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NMR Spectra of Some Metal Acetylacetonates*[1]

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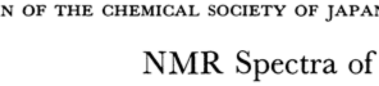
The NMR spectra of a series of complexes, XX′Sn(acac)$_2$ (X, X′ =alkyl, aryl and halogen), $(CH_3)_2Pb(acac)_2$, $Cl_2Ti(acac)_2$, $Cl_2Ge(acac)_2$, $Cl_4Sb(acac)$ and $(C_6H_5)Cl_3Sb(acac)$, have been studied in chloroform. A linear relationship has been found between the chemical shifts of the γ proton and those of the methyl protons of acetylacetone for various type of complexes. In XX′Sn(acac)$_2$, both τ values decrease with an increase in the electron-attracting power of the substituents, X and X′, and the chemical shifts of these protons are found to be correlated with the Sn–O and C=O stretching frequencies. This behavior can be explained in terms of the inductive effect of the substituents on the tin atom.

In order to account for the high stability of several metal acetylacetonates with a chelate structure, Calvin and Wilson[1] suggested some contribution of the benzenoid resonance (I):


(1)

in addition to the enol-type resonance (2):


(2)

However, the NMR spectra of the usual diamagnetic metal acetylacetonates, M(acac)$_n$ (n= 1—4), seem to show that there is no evidence for the contribution of the benzenoid resonance (1).[2] The chemical shifts of the γ and the methyl protons in these metal complexes are almost the same (4.60—4.80 and 7.90—8.10 ppm respectively)[2,3] as those in a free acetylacetone molecule with an enol form (4.6 and 8.0 ppm).[3] Smaller τ values would be expected if there were an appreciable contribution from the benzenoid resonance (1). On the other hand, it has been reported by Hester[4] that there is some possibility of a benzenoid resonance (1) in the chelate structure of the tris(acetylacetonato)silicon cation $[Si(acac)_3]^+[HCl_2]^-$. This was deduced from two experimental results. One of them is the fact that the τ values for both the γ and the methyl protons are fairly small (3.74 and 7.73 ppm respectively) compared with those for the usual dia-

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*[1] Portions of this paper were presented at the International Symposium on Nuclear Magnetic Resonance, Tokyo, September, 1965.

[1] M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945).

[2] R. H. Holm and F. A. Cotton, *ibid.*, **80**, 5658 (1958).

[3] J. A. S. Smith and J. D. Thwaites, *Discussions Faraday Soc.*, **34**, 143 (1962).

[4] R. E. Hester, *Chem. & Ind.*, **1963**, 1397.

magnetic metal acetylacetonates. To explain the smaller τ values of these proton resonances, Hester assumed the presence of a ring current due to the benzenoid resonance (1), as in aromatic compounds.[5] The other experimental result is the fact that the Si–O stretching frequency is higher than that of the Al–O bond in tris(acetylacetonato)aluminum, which is isoelectronic with the tris(acetylacetonato)silicon cation. Hester assumed that the higher Si–O stretching frequency was due to the increase in the partial double-bond character in the silicon-oxygen bond as a result of the fairly large contribution of the benzenoid resonance (1) in the chelate structure.

We have measured the NMR and the infrared spectra of a series of compound, XX′Sn(acac)$_2$ (X, X′ = alkyl, aryl and halogen), $(CH_3)_2Pb(acac)_2$, $Cl_2Ti(acac)_2$, $Cl_2Ge(acac)_2$, $Cl_4Sb(acac)$ and $(C_6H_5)Cl_3Sb(acac)$, in order to study the effect of the X and X′ substituents on the chemical shift of the γ and the methyl protons.

Experimental

NMR Spectra. The NMR spectra were measured in chloroform using a Varian A-60 spectrometer and two Japan Electron Optics spectrometers, models JNM-3H-60 and JNM-4H-100, operating at 60 and 100 Mc/sec respectively. Tetramethylsilane was used as an internal standard throughout the experiments.

Infrared Spectra. The infrared spectra were measured in Nujol and hexachlorobutadiene mulls using a Hitachi EPI-2G spectrometer equipped with gratings.

Preparation of the Materials. One series of compounds, XX′Sn(acac)$_2$ (X, X′ = alkyl, aryl and halogen), used in this experiment was obtained by the methods reported elsewhere.[6]

Bis(acetylacetonato)titanium Dichloride. Titanium tetrachloride was slowly added to a mixture of chloroform and carbon tetrachloride containing a small excess of acetylacetone. The mixture was then refluxed for 2 hr. The red precipitates formed were filtered and dried *in vacuo*. Mp 185°C (decomp.). (Found: Ti, 15.13%. Calcd for $C_{10}H_{14}O_4Cl_2Ti$: Ti, 15.11%.)

Bis(acetylacetonato)germanium Dichloride. A mixture of germanium tetrachloride and a small excess of acetylacetone in chloroform was refluxed for 4 hr. The white precipitates thus formed were filtered and dried *in vacuo*. Mp 240°C (decomp.) (The literature value: mp 240°C.)[7]

Acetylacetonatoantimony Tetrachloride. Antimony pentachloride and a small excess of acetylacetone were refluxed in carbon tetrachloride for 4 hr. Yellow crystals were obtained when the solution was then cooled at room temperature. The precipitates were recrystallized from chloroform and ligroin. Mp 131°C. (Found: C, 16.79; H, 1.89; Cl, 39.73%. Calcd for $C_5H_7O_2Cl_4Sb$: C, 16.56; H, 1.94; Cl, 39.10%.)

Phenyl(acetylacetonato)antimony Trichloride. In a mixture of acetylacetone and concentrated hydrochloric acid, phenylstibonic acid was dissolved. The product was then extracted by methylene chloride. Transparent crystals were obtained when some portions of the organic solvent were evaporated. The compound was dried *in vacuo*. Mp 176—178°C (decomp.). (Found: C, 33.24; H, 2.84; Cl, 25.72%. Calcd for $C_{11}H_{12}O_2Cl_3Sb$: C, 33.07; H, 3.03; Cl, 25.40%.)

Results and Discussion

The τ values of the γ and the methyl protons of the acetylacetone ring, together with the C=O and M–O stretching frequencies,[8] for the six series of complexes, XX′Sn(acac)$_2$ (X, X′ = alkyl, aryl and halogen), $(CH_3)_2Pb(acac)_2$, $Cl_2Ti(acac)_2$, $Cl_2Ge(acac)_2$, $Cl_4Sb(acac)$ and $(C_6H_5)Cl_3Sb(acac)$, are shown in Table 1. In the XX′Sn(acac)$_2$ series of compounds (X, X′ = alkyl, aryl and halogen), the Sn–O and C=O stretching frequencies change regularly with the electronegativity of the X and X′ substituents on the tin atom, and the τ values for both the γ and the methyl protons decrease with an increase in the electronegativity of X and X′. The change in the τ value of the γ proton by the change in substituents on the tin atom is found to be larger than that for the methyl protons. A linear relationship between the sum of the Hammett constant, σ^*, of the X and X′ substituents[9] and the τ values of the γ proton in these compounds is shown in Fig. 1.

When halogen atoms in bis(acetylacetonato)tin dihalides attract electrons from the tin atom, the ligands (acetylacetone, in this case) may donate some electrons to the tin atom to compensate for

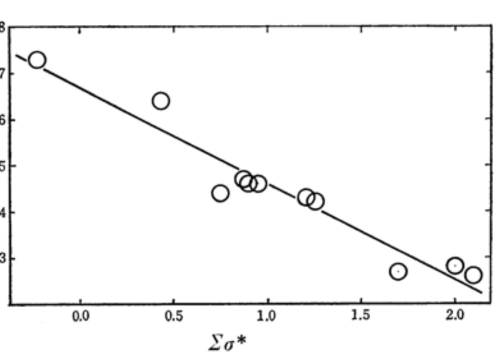

Fig. 1. Plots of the chemical shifts of the γ proton *versus* the sum of the Hammett's constant σ^* of the substituents on the tin atom for XX′Sn(acac)$_2$.

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[5] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, New York (1959), p. 180.

[6] R. Ue-eda, Y. Kawasaki, T. Tanaka and R. Okawara, *J. Organometal. Chem.*, **5**, 194 (1966).

[7] W. K. Ong and R. H. Prince, *J. Inorg. Nucl. Chem.*, **27**, 1037 (1965).

[8] Y. Kawasaki, T. Tanaka and R. Okawara, *Spectrochim. Acta*, **22**, 1571 (1966).

[9] M. S. Newman, ed., "Steric Effect in Organic Chemistry," John Wiley, New York (1956), p. 595.

TABLE 1. THE PROTON CHEMICAL SHIFTS AND THE RELEVANT INFRARED BANDS OF BIS(ACETYLACETONATO)-METAL DERIVATIVES

$XX'M(acac)_2$			τ(>C-H)	τ(>C-CH_3)	ν(C=O)b)	ν(M-O)b)
M	X	X'	ppma)	ppma)	cm^{-1}	cm^{-1}
Pb	CH_3	CH_3	4.88	8.08	1575	396
Sn	C_2H_5	C_2H_5	4.73	8.04	1572	404
	C_2H_3	C_2H_3	4.61	8.03	1563	408
	C_6H_5	C_6H_5	4.64	8.06	1564	408
	C_2H_5	Br	4.47	7.95	1560	433
	CH_3	I	4.44	7.95	1562	432
	CH_3	Br	4.46	7.95	1558	436
	CH_3	Cl	4.46	7.95	1558	435
	C_6H_5	Br	4.43c)	7.93d)	1552	438
	C_6H_5	Cl	4.42c)	7.94d)	1555	438
	I	I	4.27	7.90c)	1546	445
	Br	Br	4.28	7.86c)	1543	453
	Cl	Cl	4.26	7.84c)	1543	461
Ge	Cl	Cl	4.24	7.84c)	1544	478
Ti	Cl	Cl	3.96	7.85	1543	470
$C_6H_5SbCl_3(acac)$			4.15	7.75c)	1544	456
$SbCl_4(acac)$			3.94	7.57	1544	459

a) Measured in chloroform and $Si(CH_3)_4$ was taken as an internal standard.
b) Ref. 8.
c) Mean value of doublet.
d) Mean value of quartet.

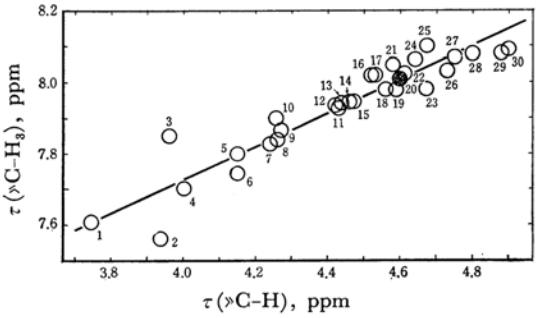

Fig. 2. Chemical shifts of the γ proton *versus* the methyl protons.
(1) $[Si(acac)_3]^+HCl_2^-$.a) (2) $Cl_4Sb(acac)$.
(3) $Cl_2Ti(acac)_2$. (4) $F_2B(acac)_2$.b)
(5) $(C_6H_5C\equiv C)_2B(acac)$.b)
(6) $(C_6H_5)Cl_3Sb(acac)$. (7) $Cl_2Ge(acac)_2$.
(8) $Cl_2Sn(acac)_2$. (9) $Br_2Sn(acac)_2$.
(10) $I_2Sn(acac)_2$. (11) $(C_6H^5)ClSn(acac)_2$.
(12) $(C_6H_5)BrSn(acac)_2$.
(13) $(CH_3)ISn(acac)_2$.
(14) $(CH_3)ClSn(acac)_2$ and $(CH_3)BrSn(acac)_2$.
(15) $(C_2H_5)BrSn(acac)_2$. (16) $Be(acac)_2$.c)
(17) $Al(acac)_3$. (18) $Zn(acac)_2$.
(19) $In(acac)_3$. (20) H(acac).c,d)
(21) $(C_2H_5)_2B(acac)$.b) (22) $(C_2H_3)_2Sn(acac)_2$.
(23) $(C_6H_5)_2B(acac)$.b) (24) $(C_6H_5)_2Sn(acac)_2$.
(25) $Th(acac)_4$.c) (26) $(C_2H_5)_2Sn(acac)_2$.
(27) $Ga(acac)_3$.c) (28) $(CH_3)_2Pb(acac)_2$.
(29) Tl(acac). (30) $(CH_3)_2Tl(acac)$.
a) Ref. 4. b) Ref. 10. c) Refs. 2 and 3.
d) Free acetylacetone molecule having an enol form.

the positive charge on this atom. As a result, the electron density in the acetylacetone ring will decrease and the τ values of the γ and the methyl protons will shift toward a lower magnetic field. At the same time, the stretching frequency of the C=O bond will become lower and that of the Sn–O bond, higher. When both substituents are less electronegative than halogen, as in ethyl groups, the τ values of the γ and the methyl protons are larger than those found for bis(acetylacetonato)tin dihalides and are almost the same as those for the free acetylacetone molecule with an enol form3) or for the usual diamagnetic metal acetylacetonates, $M(acac)_n$.3,4) The inductive effect of the X and X' substituents seems, therefore, to play a predominant role in the chemical shifts of the γ and the methyl protons in acetylacetone. Plots of the τ values of the γ proton *versus* those of the methyl protons for several types of acetylacetonato complexes3,4,10) are shown in Fig. 2, where a linear relationship is obtained. In labile complexes such as thallusacetylacetone, the τ values of both protons are the largest, while in complexes with many halogen atoms, such as acetylacetonatoantimony tetrachloride, both protons show one of the smallest τ values. Most compounds show τ values intermediate between thees two cases. The τ values of the γ and the methyl protons in the tris(acetylacetonato)silicon cation are found to be the smallest among many acetylaceto-

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10) L. H. Toporcer, R. E. Dessy and S. I. E. Green, *Inorg. Chem.*, **4**, 1649 (1965).

TABLE 2. THE VALUES OF SPIN-SPIN COUPLING CONSTANT AND THE CHEMICAL SHIFTS OF THE METHYL PROTONS ATTACHED TO METAL FOR $(CH_3)XSn(acac)_2$ AND $(CH_3)_2Pb(acac)_2$ IN CHLOROFORM

$(CH_3)XM(acac)_2$		$J_{^{119}Sn-CH_3}$ cps	$J_{^{117}Sn-CH_3}$ cps	$J_{^{207}Pb-CH_3}$ cps	τ $(M-CH_3)$ ppm
M	X				
Sn	CH_3	99.3[a)]	95.0[a)]		9.51[a)]
	I	115.2	110.4		8.79
	Br	118.5	113.7		8.96
	Cl	120.9	115.2		9.09
Pb	CH_3			154.7	7.95

a) Ref. 11.

nato complexes. As has been pointed out by Hester,[4)] this is probably due to the presence of a ring current, accompanied by a large contribution of the benzenoid resonance (1) in the chelate structure. However, the inductive effect of the silicon atom with a singly-positive charge may not be neglected in explaining the small τ values of the protons in this molecule.

Some values of the spin-spin coupling constants $J_{^{117}Sn-CH_3}$, $J_{^{119}Sn-CH_3}$, and $J_{^{207}Pb-CH_3}$, and the chemical shifts of the protons of methyl groups attached to tin and lead in $(CH_3)_2Sn(acac)_2$,[11)] $(CH_3)XSn(acac)_2$ (X=halogen), and $(CH_3)_2Pb(acac)_2$ are shown in Table 2. The $J_{^{117}Sn-CH_3}$ and $J_{^{119}Sn-CH_3}$ values in $(CH_3)XSn(acac)_2$ increase with an increase in the electronegativity of halogen. This is probable due to an increase in the s character in the Sn–C bond as a result of the rehybridization of the tin atom caused by electonegative halogen,[12)] because spin-spin coupling between tin and methyl protons in most tin compounds is explained by the Fermi contact term.[13)] One remarkable finding regarding the $J_{^{207}Pb-CH_3}$ value for $(CH_3)_2Pb(acac)_2$ is that this value is more than twice the value for tetramethyllead.[14-16)] This is different from that for $(CH_3)_2Sn(acac)_2$, because in this compound $J_{^{119}Sn-CH_3}$ is somewhat less than twice the value for tetramethyltin.[13)]

The τ values of the methyl proton signals in $(CH_3)XSn(acac)_2$ increase as the electronegativity of halogen increases, although those of acetylacetone protons are almost constant. The chemical shift of the former protons, therefore, seems to be more or less affected by the paramagnetic effect of halogen.

[11)] M. M. McGrady and R. S. Tobias, *J. Am. Chem. Soc.*, **87**, 1909 (1965).

[12)] H. Bent, *Chem. Revs.*, **61**, 275 (1961).

[13)] J. R. Holmes and H. D. Kaesz, *J. Am. Chem. Soc.*, **83**, 3909 (1961).

[14)] W. G. Schneider and A. D. Buckingham, *Discussions Faraday Soc.*, **34**, 147 (1962).

[15)] N. Flitcroft and H. D. Kaesz, *J. Am. Chem. Soc.*, **85**, 1377 (1963).

[16)] H. P. Fritz and K. E. Schwarzhans, *J. Organometal. Chem.*, **1**, 297 (1964).