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DIPOLE MOMENTS OF COMPOUNDS CONTAINING A COBALT—TIN BOND

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Summary

The molecular electric dipole moments are reported for the series of tin-substituted tetracarbonyl cobalt compounds $R_nY_{m-n}Sn\{Co(CO)_4\}_{4-m}$ (m = 1-3; $n \leqslant m$; R = alkyl, phenyl; Y = halogen). The effect of the substituents at the tin atom on the nature of the Co—Sn bond is established on calculating the $(CO)_4Co$—Sn group dipole moments. It is shown that the charge transfer in the Co—Sn bond is mainly determined by the inductive properties of the ligands attached to tin.

Introduction

The series of molecules $R_nY_{m-n}Sn\{Co(CO)_4\}_{4-m}$ (m = 1-3; $n \leqslant m$; R = alkyl, phenyl; Y = halogen) is well suited to establish the nature of the metal—metal bond. Most tin groups cause an electron shift when substituted in metal carbonyls and the molecular electric dipole moment is a good criterion for this charge effect. In connection with our previous papers treating cobalt-59 NMR [1] and FIR [2,3] measurements we now report the polar characteristics of these organometallics.

Results

Table 1 summarises the electric dipole moments obtained for the 24 tetracarbonyl cobalt compounds under study. The values obtained in the classical way according to Debye's Second Method are listed under μ_D. The dipole moments were calculated using the formula $\mu = 0.01281\sqrt{(P_{2\infty}-R_{2\infty})T}$ (Debye Units). Both the molecular polarisation $P_{2\infty}$ and the molecular refraction $R_{2\infty}$ at infinite dilution were obtained by graphical extrapolation from the linear plots of P_2 resp. R_2 values against the mole fraction of solute. No correction was made for the atomic polarisation.

TABLE 1

DIPOLE MOMENTS OF TETRACARBONYLCOBALT DERIVATIVES (DEBYE UNITS)

Carbonyl	μ_D	μ_{HHK}	μ_{CH}	μ_G	μ_H
$Me_3SnCo(CO)_4$	1.77 ± 0.06	1.76	1.75	1.76	1.79
$Ph_3SnCo(CO)_4$	1.54 ± 0.06	1.54	1.52	1.52	1.95
$Me_2ClSnCo(CO)_4$	3.03 ± 0.02	3.03	3.02	3.05	3.07
$Ph_2ClSnCo(CO)_4$	3.21 ± 0.02	3.21	3.20	3.25	3.35
$Me_2BrSnCo(CO)_4$	3.01 ± 0.02	3.01	3.00	3.03	3.06
$Me_2ISnCo(CO)_4$	2.74 ± 0.02	2.75	2.73	2.77	2.83
$Ph_2ISnCo(CO)_4$	2.80 ± 0.07	2.80	2.79	2.83	3.00
$MeCl_2SnCo(CO)_4$	4.01 ± 0.03	4.01	4.01	4.04	4.04
$PhCl_2SnCo(CO)_4$	3.98 ± 0.07	3.98	3.97	4.01	4.06
$MeBr_2SnCo(CO)_4$	3.73 ± 0.02	3.74	3.73	3.76	3.80
$MeI_2SnCo(CO)_4$	3.28 ± 0.04	3.28	3.27	3.30	3.41
$Cl_3SnCo(CO)_4$	4.97 ± 0.06	4.98	4.98	5.00	5.00
$Br_3SnCo(CO)_4$	4.32 ± 0.04	4.32	4.32	4.34	4.38
$I_3SnCo(CO)_4$	3.31 ± 0.02	3.31	3.30	3.33	3.52
$Ph_2Sn\{Co(CO)_4\}_2$	1.15 ± 0.10	1.15	1.11	1.13	1.59
$Me_2Sn\{Co(CO)_4\}_2$	1.54 ± 0.04	1.56	1.54	1.56	1.71
$PhClSn\{Co(CO)_4\}_2$	2.88 ± 0.02	2.88	2.86	2.97	3.07
$MeClSn\{Co(CO)_4\}_2$	2.98 ± 0.03	2.98	2.97	3.01	3.11
$Cl_2Sn\{Co(CO)_4\}_2$	4.04 ± 0.04	4.04	4.04	4.08	4.15
$Br_2Sn\{Co(CO)_4\}_2$	3.90 ± 0.05	3.90	3.90	3.95	4.04
$MeSn\{Co(CO)_4\}_3$	1.33 ± 0.05	1.33	1.30	1.32	1.75
$ClSn\{Co(CO)_4\}_3$	2.63 ± 0.04	2.63	2.62	2.64	2.91
$BrSn\{Co(CO)_4\}_3$	2.58 ± 0.07	2.58	2.57	2.60	2.90
$ISn\{Co(CO)_4\}_3$	2.48 ± 0.08	2.49	2.47	2.50	2.88

For comparative purposes we have calculated dipole values according to some variants, of this procedure, thus using the equations of Hedestrand, Halverstadt and Kumler [4,5] (μ_{HHK}), Cohen Hentiquez [6] (μ_{CH}) and Higasi [7] (μ_H) the factors $d\epsilon_{12}/df_2$, $d(n_{12})^2/df_2$ and $d(\rho_{12})^{-1}/df_2$ have been computed from the sets of experimental values $[\epsilon_{12}, f_2]$, $[(n_{12})^2, f_2]$ and $[\rho_{12}^{-1}, f_2]$ using a least squares fit. For handling Guggenheims method (μ_G) in practice we refer to the work of Moody and Thomas [8]. From the comparison of μ_D, μ_{HHK}, μ_{CH} and μ_G it is clearly seen that these different methods give values which are in fairly good agreement within the limits of the experimental error. The approximation of Higasi, however, fails for small dipole values.

Discussion

Assuming constant bond moments and tetrahedral angles, the following ratios of molecular moments would be expected to be observed: $\mu(ClSnX_3)/\mu(Cl_3SnX) = 1$ and $\mu(Cl_2SnX_2)/\mu(Cl_3SnX) = 1.16$, with $X = \{Co(CO)_4\}$. Taking the experimental dipole value for the trichlorotin derivative as a reference, we thus can calculate the expected molecular dipole values for the dichlorobis- and the monochlorotris(tetracarbonylcobalt)tin(IV). These values are listed in Table 2. The differences between the observed and calculated values can be explained either in terms of distortions or of altering bond or group moments.

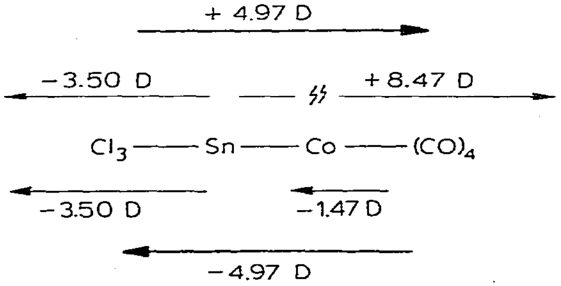
TABLE 2

OBSERVED AND CALCULATED MOLECULAR DIPOLE VALUES FOR THE SERIES $Cl_{4-n}Sn\{Co(CO)_4\}_n$ (n = 1-3) (DEBYE UNITS)

Carbonyl	$\mu_{obs.}$	$\mu_{cal.}$	Δ_{o-c}	$\mu^{cal.}_{CoSnCl = 104°C}$	Δ'_{o-c}
$Cl_3SnCo(CO)_4$	4.97	4.97	0		
$Cl_2Sn\{Co(CO)_4\}_2$	4.04	5.76	−1.72		
$ClSn\{Co(CO)_4\}_3$	2.63	4.97	−2.34	4.57	−1.94

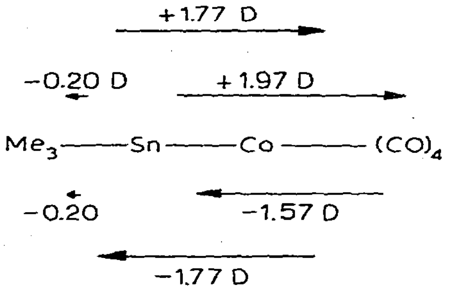
For the monocloro derivative X-ray diffraction data are available [10] which show that the tin atom has a distorted tetrahedral coordination: due to steric factors the Co—Sn—Co angles (average 114°) are increased and the Cl—Sn—Co angles (average 104°) are decreased as compared to the ideal value. Still assuming constant bond and group moments but taking into account these exact angles, a value of 4.57 D would be expected for this carbonylcomplex. Therefore we may conclude that for this particular compound the difference Δ_{o-c} is caused mainly by altering bond or group moments (~ 83%), whereas the contribution due to distortion of the tetrahedral coordination around the tin atom is rather limited (~ 17%). Since the greatest distortions are expected for the tris(tetracarbonylcobalt) derivatives $YSn\{Co(CO)_4\}_3$, $RSn\{Co(CO)_4\}_3$, this conclusion may be extended for the whole series. So, in order to simplify the calculations, the bond angles at the tin atom were taken to be equal to the tetrahedral angle and the $\mu((CO)_4Co—Sn)$ group dipole moment is regarded as the only variable.

In the calculations the following plausible values were used for the group and bond moments: Sn→Cl 3.50; Sn→Br 3.33; Sn→I 3.05 and Sn→R 0.20 D [11]. The $\mu((CO)_4Co—Sn)$ group moments are conventionally taken positive as these moments are assumed to be directed from Sn towards the CO groups. The $Cl_3SnCo(CO)_4$ has a molecular dipole moment of 4.97 D. The contribution arising from the polarity of the fragment $SnCl_3$ is 3.50 D. As a result, two values with oppositely directed dipole moments were obtained for $\overleftarrow{\mu(CO)_4Co—Sn}$ according to the sense of the over-all molecular moment: 4.97 + 3.50 = 8.47 D, or −4.97 + 3.50 = −1.47 D.



Taking into account the strong electron withdrawing capacity of chlorine, the relatively high value of 8.47 D directed away from the tin atom would be rather surprising; this value would also correspond to a very high degree of ionicity which is also unlikely for this kind of complex.

We therefore select the value of —1.47 D, which implies that the electron cloud in the group $(CO)_4Co—Sn$ is displaced towards the tin atom. An analogous procedure holds for the $Me_3SnCo(CO)_4$, so here we get 1.77 + 0.20 = 1.97 D, or —1.77 + 0.20 = —1.57 D.



A value of —1.57 D for the $\mu\overleftarrow{(CO)_4Co—Sn}$ group moment would imply an even more extensive electron shift towards tin than in the corresponding chloro derivative. This is rejected in view of the slighter electron withdrawing power of a methyl group. The alternative (1.97 D) is more acceptable because of its opposite sign in comparison with the value selected for the $\mu\overleftarrow{(CO)_4Co—Sn}$ group moment in $Cl_3SnCo(CO)_4$.

When asymmetrically substituted ligands are present, their group moment μ_L is inclined to the axis of the Sn—Co bond at an angle β which can be deduced by vector analysis. The geometry of the various partial moment vectors is shown in Fig. 1. From these data, μ_L and β, together with the observed overall molecular moment and using the cosine rule and eqns. 1 and 2, again two values were obtained for the $(CO)_4Co—Sn$ group dipole moment.

$$\mu_{exp}^2 = \mu((CO)_4Co—Sn)^2 + \mu_L^2 - 2\,\mu((CO)_4Co—Sn) \times \mu_L \cos\alpha,$$

for L = $R_2(Hal)Sn$:

$$\alpha = 180° - \beta,\ \beta = \delta + \varphi = 109°28' + \arcsin\left[\frac{\vec{r}}{\overrightarrow{\mu_L}} \sin\eta\right] \qquad (1)$$

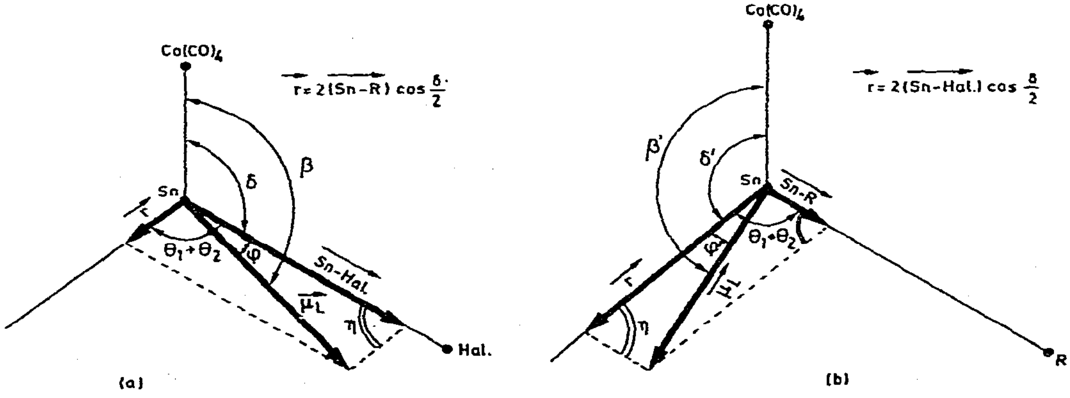


Fig. 1. Geometry of the various partial moment vectors for (a) $R_2HalSnCo(CO)_4$ and (b) $RHal_2SnCo(CO)_4$.

TABLE 3

CALCULATED GROUP DIPOLE MOMENTS FOR THE COMPOUNDS $(CO)_4Co—L$

L	μ_L (D)	$\beta(Co—Sn—\mu_L)$	$\mu(\overleftarrow{(CO)_4Co—Sn})$ (D)	
			(1)	(2)
$SnMe_3$	0.20	180°	1.97	−1.57
$SnMeCl_2$	3.93	127°37′	−0.13	4.92
$SnCl_3$	3.50	180°	−1.47	8.47
$SnPh_3$	0.20	180°	1.74	−1.34
$SnPh_2Cl$	3.37	110°12′	0.63	1.70
$SnPhCl_2$	3.93	127°37′	−0.08	4.88
$SnEt_3$ [12]	0.20	180°	2.25	−1.85
$SnMeBr_2$	3.20	110°15′	0.93	1.29
$SnMeBr_2$	3.73	127°44′	0.01	4.56
$SnBr_3$	3.33	180°	−0.99	7.65
$SnMe_2I$	2.92	110°19′	1.01	1.01
$SnMeI_2$	3.41	127°59′	0.22	3.98
SnI_3	3.05	180°	−0.26	6.36
$SnPh_2I$	2.92	110°19′	0.44	1.59

for $L = R(Hal)_2Sn$:

$$\alpha = 180° - \beta', \ \beta' = \delta' + \varphi' = \theta_1 + \theta_2 + \arcsin\left[\frac{\overrightarrow{Sn—R}}{\overrightarrow{\mu_L}} \sin\eta\right] \qquad (2)$$

The results of our calculations are summarized in Table 3. From the above dis-

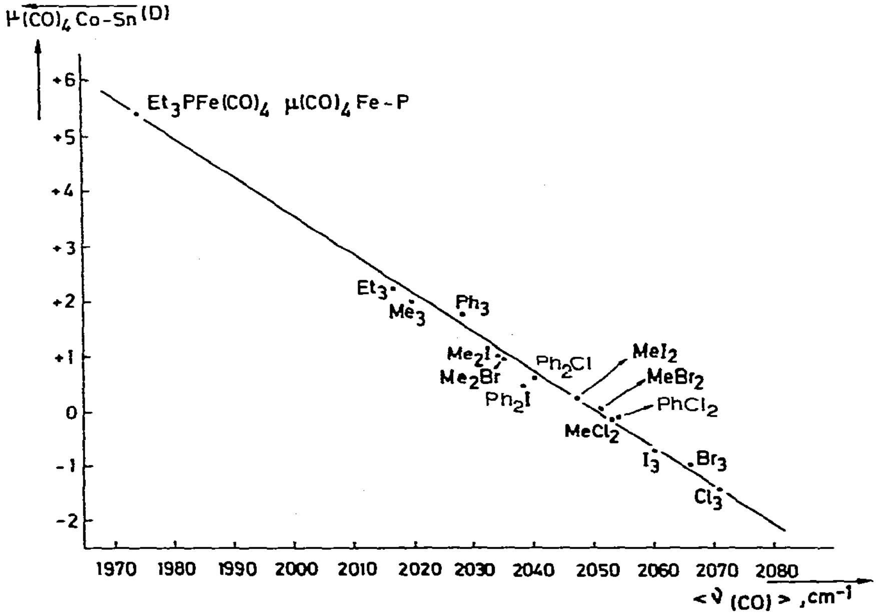


Fig. 2. Correlation between the $(CO)_4Co—Sn$ group dipole moments and the mean carbonyl stretching frequencies.

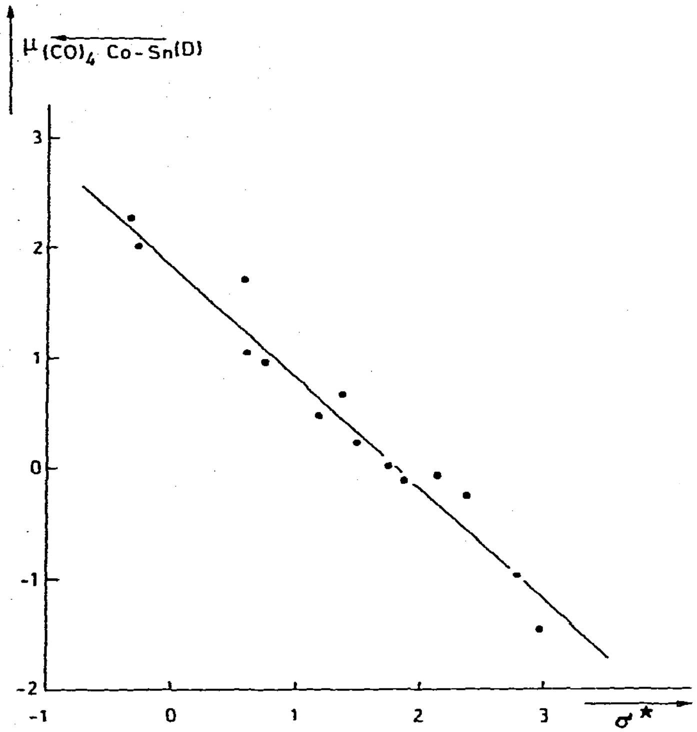


Fig. 3. Plot of $(CO)_4Co—Sn$ group dipole moments vs. Taft induction constants (σ^*) for the series $R_{3-n}Y_nCo(CO)_4$ (n = 0-3; R = Me, Et, Ph; Y = Cl, Br, I).

cussion we generalize that only the group moments of eqn. 1 are physically acceptable.

As shown in Fig. 2, a close relationship exists between the mean carbonyl stretching frequencies of the complexes and the charge transfer within the fragments $(CO)_4Co—Sn$. A similar graph has been reported by Kahn et al. [15], for the series $(CO)_4CoM'Et_3$, M' = Si, Ge, Sn, Pb. This correlation proves the transfer to be most sensitive to the nature of the ligands attached to tin since even an inversion in sign occurs. The frequency for which $\mu = 0$ is about 2050 cm^{-1}, in good agreement with the value of 2045 cm^{-1} deduced by Kahn.

A linear correlation is also found by plotting the $\mu\overleftarrow{(CO)_4Co—Sn}$ group moments versus the Taft [13] induction constants (σ^*) of the substituents at the tin atom, Fig. 3. From this relationship it is seen that the polarity of the Co—Sn bond is principally determined by the inductive properties of the substituents on tin. The same conclusion has been drawn for a series of dicarbonyl(π-cyclopentadienyl)iron compounds containing a Fe—Sn bond [14].

Experimental

The compounds were synthesized by previously described methods [9]. For the determination of electric dipole moments, measurements at a single temperature (25° ± 0.01°C) of the dielectric constant, the refractive index and the density are needed for at least four dilute benzene solutions of the compound under study. We usually work over the mole fraction range $10^{-3} < f_2 < 10^{-2}$. The tris(tetracarbonylcobalt) derivatives, however, are intensely red-purple in color, so for measuring their refraction the mole fraction has to be reduced to about 10^{-4}. The dielectric constant measurements were made with a commercial dipolemeter WTW type DM 01. The measuring cell DFL 2 was used to minimize the necessary amount of handled complex. Refractive indices were determined with a Pulfrich refractometer using the Na D line. Density measurements were made using an Aubry pycnometer with a graduated stem.

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