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The Molecular Structure of Gaseous π-Allylcobalt-tricarbonyl ($C_3H_5Co(CO)_3$)

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The structure of gaseous π-allylcobalt-tricarbonyl has been studied by electron diffraction. Satisfactory agreement between experimental and theoretical data was obtained for a model with C_s-symmetry. The cobalt atom was found to be attached to all the C-atoms in the allyl group as well as to the carbonyl C-atoms. The molecule consists of two pyramides with the cobalt atom as their common apex (Fig. 3). The parameter values are given in Table 1. The distance from Co to the central allyl C is found to be significantly shorter than the distance to the two terminal C-atoms which are equal according to symmetry. The two identical C – C bonds in the allyl group seem to be nearly equal to that in benzene. The $Co(CO)_3$ group has apparently not a threefold symmetry, the C – Co – C angle perpendicular to the plane of symmetry being larger than the two other C – Co – C angles.

The properties of the π-allyl complexes of the transition metals have recently been a subject of considerable interest.[1–3] Of the rather few published structure determinations[4–6] most are of low accuracy and to the author's knowledge no determinations of compounds in the gaseous phase have previously been performed.

EXPERIMENTAL

The sample of $C_3H_5Co(CO)_3$ was kindly supplied from Dr. S. O'Brien, Imperial Chemical Industries, Runcorn, England. The data were recorded in the usual way at the Balzer's eldigraph KD-62 in Oslo.[7,8] The photographic plates were taken at a nozzle temperature of about 30°C; three sets of plates being used. For the first set (4 plates) the electron wave-length was 0.058575 Å and the nozzle-to-plate distance 50 cm. The second set (4 plates) and the third set (3 plates) had a nozzle-to-plate distance of 25 cm and electron wave lengths 0.058561 Å and 0.58565 Å, respectively. The first set gave intensity values for s ranging from 1.5 Å^{-1} to 15.75 Å^{-1}, read off at Δs intervals of 0.125 Å^{-1}. The second and third sets gave intensities in the range $s = 3.0$ Å^{-1} – 30.0 Å^{-1} at Δs intervals of 0.25 Å^{-1}. The data were treated in the normal way,[9] and the modified molecular intensities were calculated using the modification function $s/(|f_C'||f_{Co}'|)$. All the curves were scaled, averaged and combined into a composite intensity curve in the s-range 1.5 Å^{-1} to 30.0 Å^{-1}. Fig. 1 shows this experimental intensity curve as well as the theoretical

Table 1. Structure parameters for $C_3H_5Co(CO)_3$ with standard deviations in parenthesis.

	I		II		III	
	r (Å)	u (Å)	r (Å)	u (Å)	r (Å)	u (Å)
Co–C (carbonyl)	1.8039 (0.0016)	0 054 (0.002)	1.8043 (0.0024)	0.057 (0.003)	1.8041 (0.0030)	0.056 (0.003)
C–O	1.1433 (0.0016)	0.039 (0.003)	1.1453 (0.0024)	0.039 (0.005)	1.1443 (0.0026)	0.039 (0.005)
Co–C (allyl)	1.9847 (0.0113)	0.066[a] (0.008)	1.9851 (0.0156)	0.066[a] (0.010)	1.9849 (0.0157)	0.066[a](0.010)
Co–C (allyl)	2.1004 (0.0044)		2.1011 (0.0061)		2.1007 (0.0064)	
C–C	1.3926 (0.0049)	0.045[b]	1.3889 (0.0085)	0.045[b]	1.3907 (0.0086)	0.045[b]
C–H	1.0900[b]	0.075[b]	1.0900[b]	0.075[b]	1.0900[b]	0.075[b]
	Angles (degrees)		Angles (degrees)		Angles (degrees)	
∠ CCoC	100.8 (1.0)		99.7 (0.8)		100.3 (1.0)	
∠ CCoC	111.0 (2.2)		106.9 (1.7)		109.0 (2.2)	
∠ CCC	120.9 (3.1)		125.6 (2.9)		123.2 (3.1)	
∠ HCC	120.0[b]		120.0[b]		120.0[b]	
∠ v[c]	34.2[d]		34.2[d]		36.0 (2.4)[e]	

I. Values obtained by least-squares refinement on the composite intensity curve with a diagonal weight matrix.
II. Values obtained by least-squares refinement on the intensity curves from the two nozzle-to-plate distances simultaneously. A weight matrix with off-diagonal elements included was used [11] ($P_2 = -0.58$, $P_3 = 0.08$ for the longest, and $P_2 = -0.58$, $P_3 = 0.09$ for the shortest nozzle-to-plate distance).
III. Final results. The parameter values are the average of I and II.

[a] The amplitudes were assumed equal. [b] Assumed values. [c] ∠v is the angle between the plane through the allyl group and the plane through the three C-atoms in the $(CO)_3$-group. [d] Value obtained by refining with all the other parameters kept constant at values quite near to those in column I. [e] The value was refined keeping all the other parameters constant at the values in column III.

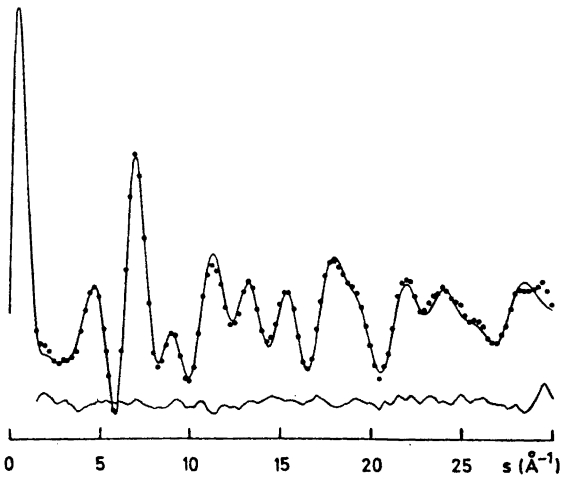

Fig. 1. Experimental (dotted) and theoretical intensity curves. The difference curve is also shown.

intensity curve which was calculated with the parameters given in Table 1, column III. The experimental and theoretical radial distribution (RD)-curves [9] were calculated by Fourier transformation of the intensity curves in Fig. 1. The two RD-curves are compared in Fig. 2. The difference curve is also shown.

STRUCTURE ANALYSES

In the initial stage of the investigation the bond parameters were taken from the experimental RD-curve, some of the angle parameters and root-mean-square amplitudes (u-values) being assumed, and some being obtained

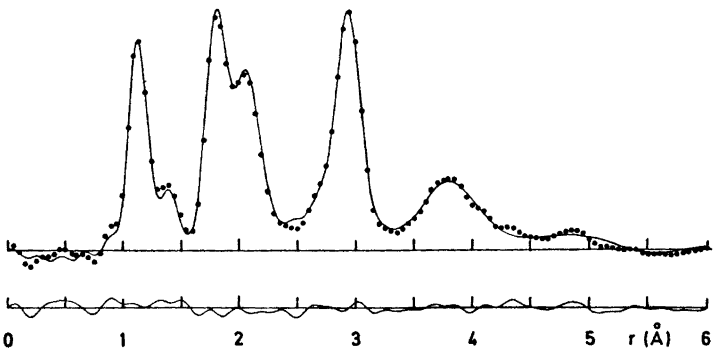

Fig. 2. Experimental (dotted) and theoretical radial distribution curves. The artificial damping constant $k = 0.0015$ Å^2. The difference curve is also shown.

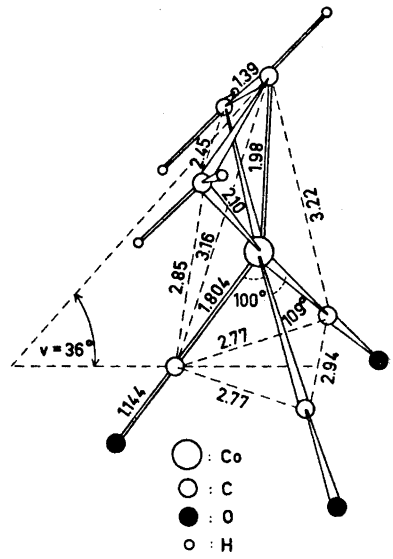

Fig. 3. The π-allylcobalt-tricarbonyl molecule with distances (in Å) and angles.

from previous structure determinations of similar molecules.[3,4,10] Fig. 3 shows the molecular model. The molecule was assumed to have a symmetry plane. Initially the $Co(CO)_3$-group was assumed to have threefold symmetry, but better agreement between experimental and theoretical curves was obtained when this assumption was discarded. Several least-squares refinements were performed. In the first calculations a diagonal weight matrix was applied,[11] and the results obtained are given in Table 1, column I; the angle v (see Fig. 3 and Table 1) being refined keeping the other parameters fixed. The results in column II were obtained with a weight matrix of the type discussed in Ref. 11 and the standard deviations in this column should therefore be more realistic than the corresponding values in column I. It is interesting to note that the standard deviations for the angle parameters are lower in column II than in column I.

DISCUSSION

The final parameters, obtained by averaging the values in Table 1, columns I and II, are given in column III together with their standard deviations. The latter are those from column II with the uncertainty in the wave length included. Because of the rather large difference in the values for two of the angle parameters in I and II, the largest set of standard deviations (I) is chosen for the angles.

The agreement between experimental and theoretical intensity curves (Fig. 1) and RD-curves (Fig. 2) is seen to be fairly satisfactory, though there are some deviations in the outer part of the RD-curve, which are probably due to experimental noise. This disagreement is reduced if a larger artificial

damping constant is used. Four observed intensity curves were obtained, each by combining data from one 50 cm plate and one 25 cm plate. Fourier transformation gave RD-curves which in the outer part deviate more from each other, than the experimental RD-curve in Fig. 2 deviates from the theoretical curve. The Co – C (carbonyl) distance and the C – O distance are believed to be quite accurately determined, and the latter show satisfactory agreement with values found in other metal carbonyls.[10,12] The distance from Co to the central C in the allyl group is significantly shorter than the two other Co – C (allyl) distances. This result is obtained in least squares calculations even if the initial paramenter values are reversed. A similar difference has been observed in related compounds.[3-4]

All the Co – C (allyl) bonds, however, are represented by one peak in the radial distribution curve at about 2.05 Å, and therefore only the average distance is well determined, and the two Co – C bond parameters given in Table 1 must have rather large standard deviations. The C – C bond in the allyl groups is nearly the same as that in benzene, however, with a large standard deviation. The u-value becomes unreasonably large (0.072 Å), when submitted to least squares refinement, but the bond length then changes less than the standard deviation (to 1.396 Å).

Though the considerable number of parameters required to describe the geometry causes some uncertainty in the interpretation of the electron diffraction data, the author feels fairly confident that the model shown in Fig. 3 is the correct one. A model with the allyl group rotated by 180° was also tried, but was abandoned since satisfactory agreement could not be obtained.

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