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STEREOISOMERISM OF DIHALODIARYL(ACETYLACETONATO)-ANTIMONY(V) COMPOUNDS

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SUMMARY

A series of dihalodiaryl(acetylacetonato)antimony(V) compounds, (p-Y-$C_6H_4)_2SbX_2$Acac (X = F, Cl, Br; Y = NO_2, Cl, H, CH_3, CH_3O), were prepared. All of these compounds are monomeric and exist in solution as a mixture of two isomers both with chelated hexacoordinate configurations. From the temperature- and solvent-dependent PMR spectra of these compounds, it is concluded that the two isomers are in equilibrium in solution. The assignments of the PMR signals to the isomers were made by considering the effects of solvent and the substituents X and Y on the spectra.

INTRODUCTION

The stereochemistry of dichlorodiphenyl(acetylacetonato)antimony(V) has recently been of considerable interest[1,2]. We have found[1] PMR spectral evidence for the presence of two kinds of acetylacetonate groups in this compound and have assumed that two chelated hexacoordinate isomers exist in equilibrium in various solvents.

In order to obtain further information on the equilibrium and to facilitate the assignment of the PMR signals to the isomers, we have prepared a series of dihalodiaryl(acetylacetonato)antimony(V) compounds, (p-$YC_6H_4)_2SbX_2$Acac, and studied, by means of PMR spectra, the effects of solvent and the substituents X and Y on the equilibrium.

EXPERIMENTAL

Preparation of (p-$YC_6H_4)_2SbCl_2Acac$ ($Y = H, CH_3$)

These compounds were prepared as reported in our previous paper[1]. Recrystallization of $(C_6H_5)_2SbCl_2$Acac from dichloromethane/petroleum ether or from benzene gave two crystal forms; the long prismatic crystal form (A) decomposes at 192° and the polyhedral form (B) decomposes at 184.5°.

Preparation of (p-$YC_6H_4)_2SbBr_2Acac$ ($Y = NO_2, Cl, H, CH_3, CH_3O$)

These compounds were synthesized in a similar manner to that reported[3].

TABLE 1

PROPERTIES OF THE COMPOUNDS $(p\text{-}YC_6H_4)_2SbX_2Acac$

Compound		*M.p. (°C)*	*Analysis found (calcd.)*		*Mol.wt.*[a]
X	*Y*	*(reported)*	*C (%)*	*H (%)*	*found (calcd.)*
F	H	121–123	48.73	4.24	392
			(49.43)	(4.15)	(413)
Cl	H	(A) 192 (dec.)	46.03	3.68	438
		(B) 184.5 (dec.)	(45.78)	(3.84)	(446)
Cl	CH_3	190 (dec.)	47.84	4.43	479
			(48.14)	(4.47)	(474)
Br	NO_2[b]	146 (dec.)	32.57	2.41	642
			(32.67)	(2.41)	(625)
Br	Cl	161 (dec.)	34.21	2.51	605
			(33.82)	(2.50)	(604)
Br	H	193 (dec.)	37.91	3.19	549
		(192–193, dec.)[c]	(38.17)	(3.20)	(535)
Br	CH_3	190–191 (dec.)	40.77	3.68	549
		(201–202, dec)[c]	(40.54)	(3.76)	(563)
Br	CH_3O	164 (dec.)	39.15	3.62	576
			(38.36)	(3.56)	(595)

[a] Molecular weights were determined in chloroform using a Mechrolab Model 302 vapor pressure osmometer or a Hitachi–Perkin–Elmer vapor pressure osmometer Model 115. [b] % N: found, 4.17; calcd., 4.48. [c] Ref. 3.

TABLE 2

RELEVANT INFRARED FREQUENCIES OF $(p\text{-}YC_6H_4)_2SbX_2Acac$ IN CHLOROFORM SOLUTION AND IN NUJOL MULL (cm^{-1})

Compound		$\nu(C{=}O)$ *solution*	$\nu(C{=}C)$ *solution*	$\nu(Sb{-}O)$ *solution*
X	*Y*	*(solid)*	*(solid)*	*(solid)*
F	H	1562	1535	445
		(1550)	(1535)	(440)
Cl	H	1555	1529	423
		(1553)[a]	(1534)[b]	(426)
Cl	CH_3	1555	1529	421
		(1550)	(1531)	(428)
Br	NO_2	1530	1522	429
		(1538)	(1520)	(425)
Br	Cl	1555	1530	429
		(1548)	(1527)	(427)
Br	H	1555	1531	420
		(1550)[c]	(1532)	(422)[d]
Br	CH_3	1552	1522	429
		(1550)[e]	(1532)	(426)[f]
Br	CH_3O	1556	1525	429
		(1543)	(1527)	(429)

[a] Reported[2] 1563. [b] Reported[2] 1537. [c] Reported[3] 1550. [d] Reported[3] 423. [e] Reported[3] 1550. [f] Reported[3] 426.

Acetylacetone was added to arylstibonic acid, p-$YC_6H_4SbO(OH)_2$, dissolved in concentrated hydrobromic acid. Extraction of the product with dichloromethane gave white crystals of only the dibromodiaryl(acetylacetonato)antimony(V), which were recrystallized from dichloromethane/petroleum ether.

Preparation of $(C_6H_5)_2SbF_2Acac$

To a solution of $(C_6H_5)_2SbCl_2Acac$ (2.23 g, 0.005 mole) in acetone (50 ml) was added dropwise a solution of silver fluoride in a minimum amount of water until precipitation of white AgCl was complete. The filtrate was evaporated under reduced pressure. The white solid residue was recrystallized from dichloromethane/petroleum ether.

All the compounds prepared are listed in Table 1 together with some physical properties.

Infrared spectra

The IR spectra were obtained in chloroform solutions and in Nujol mulls in the 4000–400 cm^{-1} region using Hitachi EPI-2G, and 225 spectrophotometers equipped with gratings and in the region of 700–200 cm^{-1} using a Hitachi EPI-L spectrophotometer with gratings. The results are listed in Table 2.

PMR spectra

The PMR spectra were measured on a Japan Electron Optics JNM-3H-60 spectrometer at 60 MHz and 20°. The results are summarized in Table 3.

RESULTS AND DISCUSSION

The IR absorption bands (see Table 2) due to the acetylacetonate group of each of these diarylantimony compounds are very similar to those reported for chelated metal acetylacetonates[4]. In addition, the presence of a characteristic strong ν(Sb–O) band[2-4] at similar position for both the solid state and in solution (Table 2), and the monomeric nature of these compounds as shown in Table 1, suggest that the antimony atom is hexacoordinated in these compounds in both states.

Stereochemistry of the complexes

The room-temperature PMR spectra of benzene and chloroform solutions of $(p\text{-}CH_3C_6H_4)_2SbCl_2Acac$ are shown together in Fig. 1. The protons of the acetylacetonate group give the resonances a and b (around 5 ppm) and c and d (around 8.5 ppm) in benzene. The intensity ratios a/c and b/d are 1/6, respectively. The appearance of these two pairs of γ- and methyl proton resonances suggests the existence of two isomers. In accordance with this, the protons of the tolyl groups give two resonances at 8.16 (e_1) and 8.05 ppm (e_2). From the integration of the signals, resonances a, c and e_1 are assignable to one isomer, while b, d and e_2 are assigned to the other.

As shown below, three octahedral configurations can be considered for these compounds. However, since each of the two isomers gives a sharp one-line resonance due to the acetylacetonate γ- and methyl protons, (III) is ruled out from the possible configurations, for in (III) the two acetylacetonate methyl groups are non-equivalent.

TABLE 3

PROTON CHEMICAL SHIFTS, τ (ppm)[a], IN THE ACETYLACETONATE LIGAND OF $(p\text{-YC}_6\text{H}_4)_2\text{SbX}_2\text{Acac}$ IN VARIOUS SOLVENTS AT 20°

Solvent	Peaks	$(p\text{-YC}_6\text{H}_4)_2\text{SbX}_2\text{Acac}$, X and Y, respectively							
		Cl *H*							
		F *H*	*Cl* *H*	*Cl* CH_3	*Br* NO_2	*Br* *Cl*	*Br* *H*	*Br* CH_3	*Br* CH_3O
C_6H_6	CH_3	8.53 8.61	8.40 8.52	8.43 8.58	[b]	8.55 8.68	8.55 8.66	[b]	[b]
	γ-H	4.96 5.35	4.75 5.28	4.92 5.35	[b]	4.91 5.51	[b]	[b]	[b]
$CHCl_3$	CH_3	7.84 7.96	7.83 7.98	7.83 7.98	7.83 7.94	7.85 8.00	7.85 8.00	[b]	7.86 8.00
	γ-H	4.20 4.58	4.15 4.60	4.19 4.61	4.19 4.57	4.16 4.62	4.18 4.65	[b]	[b]
$CDCl_3$	CH_3	7.85 7.97	7.85 8.00	7.83 7.98	7.80 7.94	7.85 7.99	7.86 8.00	7.83 7.99	7.84 7.98
			(7.87 8.04)[c]	(7.99)[d]				(8.00)[d]	
	γ-H	4.21 4.58	4.21 4.65	4.16 4.58	4.17 4.57	4.15 4.62	4.19 4.64	4.11 4.62	[b]
			(4.21 4.65)[c]	(4.61)[d]				(4.62)[d]	
$CHCl_2CHCl_2$[e]	CH_3	7.84 7.96	7.83 7.98	7.82 7.95			7.85 7.99		
CH_2Cl_2[e]	CH_3	7.83 7.95	7.88 8.01	7.86 8.00	7.81 7.95	7.85 7.98	7.85 7.98	7.86 7.98	7.86 7.98
							(7.98)[d]	(7.99)[d]	

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[a] Internal reference TMS. [b] Reliable data were not obtained because of limited solubility. [c] Ref. 2. [d] Ref. 3. [e] τ(γ-H) values were not obtained due to the appearance of the strong resonance of the solvent.

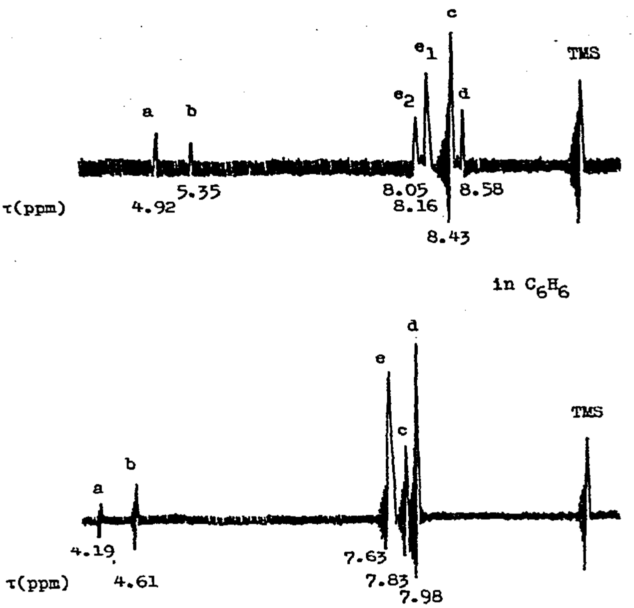
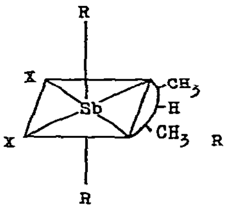
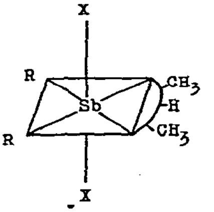


Fig. 1. Acetylacetonate PMR spectra at room temperature for $(p\text{-}CH_3C_6H_4)_2SbCl_2Acac$.

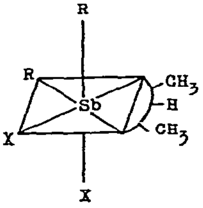
Accordingly, the presence in solution of the two isomers (I) and (II) is indicated, as previously assumed for $(C_6H_5)_2SbCl_2Acac^1$.



(I)

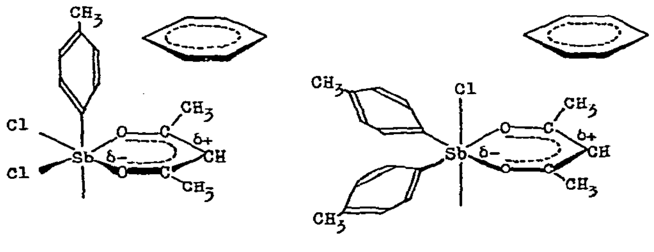


(II)



(III)

Although the methyl protons of the tolyl groups give two resonances in benzene, they show one peak (e) at a lower field (7.63 ppm) in chloroform. The fact that in benzene the resonance e_2 shows a smaller upfield shift than e_1 can be explained



(I) (II)

Fig. 2. Average geometry of the interaction between benzene and $(p\text{-}CH_3C_6H_4)_2SbCl_2Acac$.

by a contribution due to the clustering of the benzene molecules at the positive region of the solute dipole as shown in Fig. 2. This indicates that the resonances e_2, b and d arise from the *trans*-ditolyl isomer (I). This kind of benzene interaction has been postulated for some organometallic compounds[5].

Equilibrium between the trans-diaryl and cis-diaryl isomers

As shown in Fig. 3, a reversible change of the acetylacetonate methyl resonances* with temperature is observed in a 1,1,2,2-tetrachloroethane solution of $(C_6H_5)_2SbF_2Acac$**. These line-shape changes suggest that the two isomers (I) and (II) are isomerizing above ca. 100° at a rate which is rapid on the PMR time scale.

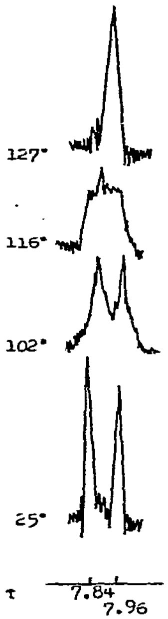


Fig. 3. Methyl region of the PMR spectra of $(C_6H_5)_2SbF_2Acac$ in 1,1,2,2-tetrachloroethane.

The observed intensity ratios of the higher field acetylacetonate methyl proton resonance to that at lower field, d/c, of $(p\text{-}YC_6H_4)_2SbX_2Acac$ in various solvents are listed in Table 4. It is apparent that the value d/c increases as the polarity of the solvent increases. There is an essentially linear relationship between the data obtained for $(C_6H_5)_2SbX_2Acac$ and the dielectric constants of the solvents. Since the *trans*-diphenyl isomer (I) is thought to be more polar than the *cis*-diphenyl isomer (II) because of the difference between the Sb–X and Sb–C_6H_5 bond moments***, the population of the isomer (I) will increase in the more polar solvent. Consequently, the higher field resonance d should be attributable to the *trans*-diphenyl isomer (I), in agree-

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* The resonances of the γ-proton are masked by the strong resonance of the solvent.

** $(C_6H_5)_2SbCl_2Acac$ in this solvent decomposes at higher temperatures.

*** Moore and Nelson[6] used 2.0 D for the Sn–Acac (pointing toward Sn) bond moment for calculating the dipole moments of hexacoordinate organotin chelate compounds.

ment with the above assignment of the PMR signals in the case of $(p\text{-}CH_3C_6H_4)_2$-$SbCl_2Acac$.

TABLE 4

THE OBSERVED INTENSITY RATIOS OF THE TWO METHYL PROTON RESONANCES, d/c, IN THE ACETYLACETONATE LIGAND FOR $(p\text{-}YC_6H_4)_2SbX_2Acac$ IN VARIOUS SOLVENTS AT 20°

Solvent	*$(p\text{-}YC_6H_4)_2SbX_2Acac$, X and Y, respectively*							
	F	*Cl*	*Cl*	*Br*	*Br*	*Br*	*Br*	*Br*
	H	*H*	*CH_3*	*NO_2*	*Cl*	*H*	*CH_3*	*CH_3O*
C_6H_6	0.36	1.5	0.75	[a]	2.5	1.5	[a]	[a]
$CHCl_3$	0.44	3.5	4.1	2.9	2.8	4.3	[a]	[a]
$CHCl_2CHCl_2$	0.89	4.9				6.6		
CH_2Cl_2	0.82	5.1	6.5	4.9	6.1	10.0	7.7	13.0

[a] Not determined because of limited solubility.

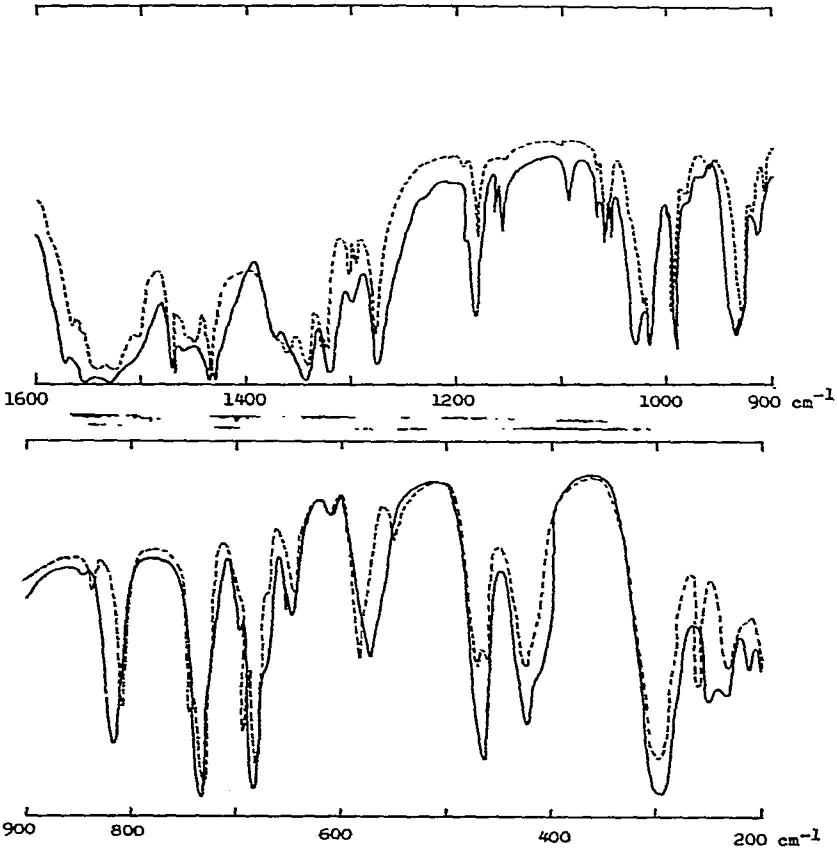

Fig. 4. Infrared spectra of $(C_6H_5)_2SbCl_2Acac$ in Nujol mull. ——, long prismatic crystal (A); ——, polyhedral crystal (B).

As shown in Table 4, a decrease in the electronegativity of the substituent Y of $(p\text{-}YC_6H_4)_2SbBr_2Acac$ causes an increase of the ratio d/c in dichloromethane and in chloroform*. This observation is consistent with the fact that the less electronegative substituent Y on the phenyl group will increase the difference in the polarities of the two isomers.

It is interesting to note that the sensitivities of the linear variation of d/c with respect to the dielectric constant of the solvents for $(C_6H_5)_2SbX_2Acac$ (X = Br, Cl, F) decrease in the order: Br > Cl $\gg$ F. This fact suggests that the covalency of the bond Sb–X increases as follows: Sb–Br < Sb–Cl $\ll$ Sb–F. This tendency is consistent with some results reported in the recent literatures[7].

The two different crystal forms (A) and (B) of $(C_6H_5)_2SbCl_2Acac$ give different crystal data[8] and different infrared spectra in the solid, as shown in Fig. 4. The X-ray structure determination of (A) by Kasai *et al.*[8] has demonstrated that the molecule is an octahedron with the two phenyl groups in *trans* positions.

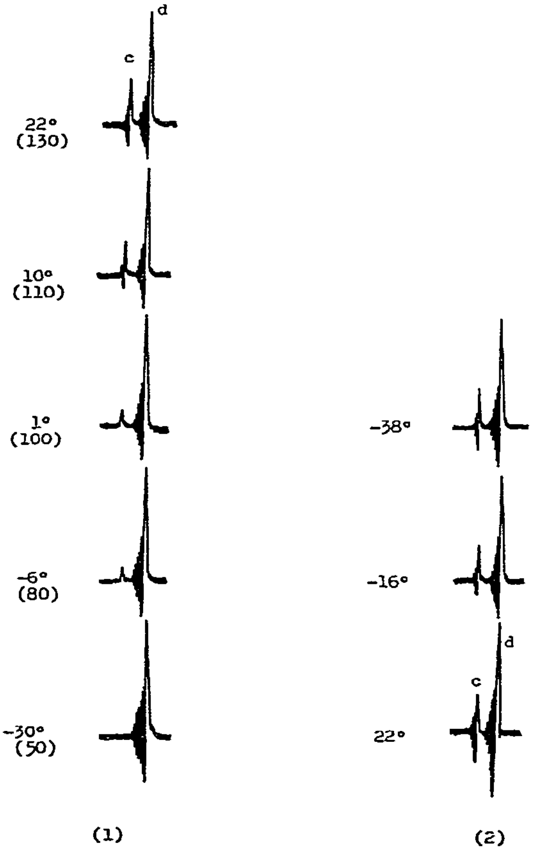

Fig. 5. Methyl PMR spectra of the crystal (A) of $(C_6H_5)_2SbCl_2Acac$ in dichloromethane at various temperatures. (1) The solution was freshly prepared below −30°. The figures in parentheses represent the times (min) from the preparation of the solution to the measurements. (2) The solution was kept at room temperature for 24 h. Ample time was allowed for each measurement.

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* In these solvents, with the exception of the difluoride analogue, the resonance d is predominant.

As shown in Fig. 5, the PMR spectrum at −30° of the solution of the isomer of known structure (A), freshly prepared below −30° in dichloromethane, reveals only one acetylacetonate methyl resonance that corresponds to the higher field resonance d of the room-temperature spectrum. With increasing temperature, however, the lower field resonance c appears and a decrease of the intensity ratio of the two resonances d/c is observed. On the other hand, the spectrum of the solution which has once been kept at room temperature gives the two methyl resonances even at −38°, and very small changes of d/c with temperature* are observed. These observations clearly prove the gradual isomerization of the isomer (I) to (II) at low temperature until the two isomers are in equilibrium in solution. These facts support the assignments of the methyl signals made above from the solvent and substituent effects.

The fact that the PMR spectral properties of (A) and (B) were found to be identical should exclude the expectation that (B) corresponds to the isomer (II)**.

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* Reproducible d/c values are observed. For example, 5.1, 5.7 and 6.5 at 20°, −10° and −26° in dichloromethane, and 1.5, 1.4 and 1.3 at 22°, 52° and 72° in benzene, respectively.

** While this paper was being prepared, we came across the information that (B) also has the *trans*-phenyl structure (I) that differs from (A) essentially only in the dihedral angle of the two phenyl ring planes[8,9].