

## Arsenic(III) and Antimony(V) Complexes of Trifluoro- $\beta$ -Diketones

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Arsenic (III) and antimony(V) complexes of trifluoro- $\beta$ -diketones of the type,  $\text{AsCl}_{3-n}(\text{CF}_3\text{COCHCOMe})_n$  and  $\text{SbCl}_4(\text{CF}_3\text{COCHOR})$  respectively (where R = Me, Et, *i*-Pr, *i*-Bu or *t*-Bu;  $n = 1-3$ ) have been synthesized and studied. These have been characterized by elemental analyses, molecular weight and molar conductance measurements, IR and NMR spectral analyses.

### INTRODUCTION

Stereochemistry and configurational rearrangements of metal complexes containing symmetrical ligands like  $\beta$ -diketones have been examined in detail<sup>1</sup>. Metal chelates derived from unsymmetrical ligands like trifluoro- $\beta$ -diketones have not been received much attention except for a few reports.<sup>2-4</sup> Metal complexes of unsymmetrical ligands also provide excellent systems to probe the origin of novel properties observed in the fluoro complexes.

### EXPERIMENTAL

Stringent precautions were taken to exclude moisture throughout the chemicals and apparatus and also during the spectral measurements. Solvent dried and purified by standard methods<sup>5</sup>. Arsenic trichloride (B.D.H.), antimony pentachloride (Aldrich) were distilled before use. Trifluoro- $\beta$ -diketones were prepared by literature procedure<sup>6</sup>. Sodium salt of trifluoroacetylacetone was prepared by the addition of benzene solution of ligand to sodium hydride (1:2 molar ratio) suspended in benzene cooled by ice bath maintained at 0°C under nitrogen atmosphere. After stirring for *ca.* 3hrs. the sodium salt is separated out by filtration, washed with benzene several times and dried at 0.1 mm Hg/50°C/10 hrs.

Arsenic and antimony were estimated by the literature procedure. Chlorine was estimated gravimetrically by standard method. Molecular weights of complexes were determined cryoscopically in benzene. Conductance was measured by conductivity bridge (Model No. L 370873, Cambridge Instruments, U.K.) at  $10^{-3}$  M concentration. Infrared spectra were recorded as nujol mulls using CsI plates in the range 4000-200  $\text{cm}^{-1}$  on a Perkin Elmer 621. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL FX 90 Q spectrometer in  $\text{CDCl}_3$  using TMS

as an internal standard.  $^{19}\text{F}$  NMR spectra were also recorded by the same instrument in  $\text{CDCl}_3$  using  $\text{CFCl}_3$  as an internal standard.

**General procedure for the preparation of arsenic (III) trifluoroacetylacetonates,  $\text{AsCl}_{3-n}(\text{CF}_3\text{COCHCOMe})_n$  (where  $n = 1 - 3$ ) (Table 1):** Arsenic trichloride dissolved in dichloromethane (ca 25 ml) was added dropwise to a suspension of stoichiometric (ca. 20 ml). The reaction mixture was refluxed for 8–10 hrs.). Separated sodium chloride was filtered and solvent was removed at reduced pressure. Finally the products dried at  $30^\circ\text{C} / 0.1 \text{ mm Hg}/4 \text{ hrs}$ .

**Preparation of antimony(V) trifluoro- $\beta$ -diketones,  $\text{SbCl}_4(\text{CF}_3\text{COCHCOR})$  (Table 1):** To stirred solution of antimony pentachloride in chloroform (ca. 20 ml) stoichiometric amount of trifluoro- $\beta$ -diketone solution (ca. 15 ml chloroform) was added dropwise. The reaction mixture was refluxed till the evolution of HCl was completely ceased (ca. 3 hrs.) The solvent was removed under reduced pressure and the liquid product was finally distilled at low pressure.

## RESULTS AND DISCUSSION

The lists of complexes with the results of their chemical analysis and other physical measurements are given in Table 1. Mono, bis and tris derivatives of arsenic (III) with trifluoroacetylacetonate have been prepared by the reaction of arsenic trichloride with sodium salts of trifluoroacetylacetonate in appropriate molar ratio in dichloromethane. Attempted preparation of Sb(III) complexes with trifluoro- $\beta$ -diketones have not been successful. In the preparation of Sb(III) derivatives, the trichloride was treated with trifluoroacetylacetonate alone or in the presence of triethylamine. The reaction always resulted into a mixture which could not be separated into their components. The reaction with sodium salt of trifluoroacetylacetonate also did not result into the desired product. Antimony pentachloride reacted readily with trifluoro- $\beta$ -diketones initially to give adducts of 1:1 composition, which readily lose hydrogen chloride even at  $-20^\circ\text{C}$  resulting into monosubstituted complex. Efforts to replace further chlorine by the ligand moiety have not been successful; the reaction with higher molar ratio of the diketones led to monosubstituted complex only.

All trifluoro- $\beta$ -diketonates of As(III) and Sb(V) are soluble in common non-polar solvents. They are non-electrolytes in nature and monomeric in benzene (cryoscopically).

IR bands of arsenic(III) trifluoroacetylacetonates and antimony(V) trifluoro- $\beta$ -diketonates are tabulated (Table 2). Absence of absorption due to  $\nu(\text{OH})$  vibration in the spectra of trifluoro- $\beta$ -diketonates suggests the deprotonation of the ligand. The bidentate mode of attachment of the ligand is suggested by the absence of bands above  $1615 \text{ cm}^{-1}$  due to free carbonyl vibration of the trifluoro- $\beta$ -diketone moiety. The observed absorption at  $1610\text{--}1580$  and  $1535\text{--}1500 \text{ cm}^{-1}$  are due to  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}=\text{C})$  vibration<sup>7</sup> respectively. The strong bands observed in the region  $1290\text{--}1130 \text{ cm}^{-1}$  are due to (C-F) stretching vibration<sup>8</sup>.

TABLE I  
PHYSICAL AND ANALYTICAL DATA OF ARSENIC (III) AND ANTIMONY (V) COMPLEXES OF TRIFLUORO- $\beta$ -DIKETONES

S.No.	Complex	Nature	M.Pt. (°C) or B.Pt. (°C/mm)	$\Lambda_m$	Analyses (%) Found (Calcd)				Mol. Wt. Found (Calcd.)
					M	Cl	C	H	
1.	AsCl <sub>2</sub> (CF <sub>3</sub> COCHCOMe)	Light Yellow solid	70	0.1	25.05 (25.03)	23.73 (23.75)	20.10 (20.03)	1.32 (1.33)	296 (299)
2.	AsCl(CF <sub>3</sub> COCHCOMe) <sub>2</sub>	Light Yellow solid	80	0.2	17.89 (17.99)	8.47 (8.52)	28.68 (28.81)	1.90 (1.92)	415 (416)
3.	As(CF <sub>3</sub> COCHCOMe) <sub>3</sub>	Yellow viscous	—	0.0	13.90 (14.03)	—	33.55 (33.71)	2.10 (2.24)	531 (534)
4.	SbCl <sub>4</sub> (CF <sub>3</sub> COCHCOMe)	Yellow liquid	110/0.2	0.2	29.15 (29.20)	33.98 (34.07)	14.35 (14.39)	0.90 (0.95)	414 (416)
5.	SbCl <sub>4</sub> (CF <sub>3</sub> COCHCOEt)	Yellow liquid	115/0.4	0.1	28.05 (28.25)	32.75 (32.96)	16.62 (16.71)	1.36 (1.39)	425 (430)
6.	SbCl <sub>4</sub> (CF <sub>3</sub> COCHCO <sup>t</sup> Pr)	Yellow liquid	120/0.6	0.1	27.28 (27.36)	31.90 (31.93)	18.84 (18.88)	1.56 (1.79)	440 (444)
7.	SbCl <sub>4</sub> (CF <sub>3</sub> COCHCO <sup>t</sup> Bu)	Yellow liquid	103/0.05	0.0	26.46 (26.53)	30.88 (30.95)	20.85 (20.92)	2.12 (2.18)	455 (458)
8.	SbCl <sub>4</sub> (CF <sub>3</sub> COCHCO <sup>t</sup> Bu)	Yellow liquid	100/0.07	0.0	26.44 (26.53)	30.70 (30.95)	20.90 (20.92)	2.15 (2.18)	452 (458)

m = Molar conductance (cm<sup>2</sup>ohm<sup>-1</sup>mole<sup>-1</sup>) of 10<sup>-3</sup> M in acetonitrile solution.  
M = As or Sb.

TABLE 2  
 IMPORTANT IR ASSIGNMENTS ( $\text{cm}^{-1}$ ) AND  $^1\text{H}$  NMR CHEMICAL SHIFTS ( $\delta$ ) OF ARSENIC (III) AND  
 ANTIMONY (V) COMPLEXES OF TRIFLUORO- $\beta$ -DIKETONES

Sl. No.	Complex	I.R. assignments			$^1\text{H}$ NMR Chemical Shifts				
		( $\text{C}^{\text{---}}\text{O}$ )	( $\text{C}^{\text{---}}\text{O}$ )	( $\text{M}^{\text{---}}\text{O}$ )	( $\text{M}-\text{Cl}$ )	$-\text{CH}_3$	$-\text{CH}_2$	$> \text{CH}$	
1.	$\text{AsCl}_2(\text{CF}_3\text{COCHCOMe})$	1600s	1522s	595s	317s	2.03	—	5.86	
2.	$\text{AsCl}(\text{CF}_3\text{COCHCOMe})_2$	1601s	1525s	582s	318s	2.03	—	5.87	
3.	$\text{As}(\text{CF}_3\text{COCHCOMe})_3$	1602s	1530s	580b	—	2.00	—	6.85d	
						2.27		7.00	
						2.97			
4.	$\text{SbCl}_4(\text{CF}_3\text{COCHCOMe})$	1600s	1522s	530s	380s	2.46	—	5.97	
					340s				
5.	$\text{SbCl}_4(\text{CF}_3\text{COCHCOEt})$	1602s	1523s	532s	361s	1.42t	2.91q	6.36	
					339s				
6.	$\text{SbCl}_4(\text{CF}_3\text{COCHCO}^i\text{Pr})$	1595s	1520s	525s	370s	—	—	—	
					318w				
7.	$\text{SbCl}_4(\text{CF}_3\text{COCHCO}^i\text{Bu})$	1598s	1520s	532s	375s	—	—	—	
					321w				
8.	$\text{SbCl}_4(\text{CF}_3\text{COCHCO}^i\text{Bu})$	1595s	1521s	530s	370s	1.42	—	6.48	
					320w				

s = strong, w = weak, b = broad, d = doublet, q = quartet, t = centre of triplet.

The far infrared region, new bands present in all the trifluoroacetylacetonates of As(III) are assignable to (As-O) and (As-Cl) stretching vibrations. These exhibit  $\nu(\text{As-O})$  absorption in the region 610–570  $\text{cm}^{-1}$ . In the chloro complexes the band due to  $\nu(\text{As-Cl})$  vibration is observed at  $317 \pm 2 \text{ cm}^{-1}$ . For monochloro complex  $\nu(\text{As-Cl})$  absorption is not of structural significance. The presence of only one band in dichloro one suggests linearity of Cl-As-Cl. This may have probably a trigonal bipyramidal geometry with a lone pair of electrons occupying an equatorial position.  $^1\text{H}$  and  $^{19}\text{F}$  NMR data of  $\text{AsCl}_2(\text{CF}_3\text{COCHCOMe})$  are not expected to be of any help in assigning the geometry.

The most plausible geometry for  $\text{AsCl}(\text{CF}_3\text{COCHCOMe})_2$ , appears to be octahedral in which the chlorine atom occupies one apical position while the lone pair may on the other apical site. The conclusion is born out of the PMR spectrum of  $\text{AsCl}(\text{CF}_3\text{COCHCOMe})_2$  which is found to be exhibit sharp resonances one due to methine and other due to methyl protons even upto  $-60^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$ .

Tris chelate of arsenic (III),  $\text{As}(\text{CF}_3\text{COCHCOMe})_3$  may exhibit two geometrical isomers i.e. *cis*(facial) and *trans*(meridional). In the *cis* isomer all the three methyl groups and methine protons are equivalent by the three fold rotation axis. In the *trans* isomer, which has no symmetry, the three methyl groups and methine protons are equivalent by the three fold rotation axis. In the *trans* isomer, which has no symmetry, the three methyl groups and the methine protons are non-equivalent. Therefore, in the absence of exchange we may assign *cis* configuration to compound which exhibits single resonance each for methyl and methine protons.

The  $^1\text{H}$  NMR spectrum of  $\text{As}(\text{CF}_3\text{COCHCOMe})_3$  at room temperature exhibits three resonances for methyl as well as methine protons. This led us to suggest tentatively a *trans* octahedral structure for the complex. However, the presence of lone pair of electrons on arsenic moiety also may distort the octahedral configuration.

Trifluoro- $\beta$ -diketonates of antimony(V) show a strong band in the infrared spectrum at around 550–520  $\text{cm}^{-1}$  due to  $\nu(\text{Sb-O})$  absorption<sup>9</sup>. (Sb-Cl) stretching absorption appears at around 385–315  $\text{cm}^{-1}$  in these complexes<sup>9</sup>. Proton NMR spectra exhibit only single resonance for each type of protons.  $^{19}\text{F}$  and  $^{13}\text{C}$  spectra are also very simple. In view of strong chelating nature of trifluoro- $\beta$ -diketonate moiety the product could be expected to antimony atom in hexacoordinate state<sup>10</sup> with octahedral configuration.

## REFERENCES

1. R.C. Mehrotra, R. Bohra and D.P. Gaut, Metal  $\beta$ -diketonates and Allied Derivatives, Academic Press (1978).
2. B.P. Bachlas and R.R. Jain, *J. Organomet. Chem.*, **82**, 359 (1974).
3. G.M. Bancroft and T.K. Sham, *Canad. J. Chem.*, **52**, 1361 (1974).

4. Ch. Sreelatha and V.D. Gupta, *Synth. React. Inorg. Met. Org. Chem.*, **29** (1988).
5. A.I. Vogel, *Text Book of Practical Organic Chemistry*, longmans, London, 4th Ed., p. 316 (1978).
6. J.C. Reid and M. Calvin, *J. Am. Chem. Soc.*, **72** 2948 (1950).
7. K.C. Joshi and V.N. Pathak, *Indian J. Chem.*, **10**, 485 (1972).
8. \_\_\_\_\_, *J. Inorg. Nucl. Chem.*, **35**, 3161 (1973).
9. S.T. Yuan and S.K. Madan, *Inorg. Chim. Acta*, **6**, 463 (1972).
10. Y. Kawasaki, T. Tanaka and R. Okawara, *Bull. Chem. Soc. Jpn.*, **40**, 1562 (1967).

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