fitted with β^2 values as large as 0.85. The results presented in Table V represent reasonably well the range of possible Δ and ϵ but give a misleading view of the magnitude of β^2.

The results obtained for both FeL_4X_2 and $Fe(phen)_2X_2$ reflect a substantial degree of ligand-t_{2g} metal orbital interaction. Most of the fittings require $|\lambda| \leqslant 80$ cm^{-1} and $\beta^2 \leqslant 0.8$. A consistent interpretation of the results requires that both of these parameters take on lower values. The theory employed should be discussed in terms of this significant ligand-metal interaction. The model assumes that "covalency" effects on the t_{2g} metal orbitals can be treated simply as an expansion of the free-ion orbitals. In other words "covalency" effects are treated simply as a reduction in the parameters λ and β^2, α^2. The angular part of the wave function is assumed to be the same as the free-ion wave function. In view of the fact that the quadrupole splitting is sensitive only to that part of the wave function close to the nucleus (the quadrupolar interaction is proportional to $\langle r^{-3}\rangle$) this would appear to be a reasonably good approximation. However, the results presented here must be considered in view of this assumption.

Magnetic Susceptibility. The average magnetic susceptibilities of these compounds have been investigated over the range 20-300° by Long and Baker.[26] The data were fitted in terms of a model which assumed axial symmetry. The fitting parameters obtained for $Fe(isoq)_4I_2$, $Fe(isoq)_4Br_2$, $Fe(isoq)_4Cl_2$, $Fe(py)_4I_2$, and $Fe(py)_4Br_2$ are in qualitative agreement with those presented here with $\Delta(Cl^-) > \Delta(Br^-) > \Delta(I^-)$. Quantitative agreement is found only for $Fe(isoq)_4Cl_2$.

An attempt was made to find better agreement by introducing the rhombic distortion parameter, ϵ, in the analysis of the susceptibility data. The magnetic susceptibility was calculated in terms of Δ, ϵ, and the "orbital reduction factor," k, by employing methods which have been described previously.[27] Introduction of this parameter was found not to improve agreement. Employing the parameters given in Tables II and III and a consistent spin-orbit coupling constant, it was found possible to reproduce qualitatively the data of $Fe(isoq)_4I_2$, $Fe(isoq)_4Br_2$, and $Fe(isoq)_4Cl_2$. This procedure gives the higher magnitudes and greater temperature dependence expected for μ_{eff} when the trend from the chloride to the iodide is followed. Exact agreement is not found, however. In view of the problems associated with the analysis of the magnetic susceptibility data which were discussed by Long and Baker,[26] it may be that exact agreement is not expected.

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Registry No. $Fe(isoq)_4I_2$, 15245-93-9; $Fe(py)_4Br_2$, 34406-12-7; $Fe(isoq)_4Br_2$, 15245-92-8; $Fe(isoq)_4Cl_2$, 15245-91-7; $Fe(py)_4(N_3)_2$, 49567-50-2; $Fe(py)_4(OCN)_2$, 49567-51-3; $Fe(1,10\text{-phen})_2(SCN)_2$, 15131-05-2; $Fe(1,10\text{-phen})_2Cl_2$, 15553-84-1; $Fe(1,10\text{-phen})_2Br_2$, 15553-83-0; $Fe(py)_4(SCN)_2$, 18251-76-8; $Fe(py)_4Cl_2$, 15245-99-5.

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Iron-57 and Antimony-121 Mossbauer Spectroscopic Studies of $[X_nSb(Fe(CO)_2(\pi\text{-}C_5H_5))_{4-n}]^+$ Species. Nature of the Iron-Antimony Bond

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A number of cations containing Fe–Sb σ bonds of the type $[X_nSb(Fe(CO)_2(\pi\text{-}C_5H_5))_{4-n}]^+$ ($X = Cl, Br, I, CF_3, C_6H_5, n\text{-}C_4H_9$; $n = 1$–3, but not all combinations), some of which have been prepared for the first time, have been studied *via* ^{57}Fe and ^{121}Sb Mossbauer spectra. These compounds are nominally isoelectronic with the extensively investigated neutral tin derivatives $X_nSn(Fe(CO)_2(\pi\text{-}C_5H_5))_{4-n}$. The ^{121}Sb isomer shifts fall between the ranges of values typically associated with Sb(III) and Sb(V); hence assignment of a formal oxidation state for antimony in these compounds has little justification. For $[R_3SbFe(CO)_2(\pi\text{-}C_5H_5)]^+$ ($R = n\text{-}C_4H_9, C_6H_5$) the ^{121}Sb quadrupole coupling constant $(e^2qQ)_{Sb}$ is positive, whereas $(e^2qQ)_{Sn}$ is negative in $(n\text{-}C_4H_9)_3SnFe(CO)_2(\pi\text{-}C_5H_5)$. Isomer shift data for ^{57}Fe, ^{119}Sn, and ^{121}Sb suggest that Fe–Sb π bonding is of more importance than Fe–Sn π bonding. The fact that Sn and Sb are essentially isoelectronic and that ^{57}Fe Mossbauer parameters are very similar in corresponding tin and antimony derivatives indicates that the positive charge in the latter complexes is not extensively delocalized onto the ligands.

Introduction

The nature of heteronuclear metal–metal bonds has been the subject of much recent discussion, particularly in compounds where a group IV element is bonded to a transition metal such as manganese, iron, or cobalt. Compounds containing Fe–Sn bonds have been rather extensively studied by Mossbauer spectroscopy,[1-8] where use of both ^{57}Fe and ^{119}Sn resonances has led to valuable insights concerning the nature

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of the Fe-Sn σ bond and the question of possible d-d π bonding. From data on a number of derivatives of the types $CpFe(CO)L \cdot SnR_3$ and $CpFeL_2 \cdot SnR_3$ ($Cp = \pi\text{-}C_5H_5$; R = Cl, CH_3, C_6H_5; L = tertiary phosphine, arsine, stibine), we have suggested[1] that the Fe-Sn bond is essentially pure σ in character. Greenwood,[5] Donaldson,[6] and their respective coworkers have reported signs of the quadrupole coupling constants e^2qQ for both iron and tin in $CpFe(CO)_2SnCl_3$. The positive e^2qQ for tin indicates an excess of p_z electron density on the tin atom, from which Donaldson[6] has concluded that the Fe-Sn bond must have predominantly σ_s character. Bryan[9] has arrived at similar conclusions on the basis of X-ray crystallographic studies.

To date the only Mossbauer study of the Fe-Sb bond using both ^{57}Fe and ^{121}Sb resonances is of the two compounds $Ph_3SbFe(CO)_4$ and $(Ph_3Sb)_2Fe(CO)_3$ ($Ph = C_6H_5$), in which the group V element acts as a two-electron donor.[10] The ^{121}Sb data were interpreted[10] as indicating very little, if any, π back-donation from filled 3d orbitals on iron to vacant 5d orbitals on antimony.

We have recently reported the preparation of a number of group V derivatives of transition metal carbonyls in which the group V element acts as a one-electron donor,[11] and it seemed attractive to investigate the Mossbauer spectra of a fairly extensive series of such compounds containing Fe-Sb σ bonds. Since isoelectronic tin and antimony derivatives having identical ligands are expected to show essentially linear correlations for both isomer shifts and quadrupole splittings, we have chosen for the present study cations of the type $[X_nSb(Fe(CO)_2Cp)_{4-n}]^+$ (X = Cl, Br, I, CF_3, C_6H_5, $n\text{-}C_4H_9$; n = 1-3, but not all combinations). The corresponding neutral tin species have been widely studied by Mossbauer spectroscopy,[1-6,12,13] and X-ray structural data are available in many cases as well.[9,14-16] Furthermore, although there is a paucity of X-ray data for compounds with Fe-Sb bonds, the structures of two of the present derivatives, *viz.*, $[Cl_2Sb(Fe(CO)_2Cp)_2]_2[Sb_4Cl_{14}]$[17] and $[ClSb(Fe(CO)_2Cp)_3]_2[FeCl_4] \cdot CH_2Cl_2$,[18] have been published. Both compounds consist of discrete cations in which the antimony atom is in a very distorted tetrahedral environment, associated with large, replaceable anions ($Sb_4Cl_{14}^{2-}$ and $FeCl_4^{2-}$, respectively). The corresponding tin compounds consist of four-coordinate neutral species.[14-16]

Experimental Section

The ^{121}Sb Mossbauer spectra were determined with a 1-mCi $Ba^{121}SnO_3$ source (New England Nuclear) at liquid nitrogen temperature and the absorber at 8.5-9.0°K in a Janis Model 6DT cryostat. Absorbers containing 8-10 mg/cm^2 of Sb were used without dilution in a copper cell with Mylar windows. The spectrometer consisted of an Austin Science Associates S-3 drive and linear motor, a $Xe\text{-}CO_2$ proportional counter and a Nuclear-Chicago Model 24-2 multichannel analyzer operating in the time mode. The single-channel analyzer was set on the escape peak of the 37-keV ^{121}Sb γ ray. The velocity scale was calibrated using a metallic iron foil absorber and a 10-mCi ^{57}Co(Cu) source. The data points were computer fitted either to a single lorentzian or to an eight-line quadrupole-split pattern using the appropriate Clebsch-Gordan coefficients for the intensities. The value $R = 1.34$[19] was used throughout. In the final data reduction step, after parameters were derived for each half of the mirror-image spectra, the spectra were folded, using the velocity determined from the best least-squares fit to the iron foil calibration. This generally resulted in an increase in line width of 0.05-0.10 mm sec^{-1}. For spectra with $\eta \neq 0$ appropriate combinations of Clebsch-Gordon coefficients were used to calculate the intensities for the 12 possible transitions, and the integrals were performed assuming randomly oriented polycrystalline samples. The ^{57}Fe Mossbauer spectra were recorded with the ^{57}Co(Cu) source at room temperature and the absorbers at 80°K, using a spectrometer previously described.[20a] One determination of the sign of the electric field gradient at iron was made employing magnetic perturbation techniques as reported elsewhere.[20b] Infrared spectra (CH_2Cl_2 solution) were obtained on a Perkin-Elmer 457 spectrophotometer calibrated with H_2O vapor and DCl gas.

(π-Cyclopentadienyl)dicarbonyl(triphenylstibine)iron hexafluorophosphate was prepared by the method of Davison, *et al.*[21] Except for the new compounds described below, the others used in this study were prepared as reported previously.[11] Microanalyses were performed by Mr. Peter Borda of this department and Drs. F. and E. Pascher, Mikroanalytisches Laboratorium, Bonn, West Germany.

Diphenylbis((cyclopentadienyl)dicarbonyliron)antimony Hexafluorophosphate, $[(C_6H_5)_2Sb(Fe(CO)_2(\pi\text{-}C_5H_5))_2][PF_6]$. A THF solution of 6.8 mmol of $NaFe(CO)_2(\pi\text{-}C_5H_5)$ was added to 1.2 g (3.14 mmol) of $(C_6H_5)_2SbCl_3$ in THF cooled to −80°. After the addition to this mixture of 1.0 g of NH_4PF_6 in acetone, the stirred solution was allowed to warm to room temperature. After 15 min the filtered solution was evaporated to dryness *in vacuo* and the solid residue extracted with CH_2Cl_2. This extract was reduced to a small volume and n-pentane was added slowly; the orange crystals so produced were recrystallized twice from CH_2Cl_2 by pentane addition; yield 0.5 g. *Anal.* Calcd for $[(C_6H_5)_2Sb(Fe(CO)_2Cp)_2][PF_6]$: C, 40.2; H, 2.6; N, 0.0; Cl, 0.0. Found: C, 39.9; H, 2.8; N, 0.0; Cl, 0.0. Conductivity in acetone is 145 cm^2 Ω^{-1} mol^{-1}. ν(CO), cm^{-1}: 2045 m, 2027 s, 1994 s, 1985 s.

Phenyltris((cyclopentadienyl)dicarbonyliron)antimony Hexafluorophosphate, $[C_6H_5Sb(Fe(CO)_2(\pi\text{-}C_5H_5))_3][PF_6]$. A THF solution of 8.5 mmol of $NaFe(CO)_2(\pi\text{-}C_5H_5)$ was added to 1.3 g (2.85 mmol) of $[C_5H_5NH^+][C_6H_5SbCl_5^-]$ in the same solvent at −80°. The red solution was treated with an acetone solution of 0.5 g of NH_4PF_6 after warming to room temperature. The solution was filtered and evaporated to dryness *in vacuo*. The residue was extracted with CH_2Cl_2; the extract was reduced in volume and then treated with n-pentane, giving dark oily crystals. These were recrystallized once from CH_2Cl_2-n-pentane and twice from acetone by addition of ether, giving 0.2 g of small red crystals. *Anal.* Calcd for $[C_6H_5Sb(Fe(CO)_2Cp)_3][PF_6]$: C, 37.1; H, 2.3; N, 0.0; Cl, 0.0. Found: C, 36.7; H, 2.2; N, 0.0; Cl, 0.0. Conductivity in acetone is 142 cm^2 Ω^{-1} mol^{-1}. ν(CO), cm^{-1}: 2037 w, 2019 s, 1981 s, br.

Tri-*n*-butyl((cyclopentadienyl)dicarbonyliron)antimony Hexafluorophosphate, $[(C_4H_9)_3Sb(Fe(CO)_2(\pi\text{-}C_5H_5))][PF_6]$. A mixture of 1.15 g (3.93 mmol) of $(C_4H_9)_3Sb$ and 0.65 g (3.07 mmol) of $ClFe(CO)_2(\pi\text{-}C_5H_5)$ in 20 ml of toluene was warmed to 50° for 5 min, cooled, and treated with n-pentane to precipitate yellow crystals (1.0 g). These were dissolved in CH_2Cl_2 and the solution was treated with 0.4 g of NH_4PF_6 in acetone. Addition of ether to the filtered solution afforded an oil which set to crystals on standing. These were purified by recrystallization from CH_2Cl_2-n-pentane, followed by recrystallization from 1 ml of acetone by addition of 50 ml of ether, evaporation to 10 ml, and further ether addition; yield 0.3 g. *Anal.* Calcd for $[(C_4H_9)_3SbFe(CO)_2Cp][PF_6]$: C, 37.2; H, 5.2; N, 0.0; Cl, 0.0. Found: C, 36.8; H, 5.0; N, 0.0; Cl, 0.0.

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$[ISb(Fe(CO)_2(\pi\text{-}C_5H_5))_3][I_3]$. Reaction of NaI (1.0 g) with 1.1 g of $[BrSb(Fe(CO)_2(\pi\text{-}C_5H_5))_3]_2[FeBr_4]$[11] in acetone gave a deep purple-red solution. This was centrifuged, evaporated to dryness, and extracted with 40 ml of CH_2Cl_2. The extract was filtered and treated slowly with 50 ml of *n*-pentane giving an oil which set to crystals. These were recrystallized from CH_2Cl_2 by pentane addition giving 0.4 g of deep red crystals of product. *Anal.* Calcd for $[ISb(Fe(CO)_2Cp)_3][I_3]$: C, 21.8; H, 1.3; I, 43.7. Found: C, 21.3; H, 1.6; I, 43.2. ν(CO), cm^{-1}: 2042 m, 2027 s, 2015 sh, 1991 s.

Iodotris((cyclopentadienyl)dicarbonyliron)antimony Hexafluorophosphate, $[ISb(Fe(CO)_2(\pi\text{-}C_5H_5))_3][PF_6]$. A solution of 0.4 g of the above I_3^- salt in 2.5 ml of CH_2Cl_2 was treated with 0.4 g of $NaPF_6$ in 5 ml of methanol. After 0.5 hr at room temperature 3 ml of pentane was added and the solution was filtered. A further 5 ml of pentane was added to the filtrate and the solution was evaporated to about 10 ml, affording 0.3 g of brown crystals of product, which were recrystallized from CH_2Cl_2-*n*-pentane. *Anal.* Calcd for $[ISb(Fe(CO)_2Cp)_3][PF_6]$: C, 27.3; H, 1.6; I, 13.7. Found: C, 27.2; H, 1.8; I, 13.5.

Results and Discussion

Syntheses. In order to complete the series $[Ph_nSb(Fe(CO)_2Cp)_{4-n}][PF_6]$ ($n = 1$-3) and $[XSb(Fe(CO)_2Cp)_3][PF_6]$, the new compounds $[Ph_2Sb(Fe(CO)_2Cp)_2Cp)_2][PF_6]$, $[PhSb(Fe(CO)_2Cp)_3][PF_6]$, and $[ISb(Fe(CO)_2Cp)_3][PF_6]$ as well as $[Bu_3SbFe(CO)_2Cp][PF_6]$ were synthesized. The two phenyl derivatives were prepared by treatment of Ph_2SbCl_3 and $[PhSbCl_5][pyH]$ with 2 and 3 equiv of $NaFe(CO)_2Cp$, respectively, followed by isolation of the cations as PF_6^- salts.

$$Ph_2SbCl_3 + 2NaFe(CO)_2Cp \rightarrow [Ph_2Sb(Fe(CO)_2Cp)_2]^+ + Cl^- + 2NaCl \xrightarrow{NH_4PF_6} [Ph_2Sb(Fe(CO)_2Cp)_2][PF_6]$$

$$[PhSbCl_5][pyH] + 3NaFe(CO)_2Cp \rightarrow [PhSb(Fe(CO)_2Cp)_3]^+ + pyHCl + 3NaCl + Cl^- \xrightarrow{NH_4PF_6} [PhSb(Fe(CO)_2Cp)_3][PF_6]$$

The iodo derivative was obtained by reaction of the previously prepared $[BrSb(Fe(CO)_2Cp)_3]_2[FeBr_4]$[11] with KI in acetone solution. The elemental analysis of the product of this reaction was consistent with $[ISb(Fe(CO)_3Cp)_3][I_3]$, while the identity of the cation was confirmed by the isolation of the PF_6^- salt.

$$[BrSb(Fe(CO)_2Cp)_3]^+ + I^- \rightarrow [ISb(Fe(CO)_2Cp)_3][I_3] \xrightarrow{NH_4PF_6} [ISb(Fe(CO)_2Cp)_3][PF_6]$$

Finally, $[Bu_3SbFe(CO)_2Cp][PF_6]$ was prepared by the replacement of Cl^- from $ClFe(CO)_2Cp$ with Bu_3Sb, followed by treatment with NH_4PF_6.

$$ClFe(CO)_2Cp + Bu_3Sb \rightarrow [Bu_3SbFe(CO)_2Cp]Cl \xrightarrow{NH_4PF_6} [Bu_3SbFe(CO)_2Cp][PF_6]$$

^{121}Sb Mossbauer Parameters. The ^{121}Sb Mossbauer spectra of compounds containing tetracoordinate antimony species such as those reported here are expected to follow certain trends, which may be illustrated by a preliminary consideration of the data given in Table I. First, since these derivatives should be isoelectronic with the corresponding neutral tin species, an additive model[22,23] for the quadrupole coupling constants e^2qQ should be applicable,[24] and there should be a more or less direct correlation with ^{119}Sn quadrupole splittings (QS). Thus, on the basis of ^{119}Sn data $|e^2qQ|$ in the series $[XSb(Fe(CO)_2Cp)_3]^+$ is expected to increase with changes in X in the order Bu, Ph < I < Br, Cl (Bu = *n*-C_4H_9; Ph = C_6H_5), as observed. Second, in compounds containing cations of the type $[X_2Sb(Fe(CO)_2Cp)_2]^+$ if the X-Sb-X angle is considerably less than 109.5° (as indeed it is in $[Cl_2Sb(Fe(CO)_2Cp)_2]_2[Sb_4Cl_{14}]$[17]), the asymmetry parameter η should be less than unity but considerably greater than zero, and e^2qQ should be opposite in sign but of approximately the same magnitude as in the corresponding $[XSb(Fe(CO)_2Cp)_3]^+$ derivatives.[23,25] Table I shows that this is in fact the case (see also Figure 1). It should be noted that the η values observed (0.44, 0.46) for the $[Cl_2Sb(Fe(CO)_2Cp)_2]^+$ species are slightly smaller than that reported (0.65)[25] for the corresponding tin compound $Cl_2Sn(Fe(CO)_2Cp)_2$. This is consistent with the fact that Fe-Sb-Fe > Fe-Sn-Fe.[14,17] Third, the e^2qQ value for $[Sb(Co(CO)_3PPh_3)_4]^+$ is zero within experimental error, as anticipated for a tetrahedral antimony derivative with four identical ligands.

A closer look at the systematics of the ^{121}Sb quadrupole coupling constants is of interest. There are two major contributions to the electric field gradient (efg) at antimony.[26] One is the effect due to charges on the ligands and to external charges which together form the lattice contribution to the efg, q_{LAT}. The second is the valence contribution q_{VAL} due to an asymmetric distribution of electrons in the bonding orbitals. In the compound $[Sb(Co(CO)_3PPh_3)_4]\cdot[PF_6]$ one expects that $q_{VAL} \simeq 0$ so that only q_{LAT} should contribute to the efg. Since $e^2qQ = 0$, with a line width of 2.9 mm sec^{-1}, an upper limit of a few millimeters per second may be set for any contribution from q_{LAT}. Similar conclusions may be drawn from data for $[Ph_4Sb][ClO_4]$, where again $e^2qQ = 0$ with a line width of 2.6 mm sec^{-1}.[19] It is thus clear that in the present derivatives q_{VAL} makes the dominant contribution to the efg at the antimony nucleus.

Perhaps the most interesting ^{121}Sb e^2qQ results reported here are those for the organoantimony derivatives. For both $[R_3SbFe(CO)_2Cp]^+$ complexes (R = Bu, Ph), e^2qQ is apparently positive (see Figure 2). In contrast, the sign of $e^2qQ(^{119}Sn)$ in $Bu_3SnFe(CO)_2Cp$ is reported[5] to be negative, and a negative $e^2qQ(^{119}Sn)$ has been predicted[8,12] for $Ph_3SnFe(CO)_2Cp$ also. Since the sign of the quadrupole moment Q for ^{119}Sn is the same as the sign of Q_{gr} (and Q_{ex}) for ^{121}Sb, these results indicate that the principal component of the efg tensor, V_{zz}, is opposite in sign in the antimony and tin compounds. For the antimony derivatives reported here it is apparent from trends in the isomer shift (*vide infra*) that the electron density in the region of the bonds decreases in the order Sb-M ⩾ Sb-R > Sb-X, and the same ordering is deduced from data on corresponding tin compounds.[5] On this basis alone one would expect e^2qQ to be positive for both antimony and tin in the triorgano derivatives. However, because of the fairly small difference in electron density at Sb between Sb-M and Sb-R bond directions (and at Sn between Sn-M and Sn-R bond directions), relatively minor changes in p-electron donor and acceptor properties between R and M groups *vis a vis* tin and antimony could presumably account for the observed sign reversal.

It is interesting to note that in the compounds $Ph_3SbFe(CO)_4$ and $(Ph_3Sb)_2Fe(CO)_3$, $e^2qQ(^{121}Sb)$ is also positive.[10] In fact, the values of ^{121}Sb e^2qQ and isomer shift δ for these compounds ($e^2qQ = +9.0$, $+10.9$ mm sec^{-1}; $\delta = -6.62$, -6.65 mm sec^{-1}, respectively) are nearly identical with those of $[Ph_3SbFe(CO)_2Cp]^+$. Thus, while it is usual to consider that in one case antimony is acting as a two-electron donor

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Table I. ^{121}Sb Mossbauer Parameters[a]

Compd	δ,[b] mm sec^{-1}	e^2qQ, mm sec^{-1}	η	Γ, mm sec^{-1}	χ^2 [c]
$[Cl_2Sb(Fe(CO)_2Cp)_2][PF_6]$	−9.3 ± 0.2	+29.0 ± 1.0	0.46 ± 0.05	2.8 ± 0.1	206
	(−9.4 ± 0.1)	(+31.4 ± 1.1)	(0.0)	(2.7 ± 0.1)	(263)
$[Cl_2Sb(Fe(CO)_2Cp)_2][Cr(SCN)_4(NH_3)_2]$	−9.1 ± 0.2	+28.7 ± 0.5	0.44 ± 0.04	2.9 ± 0.1	183
	(−9.2 ± 0.2)	(+30.2 ± 0.6)	(0.0)	(2.9 ± 0.1)	(213)
$[Br_2Sb(Fe(CO)_2Cp)_2][PF_6]$	−9.6 ± 0.3	26.6 ± 0.4	0.44 ± 0.06	3.0 ± 0.1	203
	(−9.7 ± 0.3)	(+28.6 ± 0.4)	(0.0)	(3.0 ± 0.1)	(334)
$[(CF_3)_2Sb(Fe(CO)_2Cp)_2][Cr(SCN)_4(NH_3)_2]$	−8.3 ± 0.2	+18.3 ± 0.7	0.68 ± 0.08	2.4 ± 0.1	187
	(−8.4 ± 0.2)	(+20.1 ± 0.9)	(0.0)	(3.4 ± 0.2)	(265)
$[ClSb(Fe(CO)_2Cp)_3][FeCl_4]$	−8.8 ± 0.1	−23.9 ± 1.7	0.0	3.1 ± 0.1	198
$[BrSb(Fe(CO)_2Cp)_3][PF_6]$	−8.6 ± 0.3	−23.8 ± 0.7	0.0	3.1 ± 0.1	225
$[ISb(Fe(CO)_2Cp)_3][I_3]$	−8.8 ± 0.3	−20.5 ± 1.0	0.0	3.1 ± 0.1	191
$[ISb(Fe(CO)_2Cp)_3][PF_6]$	−8.8 ± 0.2	−22.4 ± 0.2	0.0	2.9 ± 0.1	205
$[PhSb(Fe(CO)_2Cp)_3][PF_6]$	−7.9 ± 0.1	Unresolved	0.0	3.2 ± 0.1	205
$[Ph_2Sb(Fe(CO)_2Cp)_2][PF_6]$	−7.0 ± 0.2	−7.0 ± 0.4	0.43 ± 0.16	2.8 ± 0.1	116[d,e]
	(−7.0 ± 0.2)	(−6.8 ± 0.4)	(0.0)	(2.9 ± 0.1)	(118)[d,e]
	(−7.0 ± 0.2)	(+3.4 ± 1.4)	(0.0)	(3.4 ± 0.1)	(158)[d]
$[Ph_3SbFe(CO)_2Cp][PF_6]$ (run 1)	−6.7 ± 0.2	+9.6 ± 0.5	0.0	2.8 ± 0.1	149
	(−6.5 ± 0.2)	(−4.5 ± 1.3)	(0.0)	(3.6 ± 0.2)	208
(run 2)	−6.7 ± 0.2	+9.4 ± 0.4	0.0	2.9 ± 0.1	72[d]
	(−6.5 ± 0.2)	(−2.9 ± 2.2)	(0.0)	(4.0 ± 0.2)	(147)[d]
$[Bu_3SbFe(CO)_2Cp][PF_6]$	−6.9 ± 0.1	+6.9 ± 0.5	0.0	2.9 ± 0.1	169
	(−6.8 ± 0.1)	(−4.2 ± 0.8)	(0.0)	(3.3 ± 0.1)	(200)
$[Sb(Co(CO)_3PPh_3)_4][PF_6]$	−8.7 ± 0.2	0.0	0.0	2.9 ± 0.1	185

[a] Samples contained *ca.* 10 mg of Sb/cm^2 and gave absorption intensities of *ca.* 10–25% at 8.5°K. Values in parentheses are alternate fits of the data. In most cases we feel there is a significant reduction in χ^2 for our preferred solution. [b] Isomer shifts are relative to a $Ba^{121}SnO_3$ source at 80°K. [c] Approximately 180 degrees of freedom unless otherwise noted. [d] Approximately 100 degrees of freedom. [e] No significant improvement in fit for $\eta \neq 0$.

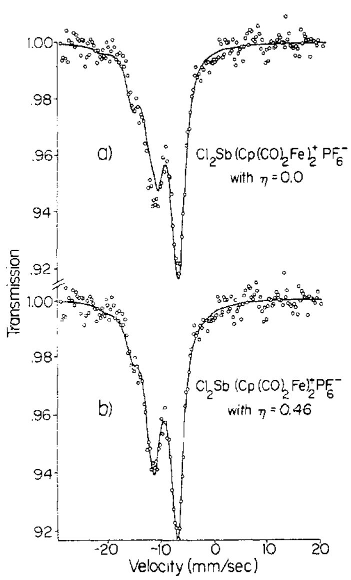

Figure 1. ^{121}Sb Mossbauer spectrum of $[Cl_2Sb(Fe(CO)_2Cp)_2][PF_6]$ at 8.5°K, showing alternate fits of the data. In (a) the asymmetry parameter $\eta = 0$, while in (b) $\eta = 0.46$. The improvement in fit for $\eta \neq 0$ is readily apparent.

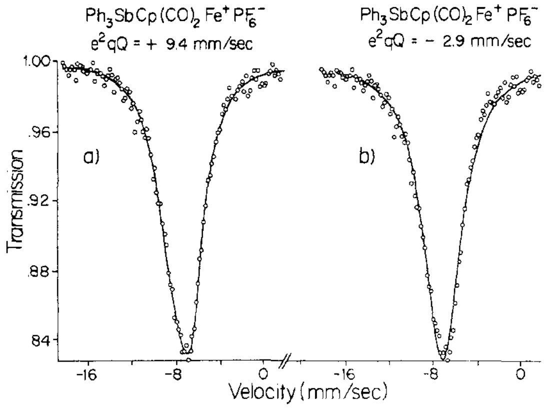

Figure 2. ^{121}Sb Mossbauer spectrum of $[Ph_3SbFe(CO)_2Cp][PF_6]$ at 8.5°K, showing alternate fits of the data. In (a) the fitting parameters were $\delta = -6.7$ mm sec^{-1}, $e^2qQ = +9.4$ mm sec^{-1}, $\Gamma = 2.9$ mm sec^{-1}, and $\eta = 0$. In (b), $\delta = -6.5$ mm sec^{-1}, $e^2qQ = -2.9$ mm sec^{-1}, $\Gamma = 4.0$ mm sec^{-1}, and $\eta = 0$. The fit with $e^2qQ > 0$ is clearly preferable.

to iron and in the other as a one-electron donor, the overall electron configuration on Sb and the electron density in the Sb-Fe bonds are essentially the same in both cases and the distinction is a purely formal one.

In the series $[Ph_nSb(Fe(CO)_2Cp)_{4-n}]^+$ ($n = 1$-3), $|e^2qQ|$ at Sb decreases with decreasing n. If we assume the bond angles are such that Fe-Sb-Fe > Fe-Sb-R > R-Sb-R, as expected on the basis of X-ray structural data for similar tin[14-16] and phosphorus[27a] derivatives and the known structure of $(CH_3)_3SbFe(CO)_4$,[27b] we find that the molecular orbital treatment of Clark, *et al.*,[23] predicts just the reverse order of $|e^2qQ|$ values. It should be noted that Clark's model[23] assumes that the contributions of the ligands to the efg are constant throughout such a series. However, there is evidence from ^{57}Fe QS data discussed below that this is not the case, since $(\Delta E_Q)_{Fe}$ is found to decrease in the order $[Ph_3SbFe(CO)_2Cp]^+ > [Ph_2Sb(CO)_2Cp)_2]^+ > [PhSb(Fe(CO)_2Cp)_3]^+$, indicating changes in the electron distribution in the Fe-Sb bonds. The observed trend in $|e^2qQ|$ values is probably best rationalized in terms of this effect which would produce a decrease in the difference of relative efg contributions from $Fe(CO)_2Cp$ and Ph.

The second parameter of interest is the ^{121}Sb isomer shift δ_{Sb}. Typical ranges of values for δ_{Sb} are −19 to −9 mm sec^{-1} for Sb(III) compounds and −7 to +4 mm sec^{-1} for Sb(V) compounds[28] (relative to $Ca^{121}SnO_3$). Normally, δ_{Sb} for organoantimony(III) derivatives fall at the most positive end of the range for Sb(III) while those for organoantimony(V) fall at the most negative end of the range for Sb(V).[19] The δ_{Sb} values for the present series of compounds lie be-

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(27) (a) H. J. Plastas, J. M. Stewart, and S. O. Grim, *Inorg. Chem.*, 12, 265 (1973); (b) J. J. Legendre, C. Girard, and M. Huber, *Bull. Soc. Chim. Fr.*, 1998 (1971).

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tween −9.6 and −6.7 mm sec^{-1}, neatly spanning the range of values from Sb(III) to Sb(V).

If the arguments of Zuckerman and coworkers[2,29] in assigning oxidation states to the corresponding isoelectronic tin species as Sn(IV) are used, our compounds must be regarded as derivatives of Sb(V). However, δ_{Sb} of organoantimony compounds such as $(p\text{-}ClC_6H_4)_3Sb$ and $(p\text{-}CH_3OC_6H_4)_3Sb$,[30] which certainly would be regarded as Sb(III) derivatives, are more positive (*i.e.*, more "Sb(V)-like") than those of $[X_2Sb(Fe(CO)_2Cp)_2]^+$ (X = Cl, Br). Similarly at the other end of the scale if we were to regard the present species as derivatives of Sb(III), where for example R_3Sb: acts as a two-electron donor toward iron, we find some compounds such as Ph_3SbI_2[19] with shifts more negative than those of $[R_3SbFe(CO)_2Cp]^+$ (R = Ph, Bu). This apparent dichotomy is perhaps not surprising in view of the fact that the isomer shift results from the particular electronic configuration about the metal nucleus which is essentially a continuous function, while the oxidation number is a discontinuous function. Thus the assignment of a particular oxidation state for antimony in compounds of this type has little justification.

It has been suggested[31,32] that δ_{Sn} should be used to assign the *valency* of tin rather than the formal oxidation state. On this basis the isomer shifts of our tetravalent antimoney compounds span the range from trivalent to pentavalent antimony derivatives, behavior which in no way seems unusual.

In the compounds $[X_2Sb(Fe(CO)_2Cp)_2]^+$ (X = Ph, CF_3, Br, Cl) the s-electron density at the antimony nucleus increases (δ_{Sb} becomes more negative) as the electronegativity of X increases. The explanation for this effect parallels that for tin-transition metal complexes,[2,6] where the relative amounts of p-character used in the M-X bonds and thus the amount of s-character in the M-Fe bonds increase in the order Ph < CF_3 < Br, Cl. Since the s-electron density at the Sb nucleus increases with increasing s character of the Sb-Fe bond, the $Fe(CO)_2Cp$ group is a better donor than halogen, CF_3, or Ph groups.

For a series such as $[X_{4-n}Sb(Fe(CO)_2Cp)_n]^+$ the greater donor strength of the $Fe(CO)_2Cp$ moiety is expected to dominate the trend in s-electron density so that δ_{Sb} should become more negative as *n* increases. This trend is observed for $[Ph_{4-n}Sb(Fe(CO)_2Cp)_n]^+$, but both $[X_2Sb(Fe(CO)_2Cp)_2]^+$ (X = Cl, Br) complexes have δ_{Sb} values more negative than those of the corresponding $[XSb(Fe(CO)_2Cp)_3]^+$ derivatives. This suggests that in the dihalides the s character in the X-Sb bonds is already so low that replacement of an X by $Fe(CO)_2Cp$ leads to little if any increase in the total s character in the Fe-Sb bonds, and the isomer shift is thus dominated by an increase in p shielding.

While it is clear from the above discussion that the systematics of ^{121}Sb isomer shifts show many parallels to the corresponding ^{119}Sn systems,[33,34] it is worth examining the correlation in more detail. Using the data of Ruby, *et al.*[35] (with a correction of +0.20 mm sec^{-1} for a systematic error in their ^{119}Sn parameters[36]), one obtains the linear correlation between $\delta_{^{121}Sb}$ and $\delta_{^{119}Sn}$ for isoelectronic antimony and tin compounds shown in Figure 3. Ruby's[35] values for $\delta_{^{121}Sb}$ were converted to a scale relative to $Ba^{121}SnO_3$ (=$\delta_{^{121}Sb}$ relative to $Ca^{121}SnO_3$) using the value[35-37] −8.62 mm sec^{-1} for the isomer shift of InSb relative to $Ba^{121}SnO_3$. Similarly, a value of 1.95 mm sec^{-1} for the isomer shift of α-^{119}Sn relative to $Ba^{119}SnO_3$ (=SnO_2) was used to convert the corrected $\delta_{^{119}Sn}$ values of ref 34 (accepted values are 2.0[38] to 2.1 mm sec^{-1} [28]). This procedure was adopted since the points β-^{119}Sn, β-^{121}Sn and $^{119}SnO_2$, $^{121}Sb_2O_5$ were available independently as a cross check.[37] We have gathered in Table II the available isomer shift data for nominally isoelectronic pairs of antimony and tin compounds of the types $[X_{4-n}Sb(Fe(CO)_2Cp)_n]^+$ and $X_{4-n}Sn(Fe(CO)_2Cp)_n$, and these points are also displayed in Figure 3. It should be noted that in the region below the straight line $\psi_s^2(^{121}Sb) > \psi_s^2(^{119}Sn)$, while the opposite is true in the region above the line.

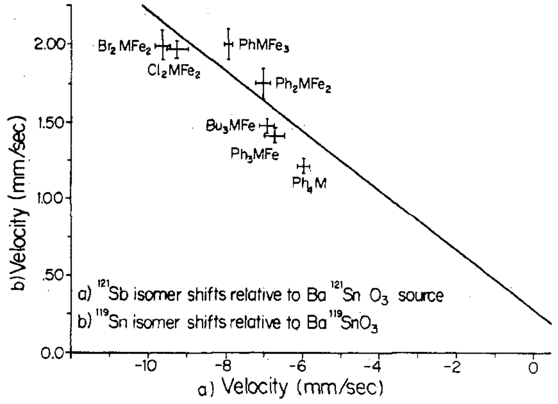

Figure 3. Correlation of ^{119}Sn and ^{121}Sb isomer shifts. The straight line is based on the assumption of equivalent s-electron densities at the two nuclei. In labeling the points we have used the notation M = Sn or Sb^+ and Fe = $Fe(CO)_2Cp$.

For the compounds $[Ph_{4-n}Sb(Fe(CO)_2Cp)_n]^+$ and $Ph_{4-n}Sn(Fe(CO)_2Cp)_n$ it appears (Figure 3) that there is a trend toward somewhat less than equivalent electron densities at the ^{121}Sb nucleus as *n* increases. It is difficult to establish if this apparent trend is really significant in view of the uncertainties involved in the slope and position of the isoelectronic line. If the trend is a real one, it implies that the *difference* in the amount of s density donated by phenyl and by $Fe(CO)_2Cp$ is less for ^{121}Sb than for ^{119}Sn. The most likely explanation of this effect is an increase in any d-d π interaction in the Sb-Fe bond over that in the Sn-Fe bond. This would be expected since the greater Z_{eff} of antimony will contract its 5d orbitals and lower them in energy relative to tin, so that any Fe→M back-π-donation should be enhanced for M = Sb. This interaction should lead to a lowering of the s-electron density at ^{121}Sb relative to ^{119}Sn by increased shielding as the number of $Fe(CO)_2Cp$ groups is increased.

While there remains some uncertainty on the basis of ^{121}Sb Mossbauer data concerning the π character of the Fe-Sb bond, it is clear that the ^{121}Sb isomer shifts are determined primarily by σ-bonding effects and that any possible π interactions play a purely secondary role.

^{57}Fe Mossbauer Parameters. The ^{57}Fe isomer shifts in the present derivatives (Table III) fall in a narrow range which is nearly the same as that reported for $Fe(CO)_2Cp$ groups bond-

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(38) Reference 26, p 374.

Table II. Isomer Shifts of Nominally Isoelectronic Antimony and Tin Complexes

Compd	δ_{Sb}, mm sec^{-1} (rel to $Ba^{121}SnO_3$)	Ref	Compd	δ_{Sn}, mm sec^{-1} (rel to $Ba^{119}SnO_3$)	Ref
$[Cl_2Sb(Fe(CO)_2Cp)_2][Cr(SCN)_4(NH_3)_2]$	−9.3	*a*	$Cl_2Sn(Fe(CO)_2Cp)_2$	1.95, 1.98	*d, e*
$[Cl_2Sb(Fe(CO)_2Cp)_2][PF_6]$	−9.1	*a*			
$[Br_2Sb(Fe(CO)_2Cp)_2][PF_6]$	−9.6	*a*	$Br_2Sn(Fe(CO)_2Cp)_2$	1.99[j]	*f*
$[PhSb(Fe(CO)_2Cp)_3][PF_6]$	−7.9	*a*	$PhSn(Fe(CO)_2Cp)_3$	2.00[j]	*g*
$[Ph_2Sb(Fe(CO)_2Cp)_2][PF_6]$	−7.0	*a*	$Ph_2Sn(Fe(CO)_2Cp)_2$	1.74[j]	*g*
$[Ph_3SbFe(CO)_2Cp][PF_6]$	−6.7	*a*	$Ph_3SnFe(CO)_2Cp$	1.43,[j] 1.41	*g, h*
$[Ph_4Sb][ClO_4]$	−5.9	*b*	Ph_4Sn	1.20,[j] 1.22	*g, i*
$[Ph_4Sb][BF_4]$	−6.0	*c*			
$[Bu_3SbFe(CO)_2Cp][PF_6]$	−6.9	*a*	$Bu_3SnFe(CO)_2Cp$	1.47	*e*

[a] This work. [b] Reference 10. [c] Reference 30. [d] Reference 3. [e] Reference 5. [f] Reference 6. [g] Reference 4. [h] Reference 1. [i] H. A. Stockler and H. Sano, *Trans. Faraday Soc.* 64, 577 (1968). [j] Converted to $Ba^{119}SnO_3$ scale assuming $\delta(\alpha\text{-}Sn) = +2.10$ mm sec^{-1}.

Table III. ^{57}Fe Mossbauer Parameters[a]

Compd	δ,[b] mm sec^{-1}	ΔE_Q,[c] mm sec^{-1}	Γ,[d] mm sec^{-1}
$[Cl_2Sb(Fe(CO)_2Cp)_2][Cr(SCN)_4(NH_3)_2]$	0.40	1.83	0.26
$[Cl_2Sb(Fe(CO)_2Cp)_2][PF_6]$	0.40	1.86	0.25
$[Cl_2Sb(Fe(CO)_2Cp)_2][Sb_4Cl_{14}]$	0.40	1.81	0.26
$[Br_2Sb(Fe(CO)_2Cp)_2][PF_6]$	0.40	1.83	0.26
$[(CF_3)_2Sb(Fe(CO)_2Cp)_2][PF_6]$	0.42	1.80	0.23
$[ClSb(Fe(CO)_2Cp)_3][FeCl_4]$	0.39	1.73	0.25
$[BrSb(Fe(CO)_2Cp)_3][PF_6]$	0.38	1.72	0.26
$[ISb(Fe(CO)_2Cp)_3][PF_6]$	0.39	1.71	0.26
$[ISb(Fe(CO)_2Cp)_3][I_3]$	0.40	1.74	0.27
$[PhSb(Fe(CO)_2Cp)_3][PF_6]$	0.41	+1.73[e]	0.26
$[Ph_2Sb(Fe(CO)_2Cp)_2][PF_6]$	0.39	1.74	0.26
$[Ph_3SbFe(CO)_2Cp][PF_6]$	0.41	1.86	0.23
$[Bu_3SbFe(CO)_2Cp][PF_6]$	0.38	1.87	0.24

[a] All measurements on neat solids with absorbers at 80°K and $^{57}Co(Cu)$ source at room temperature. [b] Isomer shift relative to sodium nitroprusside; estimated error ±0.01 mm sec^{-1}. [c] Quadrupole splitting; estimated error ±0.01 to ±0.02 mm sec^{-1}. [d] Full width at half-maximum; average of the two resonance lines. [e] The sign of e^2qQ was determined with both source and absorber at 4.2°K and the absorber in a longitudinal magnetic field of 30 kG.

Table IV. ^{57}Fe Mossbauer Parameters for $Fe(CO)_2Cp$ Groups Bonded to Tin and Antimony

Compd	δ, mm sec^{-1}	ΔE_Q, mm sec^{-1}	Ref	Compd	δ, mm sec^{-1}	ΔE_Q, mm sec^{-1}	Ref
$Cp(CO)_2FeSnCl_3$	0.41	+1.86	*a*				
	0.40	1.86	*b*				
	0.39	1.84	*c*				
$(Cp(CO)_2Fe)_2SnCl_2$	0.39	+1.66	*a*	$[(Cp(CO)_2Fe)_2SbCl_2]^+$	0.40	1.81–1.86	*d*
	0.36	1.68	*b*				
$(Cp(CO)_2Fe)_2Sn(NCS)_2$	0.39	+1.69	*a*				
$Cp(CO)_2FeSnBu_3$	0.38	+1.75	*a*	$[Cp(CO)_2FeSbBu_3]^+$	0.38	1.87	*d*
$Cp(CO)_2FeSnMe_3$	0.36	1.75	*c*				
$Cp(CO)_2FeSnPh_3$	0.37	1.83	*b*	$[Cp(CO)_2FeSbPh_3]^+$	0.41	1.86	*d*
	0.35	1.82	*c*				

[a] Reference 5. Isomer shift values from this reference have been converted to the sodium nitroprusside scale by the addition of 0.27 mm sec^{-1}. [b] Reference 3. [c] Reference 1. [d] This work.

ed to tin.[1,3,5] There may be a trend to slightly higher δ_{Fe} values in the antimony derivatives (see Table IV) but a lack of published information on the ^{57}Fe resonances in the tin complexes[39] and the inherent difficulty of comparing small differences in isomer shifts derived from different sources preclude detailed analysis.

It is worth considering just what changes in δ_{Fe} between isoelectronic tin and antimony complexes would be expected depending upon whether or not there is significant Fe-Sb π bonding. Since antimony should be a poorer σ donor than tin, if the Fe–Sb bond is essentially pure σ in character, the augmentation of 4s-electron density at iron will be smaller in the antimony derivatives, which should consequently show higher ^{57}Fe isomer shifts than the corresponding tin complexes. Any Fe→Sb back-π-bonding would affect δ_{Fe} in the opposite direction by deshielding. The fact that there is only a very small increase (if any) in δ_{Fe} in the antimony complexes appears to argue in favor of some π interactions in these compounds.

The ^{57}Fe quadrupole splittings, $(\Delta E_Q)_{Fe}$, show two trends which we feel are interrelated. First, in the compounds $[R_nSb(Fe(CO)_2Cp)_{4-n}]^+$ (R = Ph, n = 1-3; R = Cl, Br, n = 1, 2), $(\Delta E_Q)_{Fe}$ increases as n increases and hence as the σ-donor ability of the R_nSb moiety decreases. Similarly, in the compounds $[R_2Sb(Fe(CO)_2Cp)_2]^+$ $(\Delta E_Q)_{Fe}$ increases in the order Ph < CF_3 ⩽ Br, Cl, paralleling the increasing electronegativity of R. In both cases a decrease in Sb→Fe σ donation and thus in the charge density at Fe along the Fe–Sb bond direction (z axis) is accompanied by an increase in $(\Delta E_Q)_{Fe}$. These results clearly imply a deficiency of electron density at iron along the z axis and that V_{zz} should be positive. The ^{57}Fe Mossbauer spectrum of $[PhSb(Fe(CO)_2Cp)_3][PF_6]$ was measured in an applied longitudinal magnetic field of 30 kG, and V_{zz} was found to be positive as expected. It might also be noted that $(\Delta E_Q)_{Fe}$ is essentially constant for the compounds $[XSb(Fe(CO)_2Cp)_3]^+$ (X = Ph, I, Br, Cl). In these cases any differences due to alterations in σ-donor and π-acceptor properties of the XSb group are distributed among three iron atoms and effectively masked.

That the ^{57}Fe quadrupole interaction in these compounds, particularly those containing only one or two $Fe(CO)_2Cp$ moieties, is reasonably sensitive to details of the electron distribution about iron is apparent from the data in Table III. This, together with the fact that there are no large changes in $(\Delta E_Q)_{Fe}$ between corresponding tin and antimony compounds (Table IV), implies that the electron distribution

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[39] A number of tin derivatives of $Fe(CO)_2Cp$ have been reported in ref 4, where the ranges 0.30–0.37 mm sec^{-1} (relative to sodium nitroprusside) for ^{57}Fe isomer shifts and 1.60–1.83 mm sec^{-1} for ^{57}Fe quadrupole splittings are given. However, these authors do not quote values for individual compounds.

in the Fe-Sb bond is quite similar to that in the Fe-Sn bond. What small differences there are in $(\Delta E_Q)_{Fe}$ are consistent with the expected changes in σ-donor and π-acceptor properties between Sn and Sb. This result reinforces the conclusions drawn above from ^{57}Fe, ^{119}Sn, and ^{121}Sb isomer shift data, namely, that antimony and tin are nearly isoelectronic in these compounds. Thus in the ionic antimony derivatives most of the positive charge must reside on antimony rather than being delocalized onto the ligands. This agrees with a similar conclusion reached on the basis of crystal structure data.[18]

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Registry No. $[Sb(Co(CO)_3PPh_3)_4][PF_6]$, 38415-54-2; $[(CF_3)_2Sb(Fe(CO)_2Cp)_2][Cr(SCN)_4(NH_3)_2]$, 49772-08-9; $[Cl_2Sb(Fe(CO)_2Cp)_2][Cr(SCN)_4(NH_3)_2]$, 37279-45-1; $[Cl_2Sb(Fe(CO)_2Cp)_2][PF_6]$, 50297-90-0; $[Cl_2Sb(Fe(CO)_2Cp)_2]_2[Sb_4Cl_{14}]$, 50437-44-0; $[Br_2Sb(Fe(CO)_2Cp)_2][PF_6]$, 50297-87-5; $[(CF_3)_2Sb(Fe(CO)_2Cp)_2][PF_6]$, 49772-09-0; $[ClSb(Fe(CO)_2Cp)_3]_2[FeCl_4]$, 49772-10-3; $[BrSb(Fe(CO)_2Cp)_3][PF_6]$, 50297-88-6; $[ISb(Fe(CO)_2Cp)_3][PF_6]$, 50297-89-7; $[ISb(Fe(CO)_2Cp)_3][I_3]$, 50297-93-3; $[PhSb(Fe(CO)_2Cp)_3][PF_6]$, 50297-94-4; $[Ph_2Sb(Fe(CO)_2Cp)_2][PF_6]$, 50297-92-2; $[Ph_3SbFe(CO)_2Cp][PF_6]$, 49772-11-4; $[Bu_3SbFe(CO)_2Cp][PF_6]$, 49772-12-5; $NaFe(CO)_2Cp$, 12152-20-4; Ph_2SbCl_3, 21907-22-2; $[C_5H_5NH]^+[C_6H_5SbCl_5]^-$, 5425-93-4; Bu_3Sb, 2155-73-9; $ClFe(CO)_2Cp$, 12107-04-9; $[BrSb(Fe(CO)_2Cp)_3]_2[FeBr_4]$, 50322-06-0; ^{121}Sb, 14265-72-6; ^{57}Fe, 14762-69-7.

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Metal Ion Catalyzed Acid Hydrolysis of Acidopentaamminecobalt(III) Complexes. Kinetics and Mechanism of Metal Ion Catalyzed Hydrolysis of Oxalatopentaamminecobalt(III) Complex

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The acid hydrolysis of oxalatopentaamminecobalt(III) complex has been studied in the presence and absence of Al(III), Ga(III), In(III), Fe(III), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) ions. The metal ions are found to catalyze the aquation of the complex. The rate of aquation of the oxalato complex is described by the rate laws

$$\frac{-\mathrm{d}\ln C_t}{\mathrm{d}t} = \frac{k_0K_1/[\mathrm{H}^+] + k_1 + k_2[\mathrm{H}^+]}{1 + K_1/[\mathrm{H}^+]}$$

$$\frac{-\mathrm{d}\ln C_t}{\mathrm{d}t} = \frac{k_0K_1/[\mathrm{H}^+] + k_1 + k_2[\mathrm{H}^+] + k_3K_2K_1[\mathrm{M}^{n+}]/[\mathrm{H}^+]}{1 + K_1/[\mathrm{H}^+] + K_1K_2[\mathrm{M}^{n+}]/[\mathrm{H}^+]}$$

in the absence and presence of the catalyst metal ions, respectively. At 55° and $\mu = 0.3\ M$ (adjusted with $NaClO_4$) the values of the parameters of the rate equations are $k_0 = 0.78 \times 10^{-6}\ \text{sec}^{-1}$, $k_1 = 4.16 \times 10^{-6}\ \text{sec}^{-1}$, $k_2 = 7.5 \times 10^{-6}\ \text{sec}^{-1}\ M^{-1}$, $K_1 = 1.49 \times 10^{-2}\ M$; for Al(III), $k_3 = 701 \times 10^{-6}\ \text{sec}^{-1}$, $K_2 = 38.1\ M^{-1}$; for Ga(III), $k_3 = 568 \times 10^{-6}\ \text{sec}^{-1}$, $K_2 = 516\ M^{-1}$; for In(III), $k_3 = 100 \times 10^{-6}\ \text{sec}^{-1}$, $K_2 = 140\ M^{-1}$; for Fe(III), $k_3 = 1450 \times 10^{-6}\ \text{sec}^{-1}$, $K_2 = 610\ M^{-1}$; for Mn(II), $k_3 = 4.6 \times 10^{-6}\ \text{sec}^{-1}$, $K_2 = 10\ M^{-1}$; for Co(II), $k_3 = 14.6 \times 10^{-6}\ \text{sec}^{-1}$, $K_2 = 25.2\ M^{-1}$; for Ni(II), $k_3 = 15.4 \times 10^{-6}\ \text{sec}^{-1}$, $K_2 = 51.5\ M^{-1}$; for Cu(II), $k_3 = 83.8 \times 10^{-6}\ \text{sec}^{-1}$, $K_2 = 148\ M^{-1}$; for Zn(II), $k_3 = 7.12 \times 10^{-6}\ \text{sec}^{-1}$, $K_2 = 38.9\ M^{-1}$. The formation of binuclear species $(NH_3)_5CoC_2O_4M^{(n+1)+}$ is invoked to account for the observed kinetic patterns of the oxalato complex in the presence of the metal ions. The catalytic activities of the metal ions follow the sequences Mn(II) < Co(II) < Ni(II) < Cu(II) > Zn(II) and In(III) < Al(III) ⩽ Ga(III) < Fe(III). Parallelism between the thermodynamic stabilities and the chemical reactivities of the binuclear complexes is noted. The activation parameters for k_0, k_1, k_2, and k_3 paths have been determined. Like the k_0 and k_1 paths, aquation *via* k_3 path is believed to occur with Co–O bond fission.

Several carboxylatopentaamminecobalt(III) complexes of the type $(NH_3)_5CoCO_2RCO_2H^{2+}$ have been reported in the literature.[1,2] The cation formed by deprotonation of the unbound carboxyl group of such complexes is capable of coordination, and if this cation ligates to a polyvalent metal ion through the free carboxyl group, the resulting coordination compound will have the novel feature of containing two positive charge centers, the pentaamminecobalt(III) moiety and the associated metal ion. The carboxylate ion bridged binuclear complexes of various metal ions will undergo ligand substitution at the cobalt(III) center at rates which are likely to be dictated by the charge, size, and various other properties of the associated metal ions. It is also normally expected that the group R separating the positive charge centers will have some influence on the stabilities and the reactivities of the binuclear complexes.

The thermodynamic and kinetic aspects of the binuclear species $(NH_3)_5CoCO_2RCO_2M^{(n+1)+}$ have not been investigated as yet. We have been interested in the study of the effects of nonreducing and substitution labile metal ions on the kinetics of aquation of some suitable cationic carboxylatopentaamminecobalt(III) complexes in order to (i) examine their complexing abilities toward metal ions, (ii) estimate the catalytic efficiencies of various metal ions in promoting aquation of such cobalt(III) substrates, (iii) find a correlation between the thermodynamic stabilities and the chemical reactivities of the binuclear complexes, and (iv) explore the mechanism of aquation of such carboxylatopentaamminecobalt-

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(1) H. Taube and D. K. Sebera, *J. Amer. Chem. Soc.*, 83, 1785 (1961).

(2) R. D. Butler and H. Taube, *J. Amer. Chem. Soc.*, 87, 5597 (1965).