\[ ^{121}\text{Sb} \text{ Mössbauer spectra and} \ ^{57}\text{Fe Mössbauer spectra of antimony-containing iron carbonyl complexes: } [\text{HSb}(\text{Fe(CO)}_4)_3]^{2-} \text{ and } [\text{Sb}(\text{Fe(CO)}_4)_4]^{3-} \]

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(Received April 8, 1998)

\[ ^{121}\text{Sb} \text{Mössbauer spectra of the title complexes, whose isomer shifts are intermediate between the organoantimony(III) and organoantimony(V) compounds, suggest that considerable electrons are donated from hydrido ligand and Fe(CO)}_4 \text{fragments to the antimony atom.} \]

Introduction

Recent studies on complexes having bonds between d-block and heavy p-block elements have led to a number of exciting molecules with novel molecular structure and bonding. Remarkable examples are \([\text{E=E=Et}_{5-(\text{CO})_3}]^{11} \text{ and electron deficient molecules such as} \text{(Et}_{5} \text{Si})_2 \text{HCSb}[\text{W(CO)}_5]^{12} \text{ and (Et}_{4} \text{N})_2[\text{E}(\text{Fe(CO)}_4)_4]^{13} \text{(E=Pb, Sn).} \]

Although the number of the antimony compounds having organometallic fragments are rather few, interesting compounds have been reported; \([\text{Sb}_{2} \text{CO}_{4}(\text{CO})^{10-}(\mu-\text{CO})]^{n-} \text{ (n=1,2)}^{14} \text{ [Fe}_{2}(\text{CO})_6(\mu_4-\text{Sb})]_2[\text{Fe}_2(\text{CO})_6]^{15} \text{, Ph}_2\text{Sb}_2[\text{W(CO)}_5]^{3} \text{ and [HSb}(\text{Fe(CO)}_4)_3]^{2-} \text{ and [Sb}(\text{Fe(CO)}_4)_4]^{3-}^{16}. \]

Quite recently we have carried out Mössbauer spectroscopic study on Rf\(_2\)Sb(FeC\(_p\)L\(_2\))(RfH=C\(_6\)H\(_5\).C(C\(_3\)F\(_8\))\(_2\)OH; L\(_2\)=(CO\(_2\), (CO)(PPh\(_3\)) and (dppe) in which the organoiron fragment coordinates to the equatorial position of trigonal bipyramidal structure (tbp) of antimony atom (Scheme 1). The \(^{121}\text{Sb} \text{Mössbauer spectra have indicated that the electron distribution around the antimony atom is the intermediate between that of the [Rf}_2\text{SbIn}]^{-1} \text{ and Rf}_2\text{SbVX (X=Tol, 12 C}_1, \text{ Br) and the distortion from the ideal tbp structure is increased compared to Rf}_2\text{SbX.} \]

This is interpreted as the organoiron fragment donates more electrons to the equatorial position and the increased electron density in equatorial position causes the distortion of the tbp structure. Thus we have been interested in antimony compounds having organometallic fragments.

In this paper, we describe the \(^{121}\text{Sb} \text{ and} \ ^{57}\text{Fe Mössbauer spectra for the iron carbonylates complexes of antimony(V), i.e.,} [\text{HSb}(\text{Fe(CO)}_4)_3]^{2-} \text{ and} [\text{Sb}(\text{Fe(CO)}_4)_4]^{3-} \text{ (Scheme 2). In both compounds, the antimony atom is tetrahedrally coordinated by Fe(CO)}_4 \text{fragments in the trigonal bipyramidal arrangement and hydrido ligands. In (Et}_4\text{N})_2[\text{Sb}(\text{Fe(CO)}_4)_4]^{3-} \text{ the average Fe–Sb–Fe angle (108.0°) is quite close to the value for ideal tetrahedral structure and the average Sb–Fe distance is 2.666 Å.}^{10} \text{ On the other hand, in (PPh}_3\text{)}_2[\text{HSb}(\text{Fe(CO)}_4)_3]^{9} \text{ the average Fe–Sb–Fe angle of 115.6° is larger and the average Sb–Fe distance of 2.596 Å is shorter compared to the [Sb}(\text{Fe(CO)}_4)_4]^{3-} \text{ ion.} \]

Experimental

Samples

The \(^{121}\text{Sb} \text{ Mössbauer spectra were measured with an Austin Science S-600 spectrometer using a Cal}_2\text{InSnO}_3 \text{ source (16 MBq) and a germanium detector. Both samples are containing 15 mg Sb cm}^{-2} \text{ and the source were kept at 20 K in a cryostat equipped with a closed-cycle refrigerator. The Doppler velocity was measured with an Austin Science LA-9 laser interferometer and calibrated by measuring a} ^{57}\text{Fe Mössbauer spectrum of α-iron foil at 20 K. The values of isomer shift are referred to that of InSb at 20 K.} \]

\(^{57}\text{Fe Mössbauer spectra}

The \(^{57}\text{Fe Mössbauer spectra were obtained using a Mössbauer driving system from Wissenschaftliche Elektronik GmbH, consisting of an MDU-1200 driving unit, a DFG-1200 digital function generator and an MVT-1000 velocity transducer, incorporating with a model 5500 multichannel analyser from EG&G ORTEC. The samples containing 6 mg Fe cm}^{-2} \text{ were kept at 80 K in an Oxford Instruments CF1104 continuous gas flow cryostat and} ^{57}\text{Co(Rh) source (1.5 GBq) at room temperature. The spectra were computer fitted to Lorentzian lines on a personal computer and the values of isomer shift are given relative to α-iron foil at room temperature.} \]
Results and discussion

Figure 1 shows the $^{121}$Sb Mössbauer spectra for $(\text{Et}_4\text{N})_2[\text{HSb}\{\text{Fe(CO)}_4\}_3]$ and $(\text{Et}_4\text{N})_3[\text{Sb}\{\text{Fe(CO)}_4\}_4]$. Although we have paid much attention to prevent from decomposition, a small amount of impurities were observed for $(\text{Et}_4\text{N})_3[\text{Sb}\{\text{Fe(CO)}_4\}_4]$. The Mössbauer parameters are summarized in Table 1. The value of $e^2qQ$ for $[\text{Sb}\{\text{Fe(CO)}_4\}_4]^{3-}$ is experimentally 0 mm s$^{-1}$. This suggests that the electron distribution around the Sb atom is spherical as is expected from its molecular structure, and also indicates that the lattice contribution to the electric field gradient is negligible though the molecule has a large negative charge. The quite small value of $e^2qQ$ for $[\text{HSb}\{\text{Fe(CO)}_4\}_3]^{2-}$ shows also that the electron distribution around the Sb atom is almost spherical, suggesting the Fe(CO)$_4$ fragment donates as much electrons as H$^-$ which is known as an electron donating ligand.

Although $[\text{HSb}\{\text{Fe(CO)}_4\}_3]^{2-}$ and $[\text{Sb}\{\text{Fe(CO)}_4\}_4]^{3-}$ are formally regard as the Fe(CO)$_4^{2-}$ fragments coordinated to Sb(V) atom, the values of isomer shift are interestingly intermediate between that of typical organoaantimony(III) and organoaantimony(V) compounds.