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AN ELECTRON DIFFRACTION DETERMINATION OF THE MOLECULAR STRUCTURE OF SILYLCOBALT TETRACARBONYL IN THE GAS PHASE

A. G. ROBIETTE, G. M. SHELDRICK AND R. N. F. SIMPSON
University Chemical Laboratory, Lensfield Road, Cambridge (Great Britain)
B. J. AYLETT AND J. A. CAMPBELL
Westfield College, London N.W.3 (Great Britain)

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SUMMARY

The molecular structure of $H_3SiCo(CO)_4$ has been determined in the vapour phase by electron diffraction. The principal bond lengths are $C{-}O = 1.137 \pm 0.003$, $Co{-}C = 1.802 \pm 0.003$ and $Co{-}Si = 2.381 \pm 0.007$ Å, and the Si–Co–C angle is $81.7 \pm 0.7°$. A comparison with the reported crystal structure for $Cl_3SiCo(CO)_4$ provides some evidence for a $d \rightarrow d$ π-bonding contribution in the latter molecule.

INTRODUCTION

A number of silyl transition metal carbonyls have recently been prepared, for example by the reaction of a silicon–halogen bond with the carbonyl anion[1]. In these compounds there exists the possibility of multiple bonding between the silicon and metal atoms, through the use of the vacant silicon *d* orbitals; this would account for the observation that the silyl derivatives tend to be thermally more stable than the analogous carbon compounds. We have determined the molecular structure of silylcobalt tetracarbonyl, $H_3SiCo(CO)_4$, in the vapour phase by electron diffraction in the hope that the bond lengths and angles in this molecule would provide evidence concerning such bonding. Since it is difficult to make a reliable estimate of the length of a "normal" silicon–cobalt bond, it is desirable to determine the effect of changing the substituents on the silicon atom on the silicon–cobalt bond length; the crystal structure of (trichlorosilyl)cobalt tetracarbonyl, $Cl_3SiCo(CO)_4$, has recently been reported[2]. The molecular structures of trisilylamine[3], disiloxane[4], some disilylamines[5] and silyl pseudohalides[6,7] have provided stereochemical evidence for $2p \rightarrow 3d$ π-bonding, but no such evidence exists for multiple bonding involving silicon and second or third row elements[8].

EXPERIMENTAL

The sample of silylcobalt tetracarbonyl was prepared by two of us (B.J.A. and J.A.C.) by the reaction between silyl iodide and sodium cobalt tetracarbonyl[1] and purified by fractional condensation *in vacuo*. Intensities were recorded photographically on the Balzers KD.G2 instrument at U.M.I.S.T.[9] at nozzle to plate distances of 100, 50 and 25 cm, and converted into digital form using an automated Joyce–Loebl microdensitometer. All the calculations were carried out on the Cambridge University "Titan" computer using programs written by two of us (A.G.R. and G.M.S.). Centreing of the traces and corrections for emulsion response, sector profile and plate planarity, interpolation in even s intervals and combination of individual traces, together with subtraction of the coherent atomic scattering (hence deriving approximate scale factors), and further levelling by subtraction of a least-squares fitted cubic were carried out in a single data reduction programme. At this stage a smooth background is drawn through the molecular scattering by inspection, to allow for incoherent atomic scattering and extraneous scattering, and a second subtraction is made. An off-diagonal weighting scheme is used in our least-squares programme[8] to take into account the effects of correlation between adjacent data points. Consistent values of the wave length (0.05580 ± 0.00003 Å) were obtained by direct measurement of the accelerating voltage, and from the diffraction pattern of powdered thallous chloride.

Preliminary Fourier inversions of the data revealed some contamination of the sample. All radial distribution curves showed strong peaks at 1.14, 1.80, 2.38 and 2.84 Å which could be attributed to C–O, Co–C, Co–Si and Co–O interatomic pairs respectively. Data from some plates showed a relative deficiency in the Si–Co peak, but an otherwise normal radial distribution curve, although the peak at 1.5 Å was somewhat larger than expected; this was consistent with partial hydrolysis or thermal decomposition (possibly catalysed by the metal of the nozzle) to $HCo(CO)_4$. Subsequent refinement was therefore restricted to the 25 cm plate data which were almost unaffected; this covered the range $4.2 \leqslant s \leqslant 29.0$ Å^{-1}. The diagonal elements of the weight matrix were given the values $w_{jj} = (s-4.2)/3.3$, $4.2 \leqslant s \leqslant 7.5$; $w_{jj} = 1$, $7.5 \leqslant s \leqslant 21.0$; and $w_{jj} = (29.0-s)/8.0$, $21.0 \leqslant s \leqslant 29.0$.

REFINEMENT OF STRUCTURE

In the crystal structure of $Cl_3SiCo(CO)_4$ the molecule has C_{3v} symmetry, with staggered Si–Cl and Co–C bonds. The molecular model used in this refinement assumed (*i*) a C_{3v} molecular point group, (*ii*) staggered Si–H and Co–C bonds, (*iii*) all Co–C and all C–O bond lengths respectively equal, (*iv*) all Co–C–O groups linear, and (*v*) tetrahedral Co–Si–H angles. The realistic values for the C–O and Co–C amplitudes obtained during the refinement suggest that assumption (*iii*) is justified for this molecule. No attempt was made to refine the Si–H bond length, which was fixed at 1.48 Å. The remaining four geometrical parameters (C–O, Co–C, Si–C, and Si–C_{eq}), the amplitudes of the four distances which contributed most strongly to the molecular scattering (C–O, Co–C, Si–Co and Co–O), and the scale factor were varied simultaneously in the least-squares refinement, a total of nine parameters. The remaining amplitudes were constrained at typical values[8,10]. No corrections for shrinkage were applied, and all the distances are $r_g(1)$[11]. The complex scattering factors of Cox and Bonham[12] were employed. The refinement converged in about ten cycles, the first four of which were "damped". The methods and notation are given in our work on trisilylphosphine[8]. The final discrepancy indices were $R_G = [\tilde{U}WU/(\tilde{I}WI)]^{\frac{1}{2}} = 0.28$ and $R_D = [\Sigma w_{jj} \cdot U_j^2 / \Sigma (w_{jj} \cdot I_j^2)]^{\frac{1}{2}} = 0.22$ where I is the vector of intensities, U the vector of residuals, and W the weight matrix having the elements w_{jk}.

RESULTS AND DISCUSSION

The molecular intensity data are presented in Fig. 1, and the observed and difference radial distribution curves, $P(r)/r$, in Fig. 2. The final least-squares correlation matrix is given in Table 1. As expected $r1$(C–O) and $r3$(Co–C) are strongly

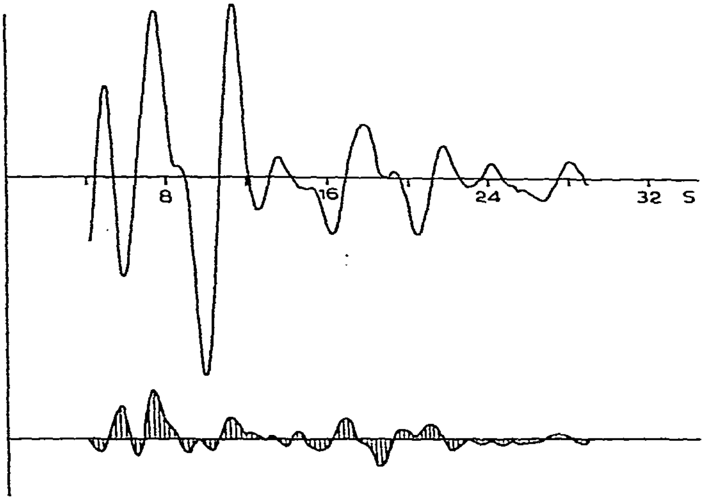

Fig. 1. Observed and weighted difference molecular intensities at a nozzle to plate distance of 25 cm.

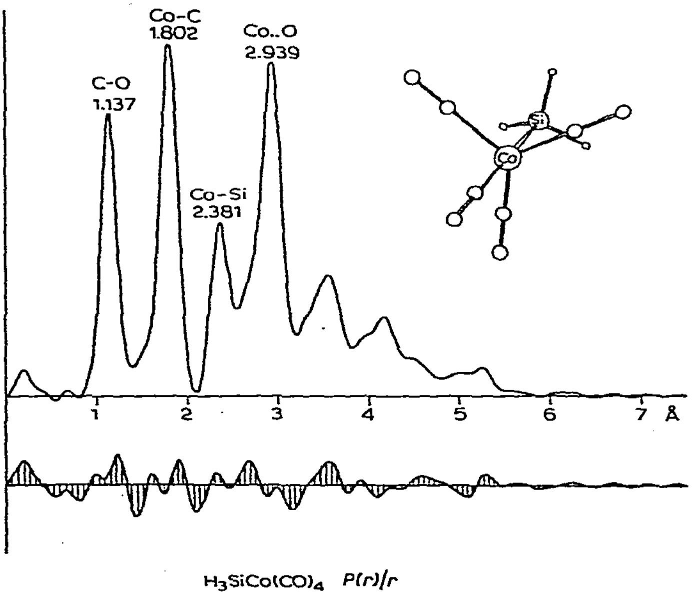

Fig. 2. Observed and difference radial distribution curves $P(r)/r$. Before the Fourier inversion the data were multiplied by: $s \cdot \exp\{-0.002s^2/[(Z_c-f_c)\cdot(Z_o-f_o)]\}$.

TABLE 1

LEAST SQUARES CORRELATION MATRIX MULTIPLIED BY 1000

$r1$	$r3$	$r4$	$r5$	$l1$	$l3$	$l4$	$l6$	$k1$
1000	−706	13	−122	7	76	48	60	102
−706	1000	−64	−66	7	−25	−10	−70	−13
13	−64	1000	228	22	47	103	73	53
−122	−66	228	1000	−163	−287	−80	−92	−464
7	7	22	−163	1000	220	122	219	364
76	−25	47	−287	220	1000	175	379	616
48	−10	103	−80	122	175	1000	187	336
60	−70	73	−92	219	379	187	1000	606
102	−13	53	−464	364	616	336	606	1000

TABLE 2

MOLECULAR PARAMETERS: INDEPENDENT DISTANCES AND AMPLITUDES

	Distance (Å)	Amplitude (Å)	a[a]
$r1$(C–O)	1.137±0.003	0.044±0.009	1.50
$r2$(Si–H)	1.480 (fixed)	0.060 (fixed)	2.00
$r3$(Co–C)	1.802±0.003	0.057±0.005	2.00
$r4$(Co–Si)	2.381±0.007	0.078±0.007	2.00
$r5$(Si–C)	2.772±0.018	0.150 (fixed)	0.00

[a] a=anharmonic constant.

MOLECULAR PARAMETERS: ANGLES

< (Si–Co–C) 81.73±0.65°
< (C–Co–C) 119.32±0.11°

TABLE 3

MOLECULAR PARAMETERS: DEPENDENT DISTANCES AND AMPLITUDES

	Distance (Å)	Amplitude (Å)
$d1$(Co–O)	2.939±0.002	0.065±0.004
$d2$(Si–C)	4.183±0.008	0.200 (fixed)
$d3$(Si–O)	5.320±0.007	0.200 (fixed)
$d4$(Si–O)	3.506±0.022	0.200 (fixed)
$d5$(C–C)	2.726±0.015	0.140 (fixed)
$d6$(C–C)	3.111±0.005	0.100 (fixed)
$d7$(C–O)	3.662±0.017	0.170 (fixed)
$d8$(C–O)	4.132±0.004	0.120 (fixed)
$d9$(O–O)	4.446±0.023	0.200 (fixed)
$d10$(O–O)	5.073±0.004	0.130 (fixed)
$d11$(H–Co)	3.195±0.006	0.150 (fixed)
$d12$(H–C)	4.880±0.007	0.150 (fixed)
$d13$(H–C)	3.078±0.019	0.150 (fixed)
$d14$(H–C)	4.116±0.015	0.200 (fixed)
$d15$(H–O)	5.978±0.007	0.150 (fixed)
$d16$(H–O)	3.515±0.026	0.150 (fixed)
$d17$(H–O)	4.953±0.020	0.200 (fixed)

correlated as individual variation in these parameters must also take into account the contribution to the molecular scattering due to the Co–O distance. The independent distances, amplitudes and bond angles are listed in Table 2, and the dependent distances and amplitudes in Table 3.

The Si–Co bond length (2.381 ± 0.007 Å) is very significantly longer than the value of 2.254 ± 0.003 Å found in $Cl_3SiCo(CO)_4$. Substitution of electron withdrawing groups on silicon would be expected[13] to contract and hence lower the energy of the "*d*" orbitals, and to increase their involvement in $d \rightarrow d$ π-bonding. This could account for the observed difference in bond lengths, but the change could also be ascribed to "electronegativity" effects. However the Si–H and C–H bond lengths tabulated by Ebsworth[14] are remarkably insensitive to change of electronegativity of the other substituents on the silicon or carbon atoms. The other parameters listed in Table 2 compare with the values 1.147 Å, 1.778 Å and 85° found for the mean C–O and Co–C distances and Si–Co–C angle respectively in $Cl_3SiCo(CO)_4$. We observe that the out-of-plane displacements of the equatorial carbonyls follows consistently the expected difference in π-acceptor capacity between the two *trans* ligands in compounds of this type, being bent away from the stronger π-acceptor. In conclusion, the comparison of the molecular structure reported here for $H_3SiCo(CO)_4$ with the crystal structure previously reported for $Cl_3SiCo(CO)_4$ provides some stereochemical evidence for $d \rightarrow d$ π-bonding in the trichloro compound. The infrared spectra have also been interpreted as implying the presence of $d \rightarrow d$ π-bonding, but the succession of approximations inherent in the method casts serious doubt upon its validity.

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