

This observation gives strong evidence that the species  $\text{Li}_2\text{Cl}_2$  may exist in these solutions, but it must be realized that the solutions are not ideal and effects such as those due to dispersion and volume must be present.

When lithium hydride is dissolved in lithium chloride the limiting value of a curve of temperature *vs.* composition approaches a value of  $\nu = 1$  in Fig. 2. For an ideal solution of  $\text{LiH}$  (un-ionized) in lithium chloride or  $\text{Li}^+$  and  $\text{H}^-$  in lithium chloride the limiting value of this function would follow a line of  $\nu = 1$ . Because of the common ion effect one cannot, therefore, distinguish between ionized and un-ionized lithium hydride in this system. There is certainly strong indication

from these data that dimerization of the  $\text{LiH}$  in lithium chloride does not occur.

Of interest to the present discussion are the data of Berkowitz and Chupka<sup>14</sup> on the mass spectrometric examination of the alkali metal halides. They found, for example, that lithium chloride has a dimer:monomer ratio of 2.50:1 for species present in the vapor phase when this vapor is in equilibrium with its condensed phase. Their data show polymerization to be a general characteristic of the lithium salts. The sodium, potassium, and rubidium salts all tend to have monomers as the predominant species present in the vapor phase.

(14) J. Berkowitz and W. A. Chupka, *J. Chem. Phys.*, **29**, 653 (1958).

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,  
BROOKHAVEN NATIONAL LABORATORY, UPTON, NEW YORK 11973

## Crystal and Molecular Structure of Manganese Pentacarbonyl Hydride<sup>1</sup>

By SAM J. LA PLACA, WALTER C. HAMILTON, AND JAMES A. IBERS

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Manganese pentacarbonyl hydride,  $\text{HMn}(\text{CO})_5$ , crystallizes with eight molecules in space group  $I2/a$  of the monoclinic system in a cell which at  $-75^\circ$  has the dimensions  $a = 12.18$ ,  $b = 6.35$ ,  $c = 19.20$  Å, and  $\beta = 93.3^\circ$ . Three-dimensional X-ray data were collected from crystals grown from the liquid phase, and the structure was solved by standard techniques. Although the H atom was not located, its profound influence on the geometry of the molecule can be inferred from the fact that the  $\text{Mn}(\text{CO})_5$  portion of the molecule shows insignificant deviations from  $C_{4v}$  symmetry: the five carbon atoms of the carbonyls occupy five of the six corners of a nearly regular octahedron; the manganese atom lies slightly above the basal plane along the fourfold axis toward the apical carbonyl group. This result is in direct contrast to claims from infrared studies that the molecule in the gas phase definitely has symmetry lower than  $C_{4v}$ , and to arguments based on the marked similarities in chemical and physical properties of  $\text{HMn}(\text{CO})_5$  and  $\text{Fe}(\text{CO})_5$  that  $\text{HMn}(\text{CO})_5$  must be a trigonal bipyramid with the H buried in the metal orbitals.

### Introduction

Based in part on chemical and physical studies of transition metal carbonyl hydrides by Hieber and his associates<sup>2</sup> and in part on spectroscopic and theoretical studies by Cotton and his associates,<sup>3-5</sup> the notion has developed that the metal-hydrogen bond in transition metal carbonyl hydrides is abnormally short and that the hydrogen exerts little, if any, influence on the geometrical arrangement of the other ligands around the metal. Thus Hieber and Wagner<sup>2</sup> describe the Mn-H group as a pseudo-Fe atom, and Cotton and Wilkinson<sup>3</sup> suggest that the proton is buried in the electron density of the metal atom. In the past few years there has accumulated evidence from diffraction studies, evidence more direct than that based on spectroscopic data and physical properties, that the hydrogen atom is at a normal distance from the metal and in fact exerts a profound influence on the geometrical arrangement of other ligands about the metal in partially and totally substituted transition metal carbonyl hydrides. For

example, Owston, Partridge, and Rowe<sup>6</sup> showed that the phosphorus and bromine atoms in  $\text{HPt}[\text{P}(\text{C}_2\text{H}_5)_3]_2\text{Br}$  were at three of the four corners of a square, with the platinum at the center.<sup>7</sup> Similarly, Orioli and Vaska<sup>8</sup> found that in  $\text{HOsBr}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_3$  the bromine, carbon, and three phosphorus atoms were at five of the six vertices of an octahedron. More recently, La Placa and Ibers<sup>9,10</sup> not only found that in  $\text{HRh}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_3$  the carbon and three phosphorus atoms were at four of the five vertices of a trigonal bipyramid, as might be expected on the basis of the earlier studies that showed the influence of hydrogen on the geometry, but they also located the hydrogen itself at the fifth vertex at a normal covalent Rh-H distance of  $1.60 \pm 0.12$  Å.

Still the argument might be made<sup>11</sup> that these substituted carbonyl hydrides differ from the parent compounds on which most of the spectroscopic data have been collected. This seems unlikely in view of the

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) W. Hieber and G. Wagner, *Z. Naturforsch.*, **13b**, 340 (1958).

(3) F. A. Cotton and G. Wilkinson, *Chem. Ind.* (London), 1305 (1956).

(4) F. A. Cotton, J. L. Down, and G. Wilkinson, *J. Chem. Soc.*, 833 (1959).

(5) F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 4425 (1958).

(6) P. G. Owston, J. M. Partridge, and J. M. Rowe, *Acta Cryst.*, **13**, 246 (1960).

(7) Similar results have been obtained by R. Eisenberg and J. A. Ibers (unpublished) on  $\text{HPt}[\text{PC}_2\text{H}_5(\text{C}_6\text{H}_5)_2]_2\text{Cl}$ .

(8) P. L. Orioli and L. Vaska, *Proc. Chem. Soc.*, 333 (1962).

(9) S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.*, **85**, 3501 (1963).

(10) S. J. La Placa and J. A. Ibers, *Acta Cryst.*, in press.

(11) J. Chatt, *Proc. Chem. Soc.*, 318 (1962).

close parallels in high-field proton chemical shifts and in the metal-hydrogen vibrational frequencies; all the evidence points to completely similar environments of the hydrogen in the parent and substituted compounds. Nevertheless, it seemed essential to investigate by diffraction methods one of the parent compounds, and for this purpose we chose manganese pentacarbonyl hydride, the most stable. This study, undertaken in preparation for a neutron diffraction study, was summarized recently.<sup>12</sup> In this paper we present in detail our X-ray evidence which shows unequivocally that the  $\text{Mn}(\text{CO})_5$  portion of the molecule has  $C_{4v}$  symmetry with the carbon atoms at five of the six vertices of an octahedron. Hence in this parent transition metal carbonyl hydride the hydrogen does exert a definite influence on the geometry of the ligands.

#### Collection of X-Ray Data

Samples of  $\text{HMn}(\text{CO})_5$  in Pyrex capillaries were kindly supplied by W. N. Lipscomb. The material had been prepared some time earlier by F. G. A. Stone. Crystals were grown from the liquid phase by cooling the capillary containing the sample in a stream of cold nitrogen gas, using a modification of the apparatus described by Post, Schwartz, and Fankuchen.<sup>13</sup> The sample temperature was held constant at  $-75^\circ$  (some  $50^\circ$  below the melting point) during the X-ray photography.<sup>14</sup> On the basis of the observed Laue symmetry  $2/m$  and the systematic absences  $h + k + l \neq 2n$  for  $hkl$  and  $h \neq 2n, l \neq 2n$  for  $h0l$ ,  $\text{HMn}(\text{CO})_5$  may be assigned to space groups  $C_{2h}^6$ - $I2/a$  or  $C_s^4$ - $Ia$  of the monoclinic system. The former space group was assumed and this assumption led to the reasonable structure described below. The cell dimensions at  $-75^\circ$  are  $a = 12.18 \pm 0.02$ ,  $b$  (unique axis)  $= 6.35 \pm 0.01$ ,  $c = 19.20 \pm 0.03$  Å.,  $\beta = 93.3 \pm 0.5^\circ$ . The calculated density for eight molecules in the cell is  $1.70$  g./cm.<sup>3</sup>, a reasonable value when compared with the density at  $20^\circ$  of the liquid of  $1.465$  g./cm.<sup>3</sup>.<sup>2</sup> The reciprocal lattice nets  $h0l$ ,  $h1l$ ,  $hk0$ ,  $hk1$ ,  $hk2$ ,  $hk3$ ,  $hk\bar{k}$ ,  $h,k,2k$ , and  $hhl$  were recorded photographically by the precession method using Mo  $K\alpha$  radiation, and in this way the intensities of 738 reflections, of which 594 were independent, were obtained. Owing to various mishaps with the low-temperature system these data were obtained in experiments from three separate crystals grown from the same capillary. The intensities were estimated visually and were reduced to structure amplitudes in the usual way. The linear absorption coefficient of  $\text{HMn}(\text{CO})_5$  for Mo  $K\alpha$  radiation is  $17.8$  cm.<sup>-1</sup> and the sample was of approximate diameter  $0.3$  mm. Thus corrections of absorption are expected to be small and were neglected. No correction was made for extinction effects.

(12) S. J. La Placa, J. A. Ibers, and W. C. Hamilton, *J. Am. Chem. Soc.*, **86**, 2288 (1964).

(13) B. Post, R. S. Schwartz, and I. Fankuchen, *Rev. Sci. Instr.*, **22**, 218 (1951).

(14) Photographs taken as low as  $-140^\circ$  indicate no phase transition between that temperature and  $-24^\circ$ .

TABLE I  
POSITIONAL PARAMETERS FOR  $\text{HMn}(\text{CO})_5$

Atom	$x^a$	$y$	$z$
Mn	-0.15152 (6)	0.2554 (3)	0.12285 (4)
C <sub>1</sub>	-0.0913 (5)	0.3666 (17)	0.2037 (4)
O <sub>1</sub>	-0.0542 (4)	0.4377 (12)	0.2537 (3)
C <sub>2</sub>	-0.1940 (5)	-0.0005 (15)	0.1589 (5)
O <sub>2</sub>	-0.2197 (5)	-0.1587 (11)	0.1781 (4)
C <sub>3</sub>	-0.1237 (5)	0.4812 (17)	0.0664 (4)
O <sub>3</sub>	-0.1108 (5)	0.6156 (12)	0.0291 (4)
C <sub>4</sub>	-0.0247 (5)	0.1283 (14)	0.0963 (4)
O <sub>4</sub>	0.0522 (4)	0.0474 (12)	0.0792 (3)
C <sub>5</sub>	-0.2906 (5)	0.3563 (14)	0.1315 (4)
O <sub>5</sub>	-0.3770 (4)	0.4204 (12)	0.1349 (4)

<sup>a</sup> Numbers in parentheses here and in subsequent tables are estimated standard deviations in the least significant figures.

Photographs of a given zone of the same crystal at the beginning and end of the photography (perhaps 100 hr. of exposure to the X-ray beam) are identical and attest to the stability of the sample. Nevertheless as the exposure progressed the transparent crystals became pink and eventually deep red, presumably owing to the formation in very small concentrations of a free-radical species, perhaps  $\cdot\text{Mn}(\text{CO})_5$ . On warming the sample, recombination evidently occurred, for the liquid was colorless and subsequent crystals were transparent before exposure to the X-ray beam.

#### Determination and Refinement of the Structure

The Mn atom was readily located on a three-dimensional Patterson function map; the five carbon and five oxygen atoms were subsequently located on a difference Fourier synthesis that had been phased by the manganese contributions to the structure factors.

The structure was refined by the least-squares technique. In these calculations the observed structure amplitudes  $|F_o|$  for all 738 reflections were included. The quantity  $\sum w(|F_o| - |F_c|)^2$  was minimized, with weights assigned as follows:  $F \geq 50$  electrons,  $w = (50/F)^2$ ;  $20 \leq F < 50$ ,  $w = 1.0$ ;  $F < 20$ ,  $w = (F/20)^2$ . The atomic scattering factors tabulated by Ibers<sup>15</sup> were employed as were the dispersion corrections tabulated by Templeton.<sup>16</sup> These dispersion corrections were applied to  $F_o$ .<sup>17</sup> In an initial set of refinements all atoms were constrained to vibrate isotropically, and the  $R$  factor or agreement factor

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

decreased smoothly to 0.080. All atoms were then allowed to vibrate anisotropically in a further series of calculations, and the  $R$ -factor decreased significantly<sup>18</sup> to 0.045. A difference Fourier synthesis, calculated at this point and based only on the independent reflections, exhibited a few peaks as high as  $0.35$  e/Å.<sup>3</sup>, but provided no convincing evidence of the hydrogen atom position.

In Table I the final positional parameters from the

(15) J. A. Ibers, "International Tables for X-ray Crystallography," Kynoch Press, Birmingham, England, 1962, Vol. 3, Table 3.3.1A.

(16) D. H. Templeton, *ibid.*, Table 3.3.2A.

(17) J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

(18) W. C. Hamilton, *ibid.*, in press.

TABLE II  
 ANISOTROPIC THERMAL PARAMETERS FOR  $\text{HMn}(\text{CO})_5$ 

Atom	$\beta_{11}^a$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Mn	0.00294 (5)	0.0151 (3)	0.00154 (2)	-0.00008 (17)	-0.000009 (25)	0.00066 (22)
C <sub>1</sub>	0.0051 (4)	0.0241 (25)	0.0020 (2)	0.0002 (10)	0.0004 (2)	-0.0002 (9)
O <sub>1</sub>	0.0088 (4)	0.0322 (22)	0.0020 (1)	-0.0035 (8)	-0.0010 (2)	-0.0022 (6)
C <sub>2</sub>	0.0049 (4)	0.0148 (17)	0.0029 (2)	0.0005 (9)	0.0003 (3)	0.0002 (9)
O <sub>2</sub>	0.0088 (5)	0.0187 (15)	0.0047 (3)	-0.0023 (8)	0.0016 (3)	0.0014 (7)
C <sub>3</sub>	0.0045 (4)	0.0270 (25)	0.0020 (2)	0.0008 (10)	0.0006 (3)	0.0037 (9)
O <sub>3</sub>	0.0087 (4)	0.0376 (26)	0.0036 (2)	0.0004 (10)	0.0017 (3)	0.0048 (8)
C <sub>4</sub>	0.0043 (4)	0.0259 (26)	0.0019 (2)	-0.0014 (9)	0.0002 (2)	-0.0005 (9)
O <sub>4</sub>	0.0060 (3)	0.0379 (26)	0.0033 (2)	0.0076 (9)	0.0017 (2)	0.0016 (7)
C <sub>5</sub>	0.0041 (4)	0.0214 (22)	0.0026 (2)	-0.0007 (10)	0.0001 (2)	0.0006 (9)
O <sub>5</sub>	0.0036 (3)	0.0333 (23)	0.0057 (3)	0.0026 (7)	0.0011 (3)	0.0010 (9)

<sup>a</sup> The general anisotropic temperature factor has the form  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .

 TABLE III  
 ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (IN Å.)

Atom	Minimum	Intermediate	Maximum
Mn	0.147 (1)	0.160 (4)	0.185 (4)
C <sub>1</sub>	0.185 (9)	0.201 (9)	0.222 (12)
O <sub>1</sub>	0.156 (10)	0.259 (9)	0.283 (8)
C <sub>2</sub>	0.172 (11)	0.193 (9)	0.234 (10)
O <sub>2</sub>	0.179 (10)	0.252 (8)	0.307 (8)
C <sub>3</sub>	0.145 (17)	0.183 (9)	0.266 (13)
O <sub>3</sub>	0.191 (12)	0.258 (8)	0.324 (11)
C <sub>4</sub>	0.175 (9)	0.189 (9)	0.234 (12)
O <sub>4</sub>	0.154 (9)	0.238 (9)	0.318 (10)
C <sub>5</sub>	0.174 (8)	0.205 (15)	0.255 (13)
O <sub>5</sub>	0.154 (7)	0.263 (10)	0.329 (9)

anisotropic refinement are given. In Table II the corresponding thermal parameters are given. In Table III we give the root-mean-square amplitudes of vibration of the atoms. In general these vibrations seem reasonable, but no interpretation in terms of rigid-body motions has been attempted. It seems advisable to defer such a treatment until after the neutron diffraction data have been obtained. In Table IV the values of  $F_o$  and  $F_c$  are given for the independent reflections. The  $F_o$  so tabulated are average values in those cases where there was more than one observation. The  $R$  factor for the data of Table IV is 0.043.

### Description of the Structure

There are no restrictions of a crystallographic nature on the symmetry of the  $\text{HMn}(\text{CO})_5$  molecule since all atoms lie in general positions in the space group. The structure described by the symmetry operations of the space group, the cell dimensions, and the parameters of Table I consists of the packing of discrete  $\text{HMn}(\text{CO})_5$  molecules of approximate symmetry  $C_{4v}$ . Part of this packing arrangement is depicted in Fig. 1. The  $\text{Mn}(\text{CO})_5$  portion of a molecule departs insignificantly from  $C_{4v}$  symmetry, and if the hydrogen is on the fourfold axis the coordination around the manganese is essentially octahedral. A symmetry as high as  $C_{4v}$  is said to be inconsistent with the infrared spectrum.<sup>4,19</sup> Since we feel that it is unlikely that the configuration in the gas phase is less symmetric than that in the solid phase, we suggest that a reinvestigation of the complex infrared spectrum is in order.

(19) W. E. Wilson, *Z. Naturforsch.*, **13b**, 349 (1958).

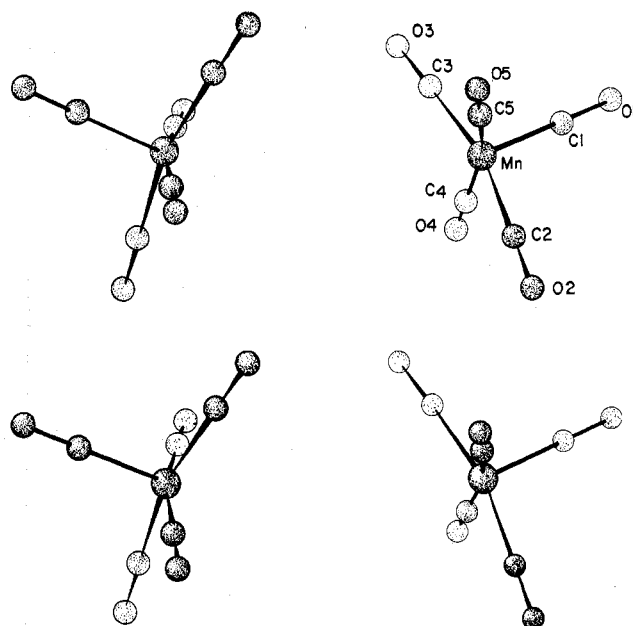


Fig. 1.—A perspective view of part of the  $\text{HMn}(\text{CO})_5$  crystal structure. The  $b$  axis is vertical; the fourfold axes lie nearly in the  $(\bar{1}01)$  plane.

In Table V the important intramolecular bond distances and angles are listed. Also listed in Table V are the standard deviations of these quantities as estimated from the error matrix. The geometry of the  $\text{Mn}(\text{CO})_5$  portion in  $\text{HMn}(\text{CO})_5$  is markedly similar to that in  $\text{Mn}_2(\text{CO})_{10}$ .<sup>20</sup> Thus in  $\text{Mn}_2(\text{CO})_{10}$  the Mn-C distances range from 1.792 to 1.855 and average  $1.823 \pm 0.006$  Å. (without an attempted correction for thermal motion) and the apical to basal C-Mn-C angles range from  $92.1$  to  $96.1^\circ$ . From the data of Table V it is clear that the Mn-C distances are comparable (mean  $1.836 \pm 0.004$  Å.), but that the C-Mn-C angles are slightly larger, as is expected since H is far less bulky than the  $\text{Mn}(\text{CO})_5$  group. In both structures the shortening of the apical Mn-C bond, if real, is surely small.

From Fig. 1 it is clear that the  $\text{HMn}(\text{CO})_5$  molecules pack in such a way that the hydrogen atoms in two adjacent molecules related by a twofold rotation point toward one another. The Mn-Mn separation is  $5.167 \pm 0.013$  Å., the angle between the fourfold axes of the

(20) L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963).

TABLE IV  
 OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS) FOR  $\text{HMn}(\text{CO})_6$ 

K	L	OBS	CAL	K	L	OBS	CAL	K	L	OBS	CAL	K	L	OBS	CAL	K	L	OBS	CAL							
0	0	763.2		0	16	38.7	38.4	1	-12	82.6	82.4	1	2	98.5	101.7	1	10	50.9	50.1	*****H12*****						
0	8	133.7	135.6	0	-16	11.6	13.4	1	16	50.1	51.7	1	-2	123.7	131.3	1	-10	38.8	38.7	0	0	17.7	15.8			
0	12	74.7	72.2	0	18	21.4	21.5	1	-16	68.3	67.9	1	4	23.5	24.0	1	12	28.6	28.0	0	2	40.9	42.6			
0	14	17.7	19.5	0	-18	59.9	61.1	1	-18	18.4	19.2	1	-4	34.8	35.5	1	-12	42.3	42.4	0	-2	30.2	30.0			
0	16	75.9	76.8	0	20	50.7	51.8	1	20	44.2	44.5	1	6	88.4	87.2	1	14	45.2	45.5	0	6	53.0	53.5			
0	18	12.3	12.2	0	22	33.3	33.3	1	-20	52.5	52.3	1	-14	21.6	21.6	1	16	24.7	23.4	0	-6	53.6	51.9			
0	20	41.0	42.6	0	-22	36.3	31.3	1	-24	26.3	25.6	1	8	43.6	42.7	1	-16	31.0	32.6	0	-8	17.8	16.3			
0	22	21.3	21.9	0	24	21.9	20.7	1	2	17.6	18.1	1	-8	38.0	38.7	1	10	18.8	18.8	0	10	30.8	26.8			
0	24	32.7	34.9	0	-24	21.9	20.7	1	10	101.4	98.7	1	10	68.1	69.6	1	-18	32.0	33.3	0	-10	59.6	61.1			
1	1	31.6	33.7	0	1	17.2	18.1	1	-10	70.3	70.3	1	-10	70.3	70.3	1	18	18.8	16.7	0	-12	25.1	25.8			
1	5	16.9	20.1	1	-1	48.6	48.5	1	2	14.1	10.7	1	12	28.9	27.4	1	-18	22.1	19.9	0	-12	19.4	19.1			
1	7	46.7	43.0	1	5	209.2	225.1	1	3	15.1	11.7	1	14	35.6	36.4	1	-20	21.8	22.2	0	-14	50.5	52.4			
1	9	23.7	21.6	1	-5	27.1	27.0	1	5	21.7	19.3	1	-14	75.0	76.9	1	-22	17.8	19.0	0	-14	17.9	17.9			
1	11	58.3	60.3	1	9	51.8	48.0	1	5	77.8	72.3	1	16	32.5	29.6	1	2	17.3	16.1	0	-14	50.5	52.4			
1	13	33.0	32.8	1	-9	10.0	11.5	1	7	24.1	10.7	1	18	39.8	40.8	1	4	22.9	24.6	0	-14	37.4	37.7			
1	15	37.2	36.9	1	-13	19.4	19.3	1	9	95.0	96.1	1	-18	45.0	47.1	1	6	39.9	37.5	0	-14	50.5	52.4			
2	0	32.2	30.7	1	17	22.7	19.2	1	5	4	54.7	51.8	1	20	19.0	17.1	1	3	2	34.4	30.6	0	-14	50.5	52.4	
2	4	135.2	136.8	1	-17	17.3	17.0	1	5	6	16.8	16.8	1	22	23.4	24.2	1	3	6	29.9	30.1	0	-14	50.5	52.4	
2	3	1	23.1	24.8	1	10	108.5	97.3	1	0	-2	173.9	175.4	1	-22	26.7	25.9	1	3	-6	38.9	37.5	0	-14	50.5	52.4
2	3	11.8	10.6	1	-10	155.6	140.9	1	5	-8	50.5	46.7	1	2	-1	21.1	21.0	1	4	2	32.4	31.0	0	-14	50.5	52.4
3	0	39.5	38.5	2	-2	146.1	141.5	1	5	-8	50.5	46.7	2	-1	24.0	24.4	1	5	0	39.5	40.8	0	-14	50.5	52.4	
3	4	13.5	9.4	2	4	27.1	27.9	1	0	-4	91.4	80.7	2	3	0	63.9	62.7	1	5	2	24.3	24.0	0	-14	50.5	52.4
3	4	88.5	91.5	2	-4	36.2	34.2	1	0	-4	61.3	66.8	2	3	0	31.4	30.2	1	5	-2	29.7	29.5	0	-14	50.5	52.4
4	8	67.4	67.2	2	6	89.3	90.6	1	0	-6	86.8	82.0	2	3	0	31.4	30.2	1	5	10	25.0	25.3	0	-14	50.5	52.4
4	8	26.8	24.2	2	-6	175.1	176.3	1	0	-8	88.4	91.1	2	3	-2	90.4	86.9	1	5	-10	20.2	20.9	0	-14	50.5	52.4
6	0	39.5	38.5	2	8	65.7	64.5	0	0	-8	107.3	100.7	2	3	6	70.5	72.6	1	4	-2	34.9	35.1	0	-14	50.5	52.4
6	0	16.8	16.4	2	-8	13.7	12.0	0	0	-10	14.1	14.6	3	6	73.6	73.0	1	4	4	28.5	28.2	0	-14	50.5	52.4	
6	12	38.2	40.1	2	10	95.9	99.6	0	0	-10	19.2	18.6	3	5	2	41.3	44.7	1	4	8	37.2	36.6	0	-14	50.5	52.4
7	7	17.4	15.5	2	-10	86.8	106.9	0	12	156.6	107.4	5	2	12	30.8	30.9	1	4	8	37.2	36.6	0	-14	50.5	52.4	
8	0	27.0	36.2	2	12	62.6	58.9	0	12	104.5	101.2	5	10	34.5	36.2	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				2	-14	68.3	79.1	0	14	17.9	15.2	5	-10	42.9	45.9	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				2	16	51.0	45.2	0	14	27.1	28.3	7	0	15.8	15.3	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				2	-16	19.8	18.3	0	16	34.8	33.1	7	2	20.9	20.5	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				2	18	53.9	46.8	0	-16	67.8	68.9	7	-2	30.8	30.4	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				2	-18	38.7	38.0	0	18	46.5	47.9	7	4	13.3	15.2	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				2	20	16.9	16.1	0	-18	35.7	37.1	7	-6	31.4	32.6	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				2	-20	17.3	15.6	0	20	28.8	29.0	7	8	19.8	13.0	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				2	22	26.7	26.0	0	-20	43.7	45.0	0	4	189.8	206.4	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				2	-22	38.2	36.2	0	22	37.8	37.7	0	6	16.0	14.9	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	-3	18.6	17.0	0	-24	28.6	30.1	0	6	18.0	17.0	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	0	33.6	32.9	1	-1	227.0	217.8	0	8	102.8	112.0	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	0	93.7	93.5	1	1	3	17.5	17.4	0	8	74.6	72.0	1	4	8	37.2	36.6	0	-14	50.5	52.4	
				3	4	32.5	32.8	1	4	29.4	28.3	1	1	47.8	46.5	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	-4	22.8	22.5	1	-5	14.4	15.6	0	-10	70.4	65.3	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	8	31.4	30.7	1	9	21.6	21.1	0	-12	48.1	49.4	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	-8	24.2	23.3	1	11	34.1	31.1	0	-12	64.8	66.1	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	10	31.8	30.1	1	-11	32.9	33.3	0	16	30.1	32.3	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	-10	80.6	89.5	1	-13	12.9	14.6	0	-14	37.8	37.7	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	10	31.8	31.2	2	0	66.0	66.8	0	16	31.3	30.4	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	-10	44.1	46.2	2	2	35.4	35.6	0	-16	53.4	52.8	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	12	112.2	113.1	2	-2	52.0	50.5	0	18	17.9	21.1	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	-12	74.9	72.7	2	4	87.3	86.4	0	-18	63.0	62.0	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	14	54.5	50.9	2	-4	72.7	72.4	0	20	35.3	35.2	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	-14	38.1	39.4	3	1	14.5	14.5	0	-20	25.5	25.3	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	16	64.1	63.1	3	-3	34.9	36.0	0	22	18.0	17.1	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	-16	58.2	60.5	4	0	72.2	70.4	0	-22	24.3	24.6	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	18	27.0	28.2	4	2	75.3	76.6	1	1	14.5	13.8	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	-18	27.0	28.2	4	-2	85.0	85.1	1	-1	13.3	11.5	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	20	43.5	42.2	4	4	75.2	75.1	1	3	20.3	18.9	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	-20	20.2	19.8	4	-4	88.9	89.3	1	-3	25.1	24.1	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	22	27.4	27.2	4	6	71.2	69.2	1	-3	25.1	24.1	1	4	8	37.2	36.6	0	-14	50.5	52.4		
				3	-22	20.4	19.8	4	-6	71.2	69.2	1	7	44.0	45.4	1	4									

interpretation of the moment it was assumed that since the molecules were "bulky" they would pack in such a way as to make *intermolecular* H-H interactions negligible. The authors thus assigned the total moment to the one *intramolecular* interaction and derived an H-H distance of 1.88 Å., which led them to the widely-quoted Fe-H distance of about 1.1 Å. (a hydrogen "buried" in the metal orbitals). The possibility of an important H-H interaction in HMn(CO)<sub>5</sub> makes unjustifiable the assumption that such an interaction does not occur in H<sub>2</sub>Fe(CO)<sub>4</sub>; in fact, if there is one such interaction (~2.4 Å. in length), then the derived Fe-H distance would be a normal one for a covalent bond (about 1.5 Å.).

Although the evidence from this and other studies,<sup>9,10</sup> and from the recent calculations of Lipscomb and his

co-workers,<sup>22,23</sup> is strongly in favor of a metal-hydrogen bond of normal length and of a hydrogen atom that occupies a definite position in the coordination polyhedron of a parent or substituted transition metal carbonyl hydride, it still seems worthwhile to settle this question beyond any doubt, and for this reason a neutron diffraction study of HMn(CO)<sub>5</sub> is now in progress.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS 02139

## The Structure of the Deca(methylisonitrile)dicobalt(II) Cation; an Isostere of Dimanganese Decacarbonyl<sup>1</sup>

BY F. A. COTTON,<sup>2</sup> T. G. DUNNE, AND J. S. WOOD

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A single crystal X-ray structure determination has been carried out on the red diamagnetic compound of empirical formula Co(CNCH<sub>3</sub>)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub>, prepared by Sacco and Freni. Since [Co(CNCH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup> is isoelectronic with Mn(CO)<sub>5</sub>, a dimeric structure analogous to that in Mn<sub>2</sub>(CO)<sub>10</sub> seemed likely and such a structure has been found. The Co-Co bond is 2.74 ± 0.01 Å. in length, the Co-C bonds are 1.82–1.92 Å. in length, and the idealized point group symmetry of the dinuclear cation is D<sub>4d</sub>. Because of the relatively high standard deviations in the coordinates of light atoms, which are at least partially caused by librational motions of the perchlorate ions, the bond angles and bond lengths within the CoCNCH<sub>3</sub> moieties have not been obtained with sufficient accuracy to provide fully conclusive evidence regarding the nature and extent of Co-C dπ-pπ bonding, but the rather short bond lengths do suggest that such bonding occurs to a significant extent.

### Introduction

Some years ago Sacco and Freni<sup>3</sup> reported that the compound Co(CNCH<sub>3</sub>)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub> could be obtained in two forms, one light blue and paramagnetic (one unpaired electron per cobalt atom) and the other red and diamagnetic. The latter is the stable one in the solid state, but solutions of either form appeared to be the same, namely, blue and paramagnetic. Since [Co(CNCH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup> is isoelectronic and nearly isosteric with Mn(CO)<sub>5</sub>, it seemed to us plausible that the red form of the compound might contain dinuclear cations, [(CH<sub>3</sub>NC)<sub>5</sub>CoCo(CNCH<sub>3</sub>)<sub>5</sub>]<sup>4+</sup>, isostructural<sup>4</sup> with Mn<sub>2</sub>(CO)<sub>10</sub>, but more easily dissociated, giving blue, paramagnetic [Co(CNCH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup> ions. In order to test this hypothesis, it seemed necessary to verify the presence of the binuclear cations in the red crystals and to show that they do in fact contain a Co-Co bond. Only by a single crystal X-ray structural study could this be done.

Such a study was therefore carried out and is described here.

### Experimental

A supply of the compound was made available to us by Professor Sacco. This consisted mainly of aggregates and dendritic growths, but, with patience, useful single crystals were eventually located. These red-brown crystals were found to belong to the orthorhombic system, with cell dimensions  $a = 13.17 \pm 0.02$ ,  $b = 12.47 \pm 0.02$ , and  $c = 12.49 \pm 0.02$  Å. The approximate density, determined by flotation, was 1.5 g. cm.<sup>-3</sup>. Taking 463 for the molecular weight of Co(CNCH<sub>3</sub>)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub> and 4 as the number of these molecules per unit cell, the density calculated is 1.50 g. cm.<sup>-3</sup>. The systematic absences  $h00$  for  $h = 2n + 1$  and  $0k0$  for  $k = 2n + 1$ , determined from precession photographs, unambiguously indicate space group P2<sub>1</sub>2<sub>1</sub>2 (No. 18).

Intensities were recorded photographically by the equi-inclination Weissenberg method using a small crystal of maximum dimension ca. 0.4 mm. and Mo K $\alpha$  radiation. Equi-inclination levels  $0kl$  through  $10kl$  were obtained by the multiple film technique and the intensities were estimated visually using a calibration wedge prepared from the same crystal. No corrections were made for absorption—the linear absorption coefficient,  $\mu$ , being 12 cm.<sup>-1</sup>. Approximately 1200 independent reflections were obtained on the levels indicated. These were corrected for Lorentz and polarization factors and, when necessary (*i.e.*, those reflec-

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