Preparation and Properties of Trichloro(acetylacetonato)-phenylantimony(V)

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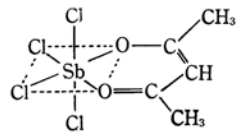
(Received November 15, 1966)

Recently preparations and properties of several penta-coordinated trialkylantimony(V) complexes[1] and hexa-coordinated tetrahalogenoantimony(V) complexes[2] were reported, but no for monoalkylantimony(V) complexes. In this note we will report a preparation and properties of trichloro(acetylacetonato)phenylantimony(V) and discuss a probable configuration on the basis of infrared and proton magnetic resonance spectra.

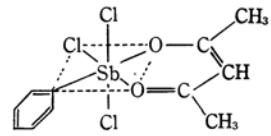
To a mixture of concentrated hydrochloric acid and acetylacetone, phenylstibonic acid was dissolved. Trichloro(acetylacetonato)phenylantimony(V) was extracted with methylene chloride. Transparent needle like crystals were obtained when some portion of organic solvent was evaporated at room temperature. 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%.

The infrared spectrum of trichloro(acetylacetonato)phenylantimony(V) was measured as mulls of Nujol and hexachlorobutadiene from 4000 cm^{-1} to 400 cm^{-1} using a Hitachi EPI-2G infrared spectrometer equipped with gratings. The general appearance of the infrared spectrum of trichloro(acetylacetonato)phenylantimony(V) is quite similar to that of tetrachloro(acetylacetonato)-antimony(V)[3] and usual metal acetylacetonates,[3,4] when vibrational bands due to the phenyl group are taken out of consideration. The C=O and C=C stretching vibrational bands have been observed at 1544 and 1521 cm^{-1}, respectively. The chelating configuration of this compound as is in tetrachloro(acetylacetonato)antimony(V) (1)[5] is, therefore, quite probable from these results.

While, the proton magnetic resonance spectrum of trichloro(acetylacetonato)phenylantimony(V) in chloroform shows a singlet at 4.15 ppm and a doublet (3.9 cps/60 Mc) at 7.75 ppm relative to internal tetramethylsilane. These signals correspond to the γ and the methyl protons, respectively. On the other hand, only two singlets have been observed at 3.94 and 7.57 ppm in the same solvent for tetrachloro(acetylacetonato)antimony-(V). From these experimental results one of the most probable configurations of trichloro(acetylacetonato)phenylantimony(V) may be a configuration (2).



(1)



(2)

Somewhat low C=O stretching frequency, high Sb-O stretching frequency (456 cm^{-1}) and small τ values of the γ and the methyl protons for trichloro-(acetylacetonato)phenylantimony(V) compared with those for dialkylbis(acetylacetonato)tin[3] and usual metal acetylacetonates[4] may be due to an inductive effect of chlorine attached to antimony as is in bis(acetylacetonato)tin dihalides. Another chracteristics in the infrared spectrum of trichloro-(acetylacetonato)phenylantimony(V) is that the C-H out of plane deformation vibration (817 cm^{-1}) is relatively higher than usual metal acetylacetonates.[4]

1) M. Shindo and R. Okawara, *J. Organometal. Chem.*, **5**, 541 (1966).
2) M. Webster, *Chem. Revs.*, **66**, 87 (1966).
3) Y. Kawasaki, T. Tanaka and R. Okawara, *Spectrochim. Acta*, **22**, 1571 (1966).
4) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, New York (1963).
5) P. J. Durrant and B. Durrant, "Introduction to Advanced Inorganic Chemistry," Longmans, London (1962).