Antimony-121 Mössbauer Spectroscopy of Some Cyanide Adducts of Antimony Pentachloride

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^{121}Sb Mössbauer spectra have been measured at 4·2 K in some cyanide adducts $SbCl_5$,NCR (R = Me, Cl, Bu^t, Ph, Et, CH_2Cl, CCl_3, $CH{=}CH_2$). Hyperfine interactions deduced from transmission integral analysis of the spectra are interpreted in terms of the varying degree of electron transfer from the cyanide to the antimony atom. The results are discussed in combination with data from nuclear quadrupole resonance and vibrational spectroscopy studies.

HYPERFINE-INTERACTION parameters measured by Mössbauer spectroscopy at the 37·15 keV level in ^{121}Sb are quite sensitive to details of the chemical bonding and electron distribution around the antimony atom.[1,2] Even in a simple approach, several mechanisms contribute to the character of such bonding: in addition to ionic and overlap contributions one must consider the influence of hybridization and polarization of nonbonding orbitals. It is, however, possible to choose a set of compounds where some of these factors are expected to be nearly constant. In an attempt to at least partially realize such a situation, we have studied ^{121}Sb Mössbauer spectra of a series of cyanide adducts of $SbCl_5$, *i.e.* $SbCl_5$,NCR (R = Me, Cl, Bu^t, Ph, Et, CH_2Cl, CCl_3, and $CH{=}CH_2$). A vibrational spectral study has shown that the antimony nucleus is octahedrally co-ordinated to five Cl groups and the N atom of the cyanide in all the complexes.[3] The aim of this work is to establish an order for the donor strength of the cyanides from measurement of the quadrupole interaction and isomer shift (i.s.). It is known that the i.s. gives access to the change in total electron density at the nucleus, while the quadrupole interaction mainly reflects asymmetry of the electron distribution around the ^{121}Sb nucleus. Both parameters are thus influenced by changes in the amount of electron transfer from the cyanide to the $SbCl_5$ moiety.

EXPERIMENTAL

Reaction of the cyanides RCN (R = Me, Cl, Bu^t, Ph, Et, CH_2Cl, CCl_3, and $CH_2{=}CH$) with $SbCl_5$ in stoicheiometric amounts was carried out in dichloromethane. The purity of the compounds was checked by chemical analysis and all manipulations took place in a dry-nitrogen atmosphere. Detailed i.r. and Raman data are reported elsewhere.[3]

Mössbauer spectra were measured against a $Ca^{121m}SnO_3$ source; both source and absorber were cooled to 4·2 K. The absorbers were carefully ground together with boron carbide, B_4C, powder; the absorber thickness was *ca.* 8 mg cm^{-2} of natural antimony. Spectra were least-squares fitted with a transmission integral to account for the quadrupole interaction as discussed previously.[2,4] The use of this procedure is essential for extracting reliable hyperfine-interaction parameters from partially resolved ^{121}Sb Mössbauer quadrupole spectra. The asymmetry parameter, η, was set equal to zero in the fitting procedure because of axial symmetry of the antimony site in these octahedrally co-ordinated compounds. This procedure is not strictly valid in all the cases, but it is reasonable to assume that η does not differ considerably from zero. Furthermore, the insensitivity of ^{121}Sb Mössbauer quadrupole spectra to small values of η has previously been demonstrated.[4]

RESULTS AND DISCUSSION

In Figure 1 we present a typical Mössbauer spectrum. Values of the quadrupole interaction and isomer shift (i.s.) deduced from Mössbauer spectra for the $SbCl_5$,NCR complexes are plotted in Figure 2. One observes a definite correlation between the quadrupole interactions (e^2q_zQ) and i.s.'s. In addition, from the spectra we note that the quadrupole interaction e^2q_zQ has a negative sign in all the compounds. The results are summarized in the Table.

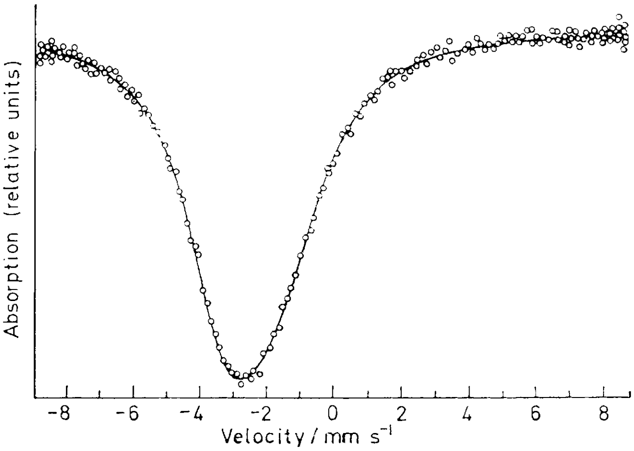

FIGURE 1 Mössbauer spectrum of the complex $SbCl_5$,NCEt against a $CaSnO_3$ source at 4·2 K, (——) represents a least-squares fit using the transmission integral formula

Neglecting the contribution from *d* electrons, the principal component of the electric-field gradient (e.f.g.) produced by *p* electrons at the ^{121}Sb nucleus

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[1] G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 59.

[2] J. M. Friedt, G. K. Shenoy, and M. Burgard, *J. Chem. Phys.*, 1973, **59**, 4468.

[3] M. Masson and M. J. F. Leroy, unpublished work; M. Burgard and J. McCordick, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 599.

[4] G. K. Shenoy and J. M. Friedt, *Nuclear Instr. Methods*, in the press; *Phys. Rev. Letters*, 1973, **31**, 419.

is as in equation (1), where R_{5p} is the Sternheimer

$$eq_z = \tfrac{4}{5}\langle r^{-3}\rangle_{5p}(1 - R_{5p})[-N_{p_z} + \tfrac{1}{2}(N_{p_x} + N_{p_y})] \quad (1)$$

antishielding factor for the $5p$ electrons and N_{p_j} ($j = x$—z) are electron populations of the various p orbitals of the antimony atom. Introducing the ionicity, i, of the Sb–Cl bonds, equation (1) becomes (2), where

$$eq_z = \tfrac{4}{5}\langle r^{-3}\rangle_{5p}(1 - R_{5p})\left(-\frac{N_C}{2} + \frac{1-i}{2}\right) \quad (2)$$

N_C represents the number of electrons in the hybrid orbital defined by the Sb–N bond. The five chlorine ligands are considered to be nearly equivalent on the basis of results of nuclear quadrupole resonance (n.q.r.) [5] and vibrational spectroscopic measurements. The quadrupole interaction thus depends on the number of electrons transferred along the Sb–N bonding direction and on the changing ionicity of the five Sb–Cl bonds. The isomer shift (i.s.) measured at the ^{121}Sb nucleus is described to a first approximation by equation (3),

$$\text{i.s.} = A - BN_s + CN_p \quad (3)$$

where A—C are positive constants and N_s and N_p represent the electron population of the $5s$ and $5p$ shells of antimony respectively. B is much larger than C. Changes in i.s. thus describe variations of the population in the $5s$ and $5p$ shells of the antimony atom.

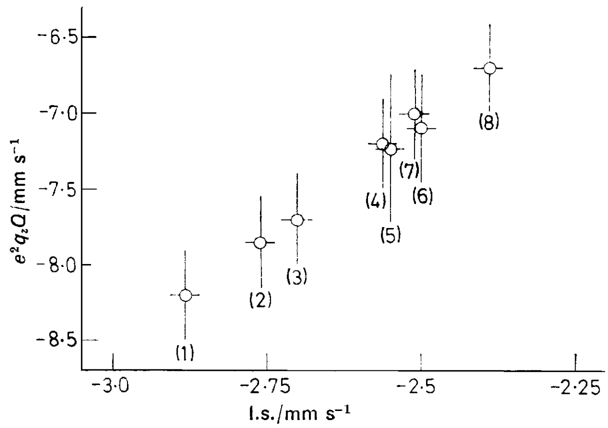

FIGURE 2 I.s. (against $CaSnO_3$) and quadrupole interaction deduced from ^{121}Sb Mössbauer spectra at 4·2 K of the complexes $SbCl_5$,NCR [R = CCl_3 (1), Cl (2), CH_2Cl (3), CH=CH_2 (4), Et (5), Me (6), Bu^t (7), and Ph (8)]

Investigation of the n.q.r. frequencies at the chlorine nuclei [5] in some of the complexes has revealed a slight increase in ionicity of the five Sb–Cl bonds with increasing donor strength of the cyanide. Changes in Sb–Cl frequencies, as measured in vibrational spectra,[3] reveal the same trend (Table). Taking these facts into account, together with equations (1)—(3), the following conclusions are drawn from the variation shown in Figure 2. (*i*) The main component of the e.f.g. tensor (eq_z) is positive in all the complexes; it follows that the electron population in the p_z orbital of the antimony atom (defined along the Sb–N bond) is always smaller than that in the p_x and p_y orbitals in the equatorial plane. The cyanide ligands are thus poorer donors to Sb than the Cl^- ions. (*ii*) The absolute value of the quadrupole interaction (e^2q_zQ) decreases with increasing donor strength of the cyanide. Since a slight increase in ionicity of the Sb–Cl bond is a consequence of the increasing donor power of the sixth ligand,[5] it is concluded that electrons donated along the Sb–N bond are increasingly redistributed towards the five chloride ions. The increase in N_{p_z} associated with a decrease of $(N_{p_x} + N_{p_y})/2$, thus results in the decrease of the difference between electron populations of the p_z and the p_x and p_y orbitals. These results are in accord with conclusions from Mössbauer data on related tin complexes $SnCl_4$,2L.[6] (*iii*) Electron populations of the various orbitals of the antimony atom are obtained from hybrid molecular orbitals in an octahedral environment [equations

Hyperfine-interaction parameters deduced from ^{121}Sb Mössbauer spectra at 4·2 K of the complexes $SbCl_5$,NCR, vibration bands (cm^{-1}) measured at 293 K, and quadrupole coupling constants (q.c.c.) at 77 K of ^{121}Sb and ^{35}Cl (from ref. 5). The error on the last significant figure is given in parentheses

R	e^2q_zQ/mm s^{-1}	I.s.[a]/mm s^{-1}	ν (MCl)			Q.c.c./MHz	
			A_1 $(SbCl_4)_{eq}$	A_1 $(SbCl)_{ax}$	E $(SbCl_4)$	^{121}Sb [b]	^{35}Cl
CCl_3	−8·2(3)	−2·88 (3)	350	303	376		
Cl	−7·85(30)	−2·76 (3)	343 349	303	373 [c] 355 [c]	236·45	52·8
CH_2Cl	−7·70(30)	−2·70(3)	349	309	370		
CH_2=CH	−7·2(3)	−2·56(3)	348	309	366		
Et	−7·23(50)	−2·55(3)	348	308	364		
Me	−7·1(3)	−2·50(3)	344 348	302	372 [c]	216·27	52·19
Bu^t	−7·0(3)	−2·51(3)	344	300	365		
Ph	−6·7(3)	−2·39(3)	342	292	367 377		

[a] Reported relative to a $CaSnO_3$ source at 4·2 K. [b] To convert to mm s^{-1} divide by 30. [c] M. Burgard and J. McCordick, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 599.

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[5] M. Burgard and E. A. C. Lucken, *J. Mol. Struct.*, 1972, **14**, 397; R. F. Schneider and J. V. Dilorenzo, *J. Chem. Phys.*, 1967, **47**, 2343.

[6] See R. V. Parish, *Progr. Inorg. Chem.*, 1972, **15**, 165.

(4)—(6)]. The charge on each electron shell of antimony

$$h_{z\pm} = \frac{1}{\sqrt{6}}s \pm \frac{1}{\sqrt{2}}p_z + \frac{1}{\sqrt{3}}d_{z^2} \quad (4)$$

$$h_{y\pm} = \frac{1}{\sqrt{6}}s \pm \frac{1}{\sqrt{2}}p_y - \frac{1}{2}d_{x^2-y^2} - \frac{1}{\sqrt{12}}d_{z^2} \quad (5)$$

$$h_{x\pm} = \frac{1}{\sqrt{6}}s \pm \frac{1}{\sqrt{2}}p_x + \frac{1}{2}d_{x^2-y^2} - \frac{1}{\sqrt{12}}d_{z^2} \quad (6)$$

is given by the product of the square of the coefficient in the hybrid orbital and the total number of electrons residing in a particular molecular orbital. The direct contribution of the *s* electrons to the i.s. dominates the screening effect due to the *p* electrons.[7] Thus the increase in i.s. with increasing donor strength of the adduct ligand implies either a decrease in *s*-electron density at the Sb nucleus or an increase in *p* shielding. There are two explanations for this result, depending on how much significance we attach to the n.q.r. results on Sb–Cl bond ionicity. (*a*) If we accept from the n.q.r. data that the ionicity of the Sb–Cl bonds slightly increases with increasing electron donation from the cyanide, then equations (4)—(6) predict that direct *s*-shell changes are dominant in the ^{121}Sb i.s. Increase in the population of h_{z+} would be outweighed by the decrease in population of the other five orbitals. In addition to the n.q.r. results, this interpretation is also supported by the i.r. frequency dependence on the cyanide, which reveals changes in ionicity of the Sb–Cl bonds along the series of complexes. (*b*) Assuming, however, that the increase in ionicity of the Sb–Cl bonds is insignificant, one has to conclude that the excess of charge transferred from the adducts preferentially occupies the p_z orbitals.[8] This explanation would be consistent with Bent's rule which assigns greater *s* character to bonds formed with the most effective donor ligands, *i.e.* the Cl^- ions in the complexes considered here. However, the preference for the p_z orbital cannot be explained in more detail. It is to be pointed out that, contrary to our results, no such difficulties exist in $SnCl_4,2L$ complexes since in these *s*-electron density increases with increasing donation. (*iv*) As a conclusion, determination of the quadrupole interaction and i.s. along the series of complexes allows classification of cyanides according to their increasing electron-donating power: $CCl_3 < Cl < CH_2Cl < CH{=}CH_2 \simeq Et < Me \simeq Bu^t < Ph$. This order agrees with those reported,[9,10] except for the position of the phenyl ligand which is usually considered to be a poor donor. The anomaly may originate from particular properties of this ligand. Furthermore, our bonding scheme is oversimplified and does not take π-bonding into account. One should, however, note that the same order of donor strength is concluded from vibrational spectra of these complexes (Table).

Conclusion.—The present results demonstrate the utility of applying ^{121}Sb Mössbauer spectroscopy to problems of molecular bonding. The higher sensitivity of the i.s.'s to chemical changes in the ^{121}Sb resonance measurements, as compared to those in ^{119}Sn or ^{125}Te, gives access to details of the chemical bond.[1,6] Although Mössbauer spectroscopy is less precise than n.q.r. for determination of quadrupole interactions, it yields in a straightforward way the sign of the interaction. The present study demonstrates the existence of electron transfer from the cyanide to the central antimony atom. However, the trends in the i.s. cannot be satisfactorily accounted for by the simple molecular-orbital picture. Determination of both the i.s. and quadrupole interaction along the series of complexes allows one to deduce an order of donating power of the cyanides. The Mössbauer effect of ^{121}Sb alone could not have provided sufficient information to draw these conclusions and the necessity of combining several techniques is evident.

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