to be bonded in a manner similar to that found in complex III.²⁵ The $\nu(\text{C-C})$

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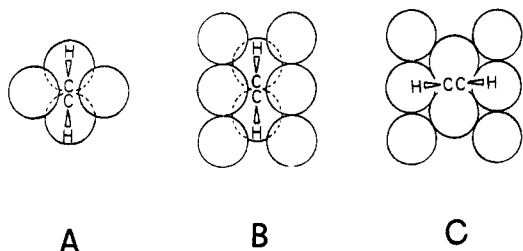


Figure 8. Schematic structures of the title complex and acetylene adsorbed on metal surfaces: A, $\text{Co}_4(\text{CO})_{12}\text{C}_2\text{H}_2$; B, acetylene on Pd(110);²⁷ C, acetylene on Ni(111).

frequencies of the species belonging to the other group fall in the range $1200\text{--}1300\text{ cm}^{-1}$, values which suggest that the adsorbed molecule is coordinated to more than three metal atoms. Complex I can be a good model for these species, as the butterfly arrangement of four metal atoms can be recognized in the (110) fcc crystal plane involving metal atoms in the first and second layer (Figure 8): an example can be the loss peak at 1240 cm^{-1} , assigned to $\nu(\text{C}\text{--}\text{C})$ of the acetylene adsorbed on Pd(110) at room temperature.²⁷

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On the other hand, the four-atom framework in the (111) fcc crystal plane can be regarded as a "flat" butterfly. The proposed structure of the acetylene adsorbed on it resembles that of complex I (Figure 8), and, actually, the loss peaks corresponding to $\nu(\text{C}\text{--}\text{C})$ have been found at 1215 cm^{-1} for Ni(111) faces²⁸ and at 1307 cm^{-1} for Cu(111) faces.²⁵

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Registry No. I, 12282-40-5; Ia, 96532-36-4; Ib, 96532-37-5; Ic, 96503-22-9; $\text{Co}_2(\text{CO})_8$, 10210-68-1; $\text{Co}_4(\text{CO})_{12}$, 17786-31-1; DCCD, 1070-74-2; HCCH, 74-86-2; $\text{H}^{13}\text{C}^{13}\text{CH}$, 35121-31-4; CaC_2 , 75-20-7; D_2O , 7789-20-0.

Supplementary Material Available: Listing of observed and calculated structure factors, thermal anisotropic parameters, and data of Figure 3 (formula of the complexes, structural values, and full bibliographic references) (21 pages). Ordering information is given on any current masthead page.

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Metal Atom Synthesis of Metallaboron Clusters. 7.¹ Synthesis and Structural Characterization of an Open-Cage Metallathiaborane Cluster Having a Triple-Decker Structure: 4,6-($\eta\text{-C}_5\text{H}_5$)₂Co₂-3,5-S₂B₂H₂

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The reaction of thermally generated cobalt atoms with cyclopentadiene, pentaborane(9), and either carbonyl sulfide or hydrogen sulfide was found to give a number of sulfur-containing clusters including the new small cage dicobaltadithiaborane cluster 4,6-($\eta\text{-C}_5\text{H}_5$)₂Co₂-3,5-S₂B₂H₂ and the previously reported compounds $\mu_3\text{-CO-(}\eta\text{-C}_5\text{H}_5\text{)}_3\text{Co}_3\text{S}$, 2,3-($\eta\text{-C}_5\text{H}_5$)₂Co₂-6-SB₅H₇, and 6,8-($\eta\text{-C}_5\text{H}_5$)₂Co₂-7,9-S₂B₅H₅. The results of an X-ray crystallographic study of 4,6-($\eta\text{-C}_5\text{H}_5$)₂Co₂-3,5-S₂B₂H₂ demonstrated that the compound has a triple-decker structure based on a pentagonal bipyramid missing one equatorial vertex, with the cobalt atoms occupying apical and the sulfur atoms equatorial positions on the open face. Such a cage geometry is consistent with the cluster's $2n + 4$ skeletal electron count but is not the pentagonal-pyramidal nido structure normally adopted by isoelectronic boron hydride and carborane cage compounds. Crystal data for 4,6-($\eta\text{-C}_5\text{H}_5$)₂Co₂-3,5-S₂B₂H₂: space group $P2_1/c$; $Z = 4$; $a = 9.847(7)\text{ \AA}$, $b = 9.939(6)\text{ \AA}$, $c = 12.565(5)\text{ \AA}$, $\beta = 94.01(5)^\circ$; $V = 1227\text{ \AA}^3$. The structure was refined by full-matrix least squares to a final R of 0.059 and R_w of 0.062 for the 1418 reflections which had $F_o^2 > 3\sigma(F_o^2)$.

Introduction

We have previously reported² the use of metal atom vaporization techniques to produce small cage metallathiaborane, 2,3-($\eta\text{-C}_5\text{H}_5$)₂Co₂-6-SB₅H₇, and metalladithiaborane, 6,8-($\eta\text{-C}_5\text{H}_5$)₂Co₂-7,9-S₂B₅H₅ and 7-($\eta\text{-C}_5\text{H}_5$)Co-6,8-S₂B₅H₈, clusters. These compounds were obtained by the cocondensation of thermally generated cobalt atoms with either pentaborane(9) or hexaborane(10)

and cyclopentadiene, followed by reaction with a sulfur source such as cyclohexene sulfide. These results led us to investigate the use other potential sulfur sources in metal atom-boron hydride reactions which might result in either higher yields or the generation of new types of cluster systems. We have now found that if metal vapors are reacted with small boron hydrides and either carbonyl sulfide or hydrogen sulfide, cage fragmentation reactions occur to generate smaller cage metallathiaboron clusters. As an example, we report here the isolation and structural characterization of a unique hybrid cluster, 4,6-($\eta\text{-C}_5\text{H}_5$)₂Co₂-3,5-S₂B₂H₂, containing equal numbers of cobalt, sulfur, and boron cage framework atoms.

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