Contribution No. 3451 from the Department of Chemistry,
University of California, Los Angeles, California 90024

Crystal and Molecular Structure of Tetracarbonyl-2-acetylphenylmanganese[1]

CAROLYN B. KNOBLER, SALLY SCHREIBER CRAWFORD, and HERBERT D. KAESZ*

Received February 7, 1975 AIC500960

The crystal and molecular structure of tetracarbonyl-2-acetylphenylmanganese, $CH_3C(\overline{O)C_6H_4Mn}(CO)_4$, has been determined by a three-dimensional X-ray diffraction study. The yellow solid crystallizes in the centrosymmetric space group $C2/c$, of the monoclinic system with a = 25.940 (7) Å, b = 5.993 (1) Å, c = 17.117 (4) Å, and β = 115.63 (2)°. Diffraction data were collected to 2θ = 55° using Mo Kα radiation and a Syntex $P\bar{1}$ automated diffractometer. The structure was solved using full-matrix least-squares refinement to a conventional discrepancy factor R_1 = 0.031 for the 1921 unique nonzero reflections. All atoms were located. The molecule contains a planar acetophenyl group chelated through acyl oxygen and ortho carbon of the phenyl ring to a cis tetracarbonylmanganese group. In the five-membered heterocyclic ring the O–Mn and C–Mn bond distances are 2.055 (2) and 2.042 (2) Å, respectively, with the O–Mn–C bond angle of 79.4 (1)°. The C–O distance in the acyl group coordinated to manganese through oxygen is 1.244 (3), lengthened significantly from that in free acetophenone, in which the C–O distance is 1.216 (2) Å.

Introduction

A large number of transition metal complexes containing intramolecular metalation of an aromatic ring are now known.[2] The recent communication, from these laboratories, which described the metalations of some aromatic ketones[3] was the first report of the directive effect of an oxygen-functional group in a metalation with a transition metal complex. The following is a structural characterization of the metalation product of acetophenone with $CH_3Mn(CO)_5$.

Experimental Section

Crystals of the complex, obtained from an ether–hexane solution[4] at −20°, were provided by R. J. McKinney of these laboratories. They are yellow and X-ray stable but slowly decompose in air and so were sealed in glass capillaries for use in the X-ray study. Examination of preliminary oscillation and Weissenberg photographs showed monoclinic symmetry. Systematic absences $l = 2n + 1$ for $h0l$ and $h + k = 2n + 1$ for all hkl indicate space group Cc or $C2/c$.

The crystal chosen for intensity measurements was a fragment of a platelet 0.125 mm × 0.175 mm × 0.425 mm along a, c, and b, respectively. It was mounted with the b axis close to the ϕ axis of a four-circle computer-controlled diffractometer (Syntex $P\bar{1}$ autodiffractometer) equipped with scintillation counter and a graphite monochromator. Fifteen of the strongest reflections (2θ = 7–21°) were used for centering and indexing. On the basis of the resulting parameters, intensity data was collected. Mo Kα radiation was used with a scan rate of 2°/min and a scan range from 1.0° below the Kα_1 peak to 1.0° above the Kα_2 peak. The takeoff angle was 4°, and background counts were recorded for a time equal to the scan time. The pulse height analyzer was set at an 85% window for Mo Kα radiation.

Intensities of three reference reflections (10,0,0, 22$\bar{6}$, and 621) were measured every 97 reflections. The variations in these standards were random and all were within 2.6% of their respective mean. A total of 3189 reflections were recorded, which included 266 space group absences, 43 duplicate $0kl$, $0k\bar{l}$ pairs, and 99 recordings of the reference reflections. The remaining 2781 unique reflections represent all those accessible to Mo Kα radiation for $2\theta \leq 55°$. These include 860 reflections with $I \leq 3\sigma(I)$, which are considered unobserved and omitted from refinement. Thus 1921 unique, observed reflections remain.

The data reduction was achieved by PI BAR[5] which employs the equations

$$I = N - (t_s/2t_b)(B_1 + B_2)$$

$$\sigma(I) = [N + (t_s/2t_b)^2(B_1 + B_2) + (0.04I)^2]^{1/2}$$

$$|F_o| = k[I/Lp]^{1/2}$$

$$\sigma(F_o) = (k/2)[\sigma(I)/I(Lp)]^{1/2}$$

In these equations, N is the total scan count, B_1 and B_2 are the individual background counts, t_s is the scan time (sec), t_b is the time (sec) each background is counted, and Lp is the correction for Lorentz and polarization effects. In the present case $t_s = 2t_b$ so that $t_s/2t_b = 1$.

After data collection, fifteen reflections (2θ = 30–45°) were used for recentering the crystal and a more accurate set of lattice parameters was determined. These are a = 25.940 (7) Å, b = 5.993 (1) Å, and c = 17.117 (4) Å, and β = 115.63 (2)° [6] at room temperature based on λ(Mo Kα) 0.71069 Å. The flotation density measured in a bromobenzene–CCl_4 solution was 1.53 g/cm^3 at room temperature and compares with the calculated value of 1.58 g/cm^3 for Z = 8.

The calculated value of μ(Mo Kα radiation) is 11.6 cm^{-1}. Calculations lead to a transmission factor range of 0.90–0.94. Thus the absorption effect is estimated to cause fluctuations of no more than ±4% in I or ±2% in $|F_o|$, and no absorption correction was felt to be necessary.

Determination and Refinement of the Structure

Although the original space group determination was not unique (Cc or $C2/c$), the $C2/c$ assignment fit the heavy-atom locations in the interpretation of the three-dimensional Patterson summation.[5] This assignment was justified by the successful refinement of the structure in space group $C2/c$.

Thus with the manganese position located by a three-dimensional Patterson summation, a Fourier synthesis[5] resulted in location of all other nonhydrogen atoms. Least-squares refinement,[5] which allowed variation of positional and anisotropic thermal parameters of manganese and later of parameters for all nonhydrogen atoms not bonded directly to hydrogen, was followed by a difference Fourier which served to locate the phenyl hydrogens. In further least-squares refinement the positions and anisotropic thermal parameters of all phenyl carbons were allowed to refine and each phenyl hydrogen was given an isotropic temperature factor 1.0 Å^2 greater than the carbon to which it is bound. A difference Fourier at this point allowed location of methyl hydrogens. These were poorly positioned, however, and so HPOSN[5] was used to determine the best tetrahedral arrangement. In the final least-squares cycles, the methyl carbon position and thermal parameters and the phenyl hydrogen position parameters and isotropic temperature factors were allowed to refine. In these cycles the methyl hydrogens were assigned fixed isotropic temperature factors of 7.0 Å^2. For some of the stronger low-order reflections, relatively large discrepancies between F_o and F_c were noted. However, an attempt to apply a secondary extinction correction did not decrease the magnitudes of most of these $|F_o| - |F_c|$ values, nor did the values of R_1 and R_2 change for the least-squares refinement before and after the application of a secondary extinction term. The refinement converged to final values of R_1 = 0.031 and R_2 = 0.037.[7]

Structure factors were calculated for all unique reflections (see supplementary Table A[8]) on the basis of the final positional and thermal parameters which are given in Tables I and II with their standard deviations. The refinement involved full-matrix least-squares procedures with anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$) applied to the form factor of manganese.[9] The atomic scattering factors used for all nonhydrogen atoms are those of Hanson, Herman, Lea, and Skillman.[10] Those employed for hydrogen were derived from Stewart, Davidson, and Simpson.[11]

In the final cycle of least-squares refinement the largest shift in a positional parameter was 0.01σ for a nonhydrogen atom and 0.02σ for a hydrogen atom. The largest thermal parameter shift was 0.06σ for a nonhydrogen atom and 0.03σ for a hydrogen atom. The standard

Table I. Atomic Positional Parameters

Atom	x^a	y^a	z^a
Mn	0.14685 (2)	0.05898 (6)	0.30470 (2)
C(1)	0.2066 (1)	0.2430 (5)	0.3748 (2)
O(1)	0.2414 (1)	0.3638 (4)	0.4155 (1)
C(2)	0.1243 (1)	0.2805 (5)	0.2273 (2)
O(2)	0.1096 (1)	0.4252 (4)	0.1784 (1)
C(3)	0.1888 (1)	−0.0823 (5)	0.2552 (2)
O(3)	0.2141 (1)	−0.1694 (5)	0.2245 (2)
C(4)	0.0787 (1)	−0.0866 (4)	0.2377 (2)
O(4)	0.0357 (1)	−0.1608 (4)	0.1956 (1)
O(5)	0.1723 (1)	−0.1787 (3)	0.4006 (1)
C(5)	0.1536 (1)	−0.1588 (4)	0.4560 (1)
C(6)	0.1139 (1)	0.0231 (4)	0.4450 (1)
C(7)	0.0872 (1)	0.0584 (6)	0.4993 (2)
C(8)	0.0495 (1)	0.2322 (6)	0.4830 (2)
C(9)	0.0391 (1)	0.3707 (5)	0.4136 (2)
C(10)	0.0653 (1)	0.3381 (5)	0.3594 (2)
C(11)	0.1036 (1)	0.1618 (4)	0.3735 (1)
C(12)	0.1739 (1)	−0.3174 (5)	0.5305 (2)
H(7)	0.093 (1)	−0.035 (5)	0.539 (2)
H(8)	0.031 (1)	0.254 (6)	0.518 (2)
H(9)	0.014 (1)	0.484 (5)	0.402 (2)
H(10)	0.056 (1)	0.440 (5)	0.312 (2)
H(12)^b	0.148	−0.433	0.523
H(12)$'^b$	0.203	−0.396	0.529
H(12)$''^b$	0.185	−0.245	0.582

[a] Estimated standard deviations in the least significant digits in these values and those in succeeding tables and text are given in parentheses following each number. [b] No standard deviations are cited for these parameters which were not allowed to vary in the refinement.

deviation in an observation of unit weight was 1.1692. The final difference Fourier showed residuals of −0.19 to +0.52 e/Å^3 with the largest positive values being in the immediate vicinity of manganese. There was a moderate (0.25 e/Å^3) amount of residual in the area of the fixed methyl hydrogens as well.

Analysis of a number of portions of the molecule for possible rigid-body motion was carried out by the program (ACA No. 1) written by Schomaker and Trueblood (1968) which is based on the treatment presented in their paper on the rigid-body motion of molecules in crystals.[12] The significant results of this analysis are given in supplementary Table B,[8] and further details are available in the dissertation of Crawford.[1a]

Results and Discussion

Overall Geometry and Molecular Motion. An ORTEP plot[5] of the ortho-metalated acetophenone molecule (**1**) is shown in Figure 1. Using the figure as a key, bond lengths and angles can be found in Tables III and IV. The structure contains a nearly planar system consisting of a phenyl ring and a five-membered manganese–tetracarbonyl-containing ring, C(5)–O(5)–Mn–C(11)–C(6), which share an edge. Table V gives least-squares plane data for the five-membered ring, for the phenyl ring (carbon skeleton only), and for the composite nine-atom system. The composite ring system is slightly bent, with an angle of 178.6° between the five- and six-membered planar rings.

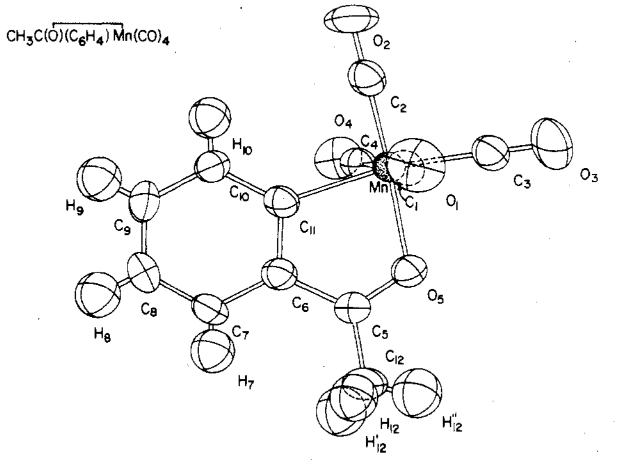


Figure 1. ORTEP plot of $CH_3C(O)C_6H_4Mn(CO)_4$. The molecule as viewed normal to the plane defined by the phenyl ring and the three-atom heterocyclic system fused to it. Thermal ellipsoids represent 50% probability.

As noted earlier, the values of the rigid-body tensors of translation (**T**), libration (**L**), and screw motion (**S**) are given in supplementary Table B for the groups of atoms also identified in Table IV. As indicated by the root-mean-square difference between observed and calculated U_{ij}, the 9-atom system is quite rigid. This low level of internal motion is maintained when equatorial carbons or equatorial and axial carbons from the carbonyl groups are considered in the calculations. It was found, however, that inclusion of the corresponding carbonyl oxygens resulted in one and one-half and nearly two-fold increases in the rms U_{ij} discrepancy over the respective values calculated for the systems which included the equatorial or equatorial and axial carbons only. The rms ΔU_{ij} values are less than the average esd of the input β_{ij}, which convert to 0.0028, 0.0032, and 0.0035 for the 9-, 11-, and 13-atom systems, respectively, when put on the scale of U. In all three analyses both the translational and librational motions are found to be quite isotropic and to be of fairly small

Table II. Atomic Thermal Parameters (×10^4)^a

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	14.51 (7)	201 (1)	30.1 (1)	3.3 (3)	11.16 (8)	0.4 (4)
C(1)	16.7 (5)	201 (8)	36 (1)	5 (2)	13.6 (7)	4 (3)
O(1)	21.6 (5)	367 (8)	56 (1)	−23 (2)	13.2 (6)	−24 (3)
C(2)	18.5 (5)	287 (9)	35 (1)	1 (2)	13.6 (7)	−5 (3)
O(2)	31.6 (6)	373 (9)	52 (1)	19 (2)	18.8 (6)	56 (3)
C(3)	20.9 (6)	314 (10)	45 (1)	6 (2)	18.4 (7)	4 (3)
O(3)	35.7 (6)	551 (11)	84 (1)	25 (2)	39.7 (9)	−26 (3)
C(4)	20.2 (6)	225 (8)	36 (1)	4 (2)	13.6 (7)	−6 (3)
O(4)	22.0 (5)	391 (8)	59 (1)	−21 (2)	8.9 (6)	−40 (3)
O(5)	16.8 (3)	232 (6)	39.9 (8)	12 (1)	14.0 (4)	12 (2)
C(5)	12.2 (4)	232 (7)	32 (1)	−2 (2)	6.9 (5)	7 (2)
C(6)	12.6 (4)	230 (7)	29 (1)	3 (1)	7.8 (5)	1 (2)
C(7)	19.8 (6)	335 (10)	36 (1)	8 (2)	15.7 (7)	14 (3)
C(8)	20.7 (6)	423 (12)	46 (1)	18 (2)	19.4 (8)	−5 (3)
C(9)	17.1 (6)	317 (10)	51 (1)	22 (2)	14.4 (8)	−7 (3)
C(10)	16.0 (5)	253 (8)	36 (1)	12 (2)	10.0 (6)	7 (3)
C(11)	12.0 (4)	206 (7)	28 (1)	−3 (1)	7.3 (5)	−8 (2)
C(12)	21.5 (6)	297 (10)	42 (1)	9 (2)	11.6 (7)	24 (3)

[a] The form of the anisotropic thermal ellipsoids is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Isotropic thermal parameters of the form $\exp[-B(\sin^2\theta/\lambda^2]$ were obtained for the hydrogen atoms H(7) (4.6 (7)), H(8) (6.5 (9)), and H(10) (3.7 (6)) and assigned for H(12), H(12)′, and H(12)″ as 7.0. No standard deviation is cited for the last parameter which was not allowed to vary in the refinement.

Table III. Observed Bond Lengths (Å)

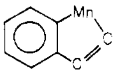
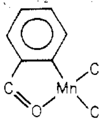
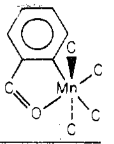
Bond	Uncor length	Cor length[a] 9-atom rigid system 	 11-atom rigid system 	 13-atom rigid system 
Mn-C(1)	1.857 (3)			1.860
Mn-C(2)	1.786 (3)		1.789	1.789
Mn-C(3)	1.849 (3)		1.853	1.852
Mn-C(4)	1.856 (3)			1.860
Mn-O(5)	2.055 (2)	2.060	2.060	2.059
Mn-C(11)	2.042 (2)	2.048	2.048	2.047
C(1)-O(1)	1.132 (3)			
C(2)-O(2)	1.150 (3)			
C(3)-O(3)	1.130 (3)			
C(4)-O(4)	1.126 (3)			
O(5)-C(5)	1.244 (3)	1.247	1.247	1.247
C(5)-C(12)	1.492 (4)			
C(5)-C(6)	1.455 (3)	1.459	1.459	1.458
C(6)-C(7)	1.394 (3)	1.399	1.398	1.397
C(7)-C(8)	1.373 (4)	1.376	1.376	1.375
C(8)-C(9)	1.377 (4)	1.380	1.380	1.379
C(9)-C(10)	1.381 (4)	1.385	1.384	1.384
C(10)-C(11)	1.397 (4)	1.401	1.401	1.400
C(11)-C(6)	1.406 (3)	1.410	1.410	1.409
C(7)-H(7)	0.85 (3)			
C(8)-H(8)	0.92 (3)			
C(9)-H(9)	0.88 (3)			
C(10)-H(10)	0.96 (3)			

Table IV. Observed Bond Angles (Uncorrected, deg)

Atoms	Angle	Atoms	Angle
C(1)-Mn-C(2)	87.2 (1)	O(5)-C(5)-C(6)	117.5 (2)
C(1)-Mn-C(3)	94.4 (1)	C(6)-C(5)-C(12)	123.8 (2)
C(1)-Mn-C(4)	169.6 (1)	C(5)-C(6)-C(11)	114.4 (2)
C(1)-Mn-O(5)	90.3 (1)	C(7)-C(6)-C(11)	121.9 (2)
C(1)-Mn-C(11)	87.8 (1)	C(5)-C(6)-C(7)	123.7 (2)
C(2)-Mn-C(3)	94.0 (1)	C(6)-C(7)-C(8)	119.6 (3)
C(2)-Mn-C(4)	88.4 (1)	C(7)-C(8)-C(9)	119.4 (3)
C(2)-Mn-O(5)	175.5 (1)	C(8)-C(9)-C(10)	121.6 (3)
C(2)-Mn-C(11)	96.8 (1)	C(9)-C(10)-C(11)	120.7 (3)
C(3)-Mn-C(4)	95.4 (1)	C(10)-C(11)-C(6)	116.8 (2)
C(3)-Mn-O(5)	90.0 (1)	C(10)-C(11)-Mn	130.9 (2)
C(3)-Mn-C(11)	169.1 (1)	Mn-C(11)-C(6)	112.2 (2)
C(4)-Mn-O(5)	93.4 (1)	C(6)-C(7)-H(7)	118 (2)
C(4)-Mn-C(11)	83.3 (1)	C(8)-C(7)-H(7)	122 (2)
O(5)-Mn-C(11)	79.4 (1)	C(7)-C(8)-H(8)	120 (2)
Mn-C(1)-O(1)	176.7 (2)	C(9)-C(8)-H(8)	121 (2)
Mn-C(2)-O(2)	179.0 (2)	C(8)-C(9)-H(9)	120 (2)
Mn-C(3)-O(3)	179.5 (3)	C(10)-C(9)-H(9)	118 (2)
Mn-C(4)-O(4)	175.2 (3)	C(9)-C(10)-H(10)	117 (2)
Mn-O(5)-C(5)	116.5 (2)	C(11)-C(10)-H(10)	123 (2)
O(5)-C(5)-C(12)	118.7 (2)		

Table V. Least-Squares Planes

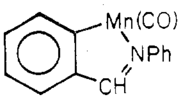
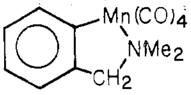
Plane[a]	Direction cosines (×10⁴) with respect to *a*	 *b*	 *c**	Description of plane	Rms dev from plane, Å ×10³
A	5714	5870	5735	9-Membered ring: phenyl C's, Mn, C(5), O(5)	3.2
B	5878	5784	5657	5-Membered ring: Mn(1), O(5), C(5), C(6), C(11)	0.4
C	5575	5929	5811	Carbon skeleton of phenyl ring	0.0

[a] Interplanar angle between planes B and C is 178.6°.

Table VI. Comparison of Selected Bond Lengths (Å)

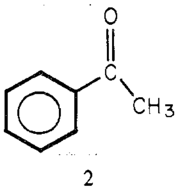
Compd	Ketone C=O	O–Mn	C–Mn	Ref
2	1.216 (2)			13
3	1.23 (1)	2.067 (7)	2.146 (10)	14
4	1.257 (8)	2.053 (5)	2.045 (7)	15
5	1.29	2.06	1.99	16
1	1.244 (3)	2.055 (2)	2.042 (2)	This study

Table VII. Comparison of Selected Bond Angles (deg) Containing Manganese

Compd	Axial C-Mn-C	Phenyl C–Mn–X (X = O, N)	Ref
cis-$CH_3Mn(CO)_4(PPh_3)$	169 (4)		19
4	175.9 (4) (Mn′) 173.1 (3) (Mn″)	79.8 (2)	15
	172.2 (4)	79.4 (3)	20
	170.4 (2)	80.2 (2)	21
1	169.6 (1)	79.4 (2)	This study

amplitude. The list of bond distances (Table III) includes values uncorrected and corrected for librational motion. The corrections applied to the bonds from manganese to the carbonyl carbons average 1.1σ. Similar corrections are indicated for carbon–carbon and carbon–oxygen bond lengths (with a maximum of 1.7σ). The manganese to ring carbon Mn–C(11) and manganese–oxygen Mn–O(5) bond lengths require corrections of 2.5σ and 3.0σ, respectively. Corrections to bond angles were 0.5σ (0.1°) or less in every case and so are omitted from Table IV. Uncorrected bond lengths will be used in comparison of the molecule with other similar molecules in the discussion which follows.

The Heterocyclic Five-Membered Ring. One of the chief points of interest in this molecule is the metalation ring fused to the phenyl group and particularly the C–O, Mn–O, and Mn–C bond lengths contained in that ring. These bond lengths may be compared with lengths of similar bonds in molecules **2**–**5**, whose structures have previously been determined. Acetophenone,[13] **2**, is the parent ketone and its structure offers a C=O bond length for comparison. Molecules **3**,[14] **4**,[15] and **5**,[16] like **1**, each have a five-membered ring containing a ketone function oxygen bonded to manganese. The pertinent data are summarized in Table VI.



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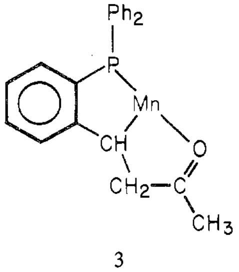

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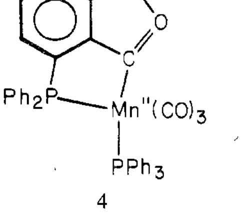

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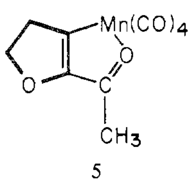


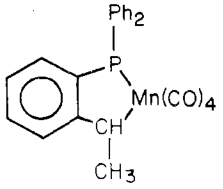
5

The free acetophenone molecule, **2**, contains the shortest

Table VIII. Comparison of Metal-Carbonyl Bond Lengths (Å)

	Carbonyl opposite oxygen-bonded ketone		Carbonyls opposite C or CO		
Compd	Mn-C	C-O	Mn-C	C-O	Ref
3	1.763 (10)	1.14 (1)	1.805 (10)	1.16 (1)	14
4	1.805 (10)	1.138 (9)	1.818 (10)	1.149 (9)	15
			1.859 (10)	1.128 (10)	
			1.847 (10)	1.139 (10)	
5	1.77	1.16	1.87	1.13	16
			1.89	1.12	
			1.84	1.14	
1	1.786 (3)	1.150 (3)	1.857 (3)	1.132 (3)	This study
			1.849 (3)	1.130 (3)	
			1.856 (3)	1.126 (3)	

C=O bond length. In the derivatives possessing five-membered Mn–O-containing rings the C=O bond is lengthened. The longest C=O length is observed for molecule **5** in which extensive delocalization is possible through resonance (see discussion in ref 16). It seems reasonable to assume that similar π-electron delocalization is responsible for the increased C=O lengths in **1** and the other metalated ketones. In addition, the Mn–O and Mn–C distances are expected to decrease with increasing delocalization. Indeed, accompanying the lengthening of the C=O bond we see shortening of the Mn–C and Mn–O bonds in compounds **3**, **1**, **4**, and **5**. That molecule **3** exhibits the longest Mn–C and Mn–O bonds is expected since extended resonance is impossible through the saturated carbon chain. Additional support for the view that shortening of the Mn–C bond results from π delocalization is given by the fact that in derivative **6**,[17] where no resonance is possible, the Mn–C bond of 2.21 (1) Å is significantly longer than the phenyl carbon to manganese bond in **1** (2.042 (2) Å), even taking into account the different hybridization of the carbon atoms.[18]



6

Further indication of delocalization is given by the C(5)–C(6) distance of 1.455 (3) Å. It is significantly shorter than the comparable bond in free acetophenone (1.494 (2) Å) through which less delocalization is expected.

Coordination Geometry around Manganese. Although manganese in molecule **1** is surrounded by six atoms within bonding distance, examination of the bond angles around manganese (first 15 entries in Table IV) indicates that its local geometry departs from octahedral in several significant ways. The angle C(1)–Mn–O(4) is 169.6°, with both C(4) and C(1) bent toward the edge defined by C(2) and C(11). The angles C(2)–Mn–C(3) and C(11)–Mn–C(2) are opened to angles of 94.0 and 96.8°, respectively, while the O(5)–Mn–C(11) angle is reduced to 79.4°. Both the bent axial C–Mn–C and the reduction in the ring angle about Mn to about 80° are found in other similar structures, as indicated in Table VII.

The metal–carbon and carbon–oxygen bond lengths of the metal carbonyl groups are influenced by the substituents in the position trans to them. Distances from manganese to carbonyl carbon atoms are found to be Mn–C(1) = 1.857 (3) Å, Mn–C(3) = 1.849 (3) Å, and Mn–C(4) = 1.856 (3) Å. The Mn–C(2) bond trans to the coordinated carbonyl oxygen, however, is only 1.786 (3) Å and is accompanied by a longer C–O distance for the carbonyl C(2)–O(2), 1.150 (3) Å, than for the other carbonyls: C(1)–O(1), 1.132 (3) Å; C(3)–O(3), 1.130 (3) Å; C(4)–O(4), 1.126 (3) Å. This no doubt results from π-electron donation to the metal by the coordinated oxygen followed by flow of metal π electrons into the antibonding π orbital of the trans CO. This results in a shortened Mn–C bond and a lengthened C–O bond as observed. The same trans relationship is evident in other structures with C=O oxygen bonded to manganese. Table VIII lists the Mn–C and C–O bond lengths for the appropriate metal–carbonyl groups in a number of these structures.

Intermolecular Distances. No unusual intermolecular contacts are found in this structure. The closest intermolecular distances are as follows: C(1)–H(12)'' ($^1/_2 - x$, $^1/_2 - y$, $1 - z$), 2.964 Å; O(2)–H(9) ($-x$, y, $^1/_2 - z$), 2.912 Å; O(4)–H(9) ($-x$, $-1 + y$, $^1/_2 - z$), 2.665 Å; O(5)–H(12)' ($^1/_2 - x$, $^1/_2 - y$, $1 - z$), 2.952 Å. These are all considerably longer than the sum of the van der Waals radii for oxygen and hydrogen (2.6 Å), while H(8)–H(9) ($-x$, $1 - y$, $1 - z$), 2.673 Å, and H(10)–H(10) ($-x$, y, $^1/_2 - z$), 2.744 Å, compare with a van der Waals value of 2.4 Å for two hydrogen atoms.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Computer time was furnished by the UCLA Campus Computing Network. The Syntex $P\bar{1}$ automated diffractometer used in this study was purchased through Departmental NSF Grant No. GP 28248. The authors thank Mr. B. T. Huie for help in use of the diffractometer.

Registry No. $CH_3C(\overline{O)C_6H_4}Mn(CO)_4$, 50831-23-7.

Supplementary Material Available. Supplementary Tables A and B, showing structure factors and rigid-body thermal parameters, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC500960-9-75.

References and Notes

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(4) The solution was prepared by adding sufficient ether to dissolve the solid in a hexane slurry, filtering the solution by suction, and blowing off ether under a stream of nitrogen until crystallization began. The solution was then heated slightly to dissolve the crystals and set aside to cool to room temperature. Crystallization was then achieved by further cooling in the freezer section of the refrigerator.

(5) The programs used in this work included the following: locally written data reduction programs; PI BAR, JBPATT, JBFOUR, and PEAKLIST, modified versions of Fourier programs written by J. Blount; local versions of ORFLS (Busing, Martin, and Levy), structure factor calculations and full-matrix least-squares refinement; SECEXT by Christensen, to correct for the effects of secondary extinction; Hope's HPOSN to calculate tentative hydrogen positions; ORTEP (Johnson), figure plotting; MGTL (Schomaker and Trueblood), analysis of possible rigid-body motion, least-squares planes; ORFFE (Busing, Martin, and Levy), distances, angles, and error com-

putations. All calculations were performed on the IBM 360-91 computer operated by the UCLA Campus Computing Network.
(6) Numbers given in parentheses throughout this paper are the estimated standard deviations and refer to the last digit given.
(7) The conventional R index, $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, and the weighted residual factor, $R_2 = (\sum w||F_o| - |F_c||^2/\sum|F_o|^2)^{1/2}$, where the weights are $w = 1/\sigma^2(F_o)$.
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Contribution No. 5050 from the Arthur Amos Noyes Laboratory of Chemical Physics,
California Institute of Technology, Pasadena, California 91125

Crystal Structure of μ-Thiocyanato-[pentaamminecobalt(III)]pentacyanocobalt(III) Monohydrate

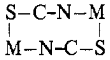
FRANK R. FRONCZEK and WILLIAM P. SCHAEFER*

Received February 7, 1975 AIC50094F

The crystal structure of μ-thiocyanato-[pentaamminecobalt(III)]pentacyanocobalt(III) monohydrate, a binuclear cobalt complex containing a single thiocyanate bridge, has been determined by single-crystal X-ray diffraction techniques using counter-measured intensity data. Crystals of $(NH_3)_5CoNCSCo(CN)_5 \cdot H_2O$ are orthorhombic, space group *Pbca* with 8 formula units per unit cell; cell dimensions are a = 14.166 (4), b = 14.549 (4), and c = 15.187 (9) Å. Anisotropic least-squares refinement fitting 2453 unique data led to a final R index of 0.050. The binuclear molecule contains two octahedral Co(III) atoms bridged by a thiocyanate ligand bonded through the sulfur atom to the pentacyanocobalt group in the "bent" configuration, with a Co–S–C angle of 101°, and in a somewhat nonlinear fashion to the pentaamminecobalt group through the nitrogen atom, with a Co–N–C angle of 169°. This bending allows a contact between ligands on opposite ends of the molecule which is interpreted as an intramolecular N–H···N hydrogen bond. A shortening of the trans Co–NH_3 distance by greater than 0.04 Å relative to the cis distances is noted.

Introduction

The thiocyanate ion has been a subject of interest in recent times as a ligand because of its ambidentate nature. The ability to coordinate through the sulfur atom (thiocyanato) or through the nitrogen atom (isothiocyanato) or both leads to possibilities of linkage isomerism. Bridging thiocyanate ligands are common but usually occur in systems which place rigid restrictions upon the bridging geometry, such as dimers of the form



Recently, singly bridged dimers of the system $(NH_3)_5Co(SCN)Co(CN)_5$ have been prepared independently in two laboratories.[1,2] Both isomers were characterized by Buckley and Wardeska through elemental analysis, infrared spectra, electronic spectra, and conductivity measurements. We are interested in these compounds because of the unique single bridge in a discrete binuclear complex and in relation to our structural studies of the analogous cyano-bridged compounds.[3,4] The structure of the thiocyanato isomer[5] $(NH_3)_5CoNCSCo(CN)_5$ is reported here in an X-ray study of the monohydrate.

Experimental Section

A sample of the compound was generously supplied by J. G. Wardeska in the form of an orange powder. Large single crystals were easily grown by dissolving this powder in 0.5 M $HClO_4$ at 50°, filtering the solution, and quickly cooling to 10°. Crystals were collected after 24 hr, washed with ethanol, and air-dried. The well-formed crystals are elongated with rectangular cross sections. Systematic extinctions judged from Weissenberg films are $0kl$ with k odd, $h0l$ with l odd, and $hk0$ with h odd. These extinctions uniquely determine the space group to be *Pbca*. The crystal chosen for data collection was elongated along c, and terminations at both ends were crumbled away to approximate a rectangular prism of dimensions 0.08 × 0.26 × 0.37 mm. This crystal was mounted with its c axis inclined about 0.5° from the ϕ axis of a Datex-automated General Electric quarter-circle diffractometer, and cell dimensions were determined by a least-squares fit using 2θ values measured for 20 reflections using graphite-monochromatized Mo Kα radiation (λ 0.71069 Å). The axial lengths, along with other pertinent crystal data, are listed in Table I. A density determination performed by flotation in a CCl_4–$CHBr_3$ mixture established that there are 8 formula units per cell and suggested that the complex is present in the crystal as the monohydrate.

Table I. Crystal Data

Formula	$(NH_3)_5CoNCSCo(CN)_5 \cdot H_2O$	Vol	3130 (1) Å^3
Formula wt	409.2	Z	8
$F(000)$	1664 electrons	ρ_{exptl}	1.77 (2) g cm^{-1}
Space group	*Pbca*	ρ_{calcd}	1.736 g cm^{-3}
a	14.166 (4) Å	λ(Mo Kα)	0.71069 Å
b	14.549 (4) Å	μ(Mo Kα)	24.9 cm^{-1}
c	15.187 (9) Å		

Intensity data were measured at room temperature using Mo Kα radiation, employing a θ–2θ scan technique and a proportional counter. All unique reflections having peak centers (the weighted mean of α_1 and α_2 lines) between the 2θ limits of 4° and 50° were scanned, and four standard reflections were remeasured every 100 measurements. Scanning widths varied linearly with 2θ, having values of 1.6° at 2θ = 7° and 1.9° at 2θ = 29°. All scans were performed at a constant