Antimony-121 Mössbauer Spectroscopic Studies of Antimony Dithiocarbamate Complexes

By **John G. Stevens** * and **Jan M. Trooster**, Laboratory of Molecular Spectroscopy, University of Nijmegen, Toernooiveld, Nijmegen, The Netherlands

Fifteen antimony dithiocarbamate complexes and five related complexes have been studied using ^{121}Sb Mössbauer spectroscopy. These include the series $Sb(S_2CNEt_2)_{3-n}X_n$ (X = Cl, Br, or I; n = 0—3), $SbR_n(S_2CNEt_2)_{3-n}$ (R = Me or Ph; n = 1 or 2), $Sb(S_2CNBu_2)_3$, $Sb(S_2CNBu_2)_2L$ (L = $0{\cdot}5Cd_2I_6$ or I_3), $SbMe_4(S_2CNEt_2)$, and $SbMe_3(S_2CNMe_2)_2$. Isomer shifts, quadrupole-coupling constants, and asymmetry parameters are used to discuss the antimony–ligand bonds and the structure. Four of the complexes studied contain Sb^V, while the others contain Sb^{III}. The sterically active lone-pair electrons are quite important in understanding the bonding and structural properties of the antimony(III) complexes.

COMPLEXES of dithiocarbamates with many different central metal ions have been extensively studied. However, only a limited amount of information on the bonding and structural properties is available for antimony complexes, since a significant number of these have been prepared only recently. In our study we investigated most of these complexes using ^{121}Sb Mössbauer spectroscopy, a technique used previously for a variety of organoantimony compounds.[1-3]

The dithiocarbamate group can occur as an ion, or a unidentate, anisobidentate (one strong and one weak metal–sulphur bond), or bidentate species. Attempts have been made using i.r. spectroscopy to distinguish between the bidentate and anisobidentate/unidentate modes by noting the absorption peaks in the 850—1 000 cm^{-1} region and assigning them to the SCS stretching frequency.[4-6] In this method a single band at *ca.* 1 000 cm^{-1} is indicative of the bidentate mode while additional peaks are assumed to be due to an anisobidentate or unidentate ligand. Often, however, the results are confusing, partially because of the complicated spectra which are usually found in this region. Only *X*-ray structural analyses have allowed unambiguous assignments of the modes of bonding of those ligands.

An interesting property of dithiocarbamate ligands is their ability to form complexes in which a transition metal is in an uncommonly high oxidation state. This occurs because of the possibility of π bonding between the metal and the ligand promoted by the strong electron-donating nitrogen atom.[7] In contrast to the transition metals, higher oxidation states of the non-transition elements (Si, Ge, Sn and P, As, Sb) cannot be explained in terms of π bonding.

Antimony(V) compounds which contain sulphur-donor ligands are rare. Since Mössbauer spectroscopy has been used successfully to obtain bonding and structural information for a number of tin dithiocarbamates [8-13], ^{121}Sb Mössbauer spectroscopy seems an excellent method of gaining a better understanding of the antimony complexes. For ^{121}Sb the excited and ground nuclear states have spins of $\frac{7}{2}$ and $\frac{5}{2}$ respectively and 12 transitions result from the quadrupole interaction. This means that, in addition to being able to determine the quadrupole-coupling (e^2qQ) and isomer-shift (δ) parameters, one can also determine the sign of the quadrupole coupling (e^2qQ) and the asymmetry parameter (η).

EXPERIMENTAL

The dithiocarbamates were prepared by the groups of J. A. Cras and J. Willemse at the University of Nijmegen and H. A. Meinema, H. F. Martens, and J. G. Noltes at the Organic Chemistry Institute TNO (Utrecht). Procedures for synthesizing these and/or the crystal structure have been reported as indicated in Tables 1 and 2, except for the $SbMe_4$-

TABLE 1

Antimony-121 Mössbauer parameters for miscellaneous antimony dithiocarbamates at 4.2 K. Errors are typical values for a change of 1.0 in χ^2

Complex	Ref.[a]	δ [b] ± 0.1 mm s^{-1}	e^2qQ ± 1.0 mm s^{-1}	η ± 0.2	Γ_a [c] ± 0.1 mm s^{-1}	$10^{-3}N_0$ [d]	t_a [e] ± 0.07	n [f] / mg cm^{-2}	f_a ± 0.03
$Sb(S_2CNEt_2)_3$	*g*, 19*d*	−6.9	7.5	0.0	1.05	110	1·22	5·0	0·43
	g, 19*d*	−6.8	7.8	0.0	1.05	40	5.6	24.6	0.41
$Sb(S_2CNBu_2)_3$	5	−6.4	7.8	0.2	1.09	78	1.35	5.0	0.48
$SbI_3(S_2CNBu_2)_2$	20	−5.5	9.4	0.5	1.20	40	1.90	7.0	0.48
$Sb(S_2CNBu_2)_2{\cdot}0{\cdot}5Cd_2I_6$	20	−5.1	10.3	0.0	1.05	47	1.14	5.0	0.41
$SbPh(S_2CNEt_2)_2$	6	−4.1	22.2	0.2	1.05	110	1.01	4.4	0.41
$SbMe(S_2CNEt_2)_2$	6	−4.0	25.1	0.2	1.07	129	0.55	4.2	0.23
$SbPh_2(S_2CNEt_2)$	6,*k*	−2.5	20.0	1.0	1.06	188	1.15	5.0	0.41
$SbMe_3(S_2CNMe_2)_2$	22	2.5	−17.4	0.4	1.11	150	1.12	5.0	0.39
$SbMe_3(S_2PEt_2)_2$	*h*	2.6	−18.7	0.2	1.20	92	1.94	9.8	0.35
$SbMe_3(mnt)$ [i]	*h*	2.3	−18.7	(0.0)	1.35	81	(1.94)	9.5	(0.37)
$SbMe_4(S_2CNEt_2)$	*j*	3.0	−2.1		1.15	109	0.74	5.0	0.27

[a] For preparation and/or structure. [b] Isomer shift relative to InSb at 4.2 K. [c] Absorber linewidth; source linewidth kept at 1.15 mm s^{-1}. [d] Number of counts per channel far from resonance. [e] Corrected for natural linewidth. [f] Absorber thickness for Sb. [g] G. E. Manoussakis and P. Karayannidis, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 71. [h] J. Willemse, unpublished work. [i] The spectrum shows a weak component due to an antimony(III) impurity. Consequently η and t_a are rather uncertain. [j] H. A. Meinema, unpublished work. [k] E. J. Kupchik and P. J. Calabretta, *Inorg. Chem.*, 1965, **4**, 973.

(S_2CNEt_2) complex which was characterized by Sb analytical analysis and n.m.r. spectroscopy. Samples used were from the original stock or specially prepared for the study. In all cases new n.m.r. and/or i.r. spectra verified their identity. The trihalides were obtained from Alfa Products (Ventron).

Lucite holders permitting sample diameters of 12 mm were used. The absorbers usually contained *ca.* 5 mg of natural antimony per cm², and therefore only small amounts of the sample were usually needed (10—30 mg). The complexes were often mixed with powdered poly(methyl methacrylate) or boron nitride. The effective absorber thickness (t_a) for most of these was between 1.0 and 2.0. This was the optimum thickness in terms of count rate, absorption intensity, and resolution. In cases in which there was any possibility of reaction in air the absorbers were prepared in a dry-nitrogen glove-box. Both the $Ni_{21}{}^{121}Sn_2B_6$ source and the absorbers were kept at liquid-helium temperature. An intrinsic germanium detector with a 200 mm² crystal was used. This has the advantage over xenon-filled proportional counters or scintillation detectors of giving a slightly increased counting rate with an extremely low background (4—5%).

TABLE 2

Antimony-121 Mössbauer parameters for $Sb(S_2CNEt_2)_{3-n}X_n$ at 4.2 K

X	n	Ref.[a]	δ[b] $\pm$0.1 mm s^{-1}	e^2qQ $\pm$1.0 mm s^{-1}	η $\pm$0.2	Γ_a[c] $\pm$0.1 mm s^{-1}	$10^{-3}N_0$[d]	t_a[e] $\pm$0.07	n[f] / mg cm^{-2}	f_a $\pm$0.03
	0	*g*	−6.9	7.7	0.0	1.05	109	1.22	5.0	0.43
I	1	*h*	−5.8	9.3	0.4	1.15	140	1.08	5.0	0.38
	2	26	−7.2	8.1	0.0	1.05	117	1.14	5.0	0.41
	3	*i*	−7.7	2.5 ± 3.0		1.3	145	0.86	5.0	0.40
Br	1	5	−6.2	9.9	0.3	1.07	158	1.26	5.0	0.45
	2	26	−7.2	10.6	0.2	1.15	153	1.11	5.0	0.40
	3	*i*	−5.9	10.7	0.3	1.36	216	0.71	5.0	0.25
Cl	1	*j*	−6.0	10.6	0.4	1.11	170	1.23	5.0	0.44
	2	26	−5.9	13.3	0.1	1.13	154	1.27	5.0	0.45
	3	*i*	−5.9	13.2	0.2	1.6	183	0.76	4.5	0.31

[a–g] As in Table 1. [h] C. A. Tsipis and G. E. Manoussakis, *Inorg. Chim. Acta*, 1976, **18**, 35. [i] Alfa Products (Ventron). [j] P. J. H. A. M. van de Leemput, unpublished work.

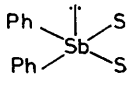
All the isomer shifts are reported relative to InSb at 4.2 K. The spectrometer was calibrated during each spectrum with a Michelson interferometer, the details of which, together with a description of the spectrometer and Dewar, are given in refs. 14 and 15. The velocity varied in a triangular way and two spectra of 512 channels each were obtained in each measurement. For the fitting procedure (see below) it is necessary that the data points lie at equidistant velocity intervals. Therefore the two spectra were linearized by an interpolation scheme, using the measured velocity. Thereafter the two spectra were added and subsequently compressed to 128 channels. This corresponds to *ca.* 8 channels per linewidth. The reduced number of channels is important since the computing time is proportional to the square of the number of channels. Data for most spectra were accumulated over 2—3 d.

All the data were fitted using a transmission-integral analysis computer routine similar to the one described by Cranshaw.[16] The Mossbauer source fraction (f_S) and source linewidth (Γ_S), however, were held constant at 0.62 and 1.15 mm s^{-1} respectively. The source fraction was determined from the maximum absorption of very thick absorbers; the source linewidth was found to give consistent results for absorbers of different thickness. The δ and e^2qQ values were not sensitive to f_S and Γ_S. Examples of observed and calculated spectra are shown in the Figure.

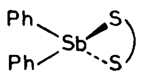
DISCUSSION

When isomer shifts are expressed relative to InSb, positive shifts imply antimony(V) and negative shifts indicate antimony(III) compounds. An examination of Table 1 shows that there are four antimony(V) complexes, $SbMe_3(S_2CNMe_2)_2$, $SbMe_3(S_2PEt_2)_2$, SbMe$_3$(mnt) [mnt = maleonitriledithiolate, $S_2C_2(CN)_2{}^{2-}$], and $SbMe_4(S_2CNEt_2)$, and six antimony(III) complexes.

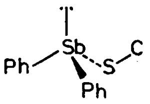
$SbR(S_2CNEt_2)_2$.—The two $SbR(S_2CNEt_2)_2$ (R = Me and Ph) complexes have similar Mössbauer parameters [see also Figure (*b*)]. Of particular note are the large positive quadrupole-coupling constants which, for axial symmetry, indicate an excess of electrons in the axial position and electron withdrawal in the equatorial position. This implies a structure in which the more electronegative atoms (the sulphurs in this case) are in the equatorial plane. Also, since η is small, there is near cylindrical symmetry. The most obvious structure is octahedral with the inclusion of sterically active lone-pair electrons in one of the six positions. Reported i.r. spectra [6] confirm this structure with the appearance of only a single intense absorption peak in the 980 ± 70 cm^{-1} region (C=S stretching frequency). The single band implies that the dithiocarbamate is bidentate.



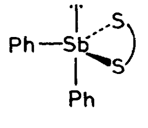
(1)



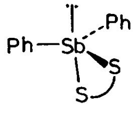
(2)



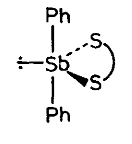
(3)



(4)

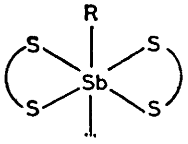


(5)



(6)

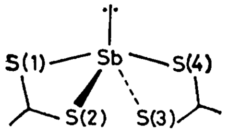
$SbPh_2(S_2CNEt_2)$ [*Figure* (*c*)].—The i.r. spectrum indicates a bidentate co-ordination of the dithiocarbamate ligand.[6] However, the five simple monomeric structures (1), (2), (4)—(6) based on bidentate co-ordination are less easily reconciled with the Mössbauer parameters observed than is (3) with unidentate dithiocarbamate. Structure (1) can be excluded since it should result in η = 0. Structure (2) which is com-



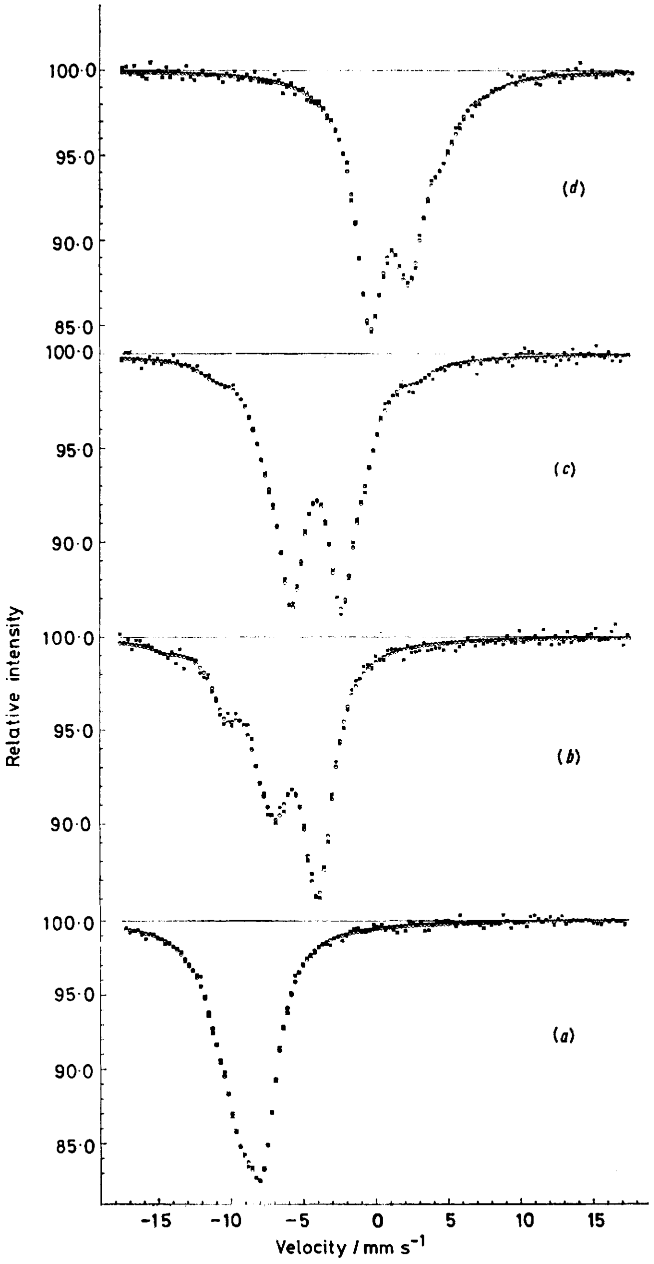
patible with $\eta = 1$ lacks a stereochemical lone pair which should exist as the complex is chemically active. Trigonal-bipyramidal structures with a lone pair in the equatorial position [such as (6)] have a considerably lower isomer shift as well as quadrupole splitting.[17,18,19a] The trigonal-bipyramidal structures (4) and (5) where the lone pair is in an axial position can be expected to have similar isomer shifts to (6). There is a close similarity with the Mössbauer parameters of $O(SbPh_2)_2$ ($\delta = -1.0$ mm s^{-1}, $e^2qQ = 21$ mm s^{-1}, $\eta = 0.9$),[19b] which has structure (3) with S replaced by O. For this compound, δ is calculated using the concept of partial chemical shifts (p.c.s.s). The p.c.s. value for the sulphur in dithiocarbamates can be approximately determined by using the average isomer-shift values for $SbX(S_2CNEt_2)_2$ (see below). These complexes apparently have three short sulphur distances, a lone pair, a long sulphur distance, and a long halide distance. The p.c.s. for sulphur then is (1/3) $(-5.9 + 8.5) = +0.8$. The p.c.s. of oxygen used by Bowen *et al.*[19c] is 1.7 mm s^{-1}. This difference in p.c.s. explains the observed difference in δ between $SbPh_2(S_2CNEt_2)$ and $O(SbPh_2)_2$.

$Sb(S_2CNR_2)_3$ (R = Et *or* Bu).—An *X*-ray structure determination has been carried out on the ethyl complex.[19d] The dithiocarbamates act as anisobidentate ligands, resulting in three short Sb–S bonds (*ca.* 2.5 Å) and three longer Sb–S bonds (*ca.* 2.9 Å). The more strongly bound S co-ordinates to Sb in an approximately trigonal configuration. A considerable gap exists in the co-ordination sphere which presumably contains the antimony lone pairs. That the Mössbauer parameters of these two complexes are almost identical indicates that the structure and bonding are also similar.

$Sb(S_2CNBu_2)_2L$.—A similar situation exists for the pair $SbI_3(S_2CNBu_2)_2$ and $Sb(S_2CNBu_2)_2\cdot 0.5Cd_2I_6$. A recent *X*-ray structure analysis (ref. 20) of the latter complex shows a distorted trigonal-bipyramidal structure with a lone pair in an equatorial position; S(X)–Sb–S(3) = 95° and S(1)–Sb–S(4) = 145°. The low symmetry precludes a prediction of the asymmetry parameter, but the value $\eta = 0.0 \pm 0.2$ is surprisingly low. Although the determination of η for low values of e^2qQ is not very accurate, the larger value of η for $SbI_3(S_2CNBu_2)_2$, which presumably has the same structure, is evident from the spectrum.



Antimony(V) *Complexes*.—While for the majority of the complexes studied antimony is in oxidation state III, $SbMe_4(S_2CNEt_2)$, $SbMe_3(S_2PEt_2)$, and $SbMe_3(mnt)$ contain Sb^V as can be concluded from the positive δ values. The Mössbauer data (specifically the fact that $e^2qQ \simeq 0$) for the $SbMe_4(S_2CNEt_2)$ complex imply an ionic structure with the methyls surrounding the antimony tetrahedrally forming a tetramethylstibonium ion and a diethyldithiocarbamate ion. In contrast with these results, a number of SbR_4X complexes have small quadrupole couplings (*ca.* 7 mm s^{-1}) [1], from which it has been concluded that these molecules are trigonal bipyr-



Antimony-121 Mössbauer spectra of (*a*) $SbBr_2(S_2CNEt_2)$, (*b*) $SbPh(S_2CNEt_2)_2$, (*c*) $SbPh_2(S_2CNEt_2)$, and (*d*) $SbMe_3(S_2CNEt_2)_2$. (■) Measured intensities; (○), intensities calculated with parameters given in Tables 1 and 2 amids. The only other complex examined by Mössbauer spectroscopy that has a tetrahedral structure about the antimony is $[SbPh_4][ClO_4]$, which has a single Lorentzian linewidth of 2.6 ± 0.2 mm s^{-1}. The isomer shift of this complex compares favourably with that of $SbMe_4(S_2CNEt_2)$, *i.e.* 2.6 ± 0.2 *versus* 3.2 ± 0.1 mm s^{-1}. Dithiocarbamate is known to be able to exist as an ion in $Na[S_2CNR_2]$ and $[NH_4][S_2CNR_2]$,[21] but few other examples are known.

The complexes $SbMe_3(S_2CNMe_2)_2$, $SbMe_3(S_2PEt_2)_2$, and $SbMe_3$(mnt) all give similar Mössbauer parameters. The relatively large negative quadrupole-coupling constants and isomer-shift values indicate trigonal-bipyramidal (t.b.p.) structures, with the methyls in equatorial positions and the sulphurs in axial positions.[1] The asymmetry value [see also Figure (*d*)] for the $SbMe_3(S_2CNMe_2)_2$ complex implies some distortion. Recent *X*-ray diffraction results [22] show this to be true with an S–Sb–S bond angle of 170° (180° for undistorted t.b.p.) and Me–Sb–Me angles of 105, 105, and 150° (*cf.* 120°). The δ and e^2qQ values of the mnt and S_2PEt_2 complexes are almost identical and only the asymmetry parameter is different, smaller in the latter case, thus signalling less distortion for the $SbMe_3(S_2PEt_2)_2$ molecule.

$Sb(S_2CNEt_2)_{3-n}X_n$.—Mössbauer data for these complexes are given in Table 2 [see also Figure (*a*) for a typical spectrum]. The values of e^2qQ for the SbX_3 complexes can be compared with those obtained by n.q.r. measurements at 77 K: $SbCl_3$, 12.8;[23] $SbBr_3$, 11.5;[24] and SbI_3, 5.7 mm s^{-1}.[24] The negative δ values for these complexes indicate that the oxidation state of antimony is III. Generally, similar structures give linear plots of δ against e^2qQ. However, for $Sb(S_2CNEt_2)_{3-n}X_n$ (n = 0—3; X = Cl, Br, or I), such plots do not show any recognizable linear relation, and there must be more than one structure for the molecules in this series. Fortunately, *X*-ray structural data are available for some of the antimony complexes or for the corresponding complexes of arsenic.

For the three $Sb(S_2CNEt_2)_2X$ complexes similar δ, e^2qQ, and η values were obtained despite differences in the electronegativity of X. This suggests that there is very weak bonding between the antimony and the halide. While *X*-ray structural data have not been reported for any of these antimony complexes, such information is available for another Group 5A complex, $AsBr(S_2CNEt_2)_2$.[25] Since the i.r. spectra for $SbBr(S_2CNEt_2)_2$ and $AsBr(S_2CNEt_2)_2$ are similar,[5] it is probable that their structures are also similar. The As–Br bond distance is 0.3 Å longer than expected for normal bonding. The other pertinent structural information is that one of the dithiocarbamates is bidentate while the other is anisobidentate with As–S distances of 2.27 and 2.82 Å. If the one weak As–S bond and the weak As–Br bond are disregarded, the resulting structure is a distorted trigonal complex with probably a sterically active lone pair in the axial position.

Inert electrons having no steric properties are expected to occupy a spherical orbital made up of a 5*s* electron contribution and equal contributions from each of the 5*p* orbitals. When a sterically active lone pair is formed, as we believe happens in $Sb(S_2CNEt_2)_2X$, it occupies a directional orbital made up of a 5*s* contribution, but unequal contributions from the 5*p* orbitals. The very small increase in e^2qQ and in δ, which is observed when the data for $Sb(S_2CNEt_2)_3$ and $Sb(S_2CNEt_2)_2X$ are compared, indicates the similarity of these species. The average increase in δ is 0.8 mm s^{-1}, suggesting a decrease in the *s* character of the lone-pair orbitals in going from $Sb(S_2CNEt_2)_3$ to $Sb(S_2CNEt_2)_2X$.

The three $Sb(S_2CNEt_2)X_2$ complexes have Mössbauer parameters which are quite different from each other: the isomer shift does not change, but the quadrupole-coupling constant increases on going from $SbCl(S_2CNEt_2)_2$ to $SbCl_2(S_2CNEt_2)$, whereas the iodo- and bromo-complexes have substantially smaller δ values and small changes in e^2qQ. The chloro-complex may have a structure similar to that reported from *X*-ray structural data for $AsBr_2(S_2CNEt_2)$,[26] which is dimeric with two Br bridges between the two arsenic centres. The two As–Br bridging distances are 2.92 and 3.07 Å compared to the other As–Br distance of 2.40 Å. Since the inductive effects of the chlorides and sulphurs are quite similar, the fact that the δ values for $SbCl_3$, which is known to be trigonal, and $SbCl_2(S_2CNEt_2)$ are equal gives added weight to our conclusion that the chloro-complex has a trigonal structure. The much lower δ values for $SbI_2(S_2CNEt_2)$ and $SbBr_2(S_2CNEt_2)$ can only be explained by their having four normal bond distances. Donaldson *et al.*[17] have reported δ values for a series of $[SbX_4]^-$ complexes in the range of −7 to −8 mm s^{-1} and describe the structures as trigonal bipyramids with a lone pair in the equatorial position.

We can, in summary, describe the bonding for the $Sb(S_2CNEt_2)_{3-n}X_n$ complexes in terms of normal bond distances which affect the Mössbauer parameters (inside the square parentheses) and weak bonds which have little effect (outside the square parentheses), as follows (where E is a sterically active lone pair):

Complex	Structure
$Sb(S_2CNEt_2)_3$	$[SbS_3E]S_3$
$Sb(S_2CNEt_2)_2X$	$[SbS_3E]SX$
$Sb(S_2CNEt_2)X_2$	$[SbS_2XE]X_2$ (X = Cl)
	$[SbS_2X_2E]$ (X = Br or I)
SbX_3	$[SbX_3E]$

One final observation is the apparently large Mössbauer fractions (see Tables 1 and 2) for these molecular crystals, which are in the range of 0.25—0.45. We have no explanation for these values at this time.

We thank Drs. J. A. Cras, J. Willemse, H. A. Meinema, and J. G. Noltes, and Mr. A. I. Martens for providing us with the antimony dithiocarbamates and for stimulating discussions.

[8/252 *Received*, *13th February*, 1978]

REFERENCES

[1] G. G. Long, J. G. Stevens, R. J. Tullbane, and L. H. Bowen, *J. Amer. Chem. Soc.*, 1970, **92**, 4230.

[2] R. G. Goel, J. N. R. Ruddick, and J. R. Sams, *J.C.S. Dalton*, 1975, 67.

[3] N. Bertazzi, T. C. Gibb, and N. N. Greenwood, *J.C.S. Dalton*, 1976, 1153.

[4] F. Bonati and R. Ugo, *J. Organometallic Chem.*, 1967, **10**, 257.

[5] G. E. Manoussakis, C. A. Tsipis, and C. C. Hadjikostas, *Canad. J. Chem.*, 1975, **53**, 1530.

[6] H. A. Meinema and J. G. Noltes, *J. Organometallic Chem.*, 1970, **25**, 139.

[7] J. Willemse, J. A. Cras, J. J. Steggerda, and C. P. Keijzers, *Structure and Bonding*, 1976, **28**, 83.

[8] J. C. May, D. Petridis, and C. Curran, *Inorg. Chim. Acta*, 1971, **5**, 511.

[9] J. Ensling, Ph. Gutlich, K. M. Hasselbach, and B. W. Fitzsimmons, *J. Chem. Soc. (A)*, 1971, 1940.

[10] J. L. K. F. de Vries and R. H. Herber, *Inorg. Chem.*, 1972, **11**, 2458.

[11] C. W. Allen and D. B. Brown, *Inorg. Chem.*, 1974, **13**, 2020.

[12] D. Petridis and B. W. Fitzsimmons, *Inorg. Chim. Acta*, 1974, **11**, 105.

[13] B. F. Hoskins, R. L. Martin, and N. Rohde, *Austral. J. Chem.*, 1976, **29**, 213.

[14] M. P. A. Viegers, Ph.D. Thesis, University of Nijmegen, 1976.

[15] M. P. A. Viegers and J. M. Trooster, *Phys. Rev.*, 1977, **B15**, 72.

[16] T. E. Cranshaw, *J. Phys. (E)*, 1974, **7**, 122, 497.

[17] J. D. Donaldson, A. Kjekshus, D. G. Nicholson, and M. J. Tricker, *Acta Chem. Scand.*, 1972, **26**, 3215.

[18] L. H. Bowen, in 'Mössbauer Effect Data Index Covering the 1972 Literature,' eds. J. G. Stevens and V. E. Stevens, Plenum, New York, 1973, p. 71.

[19] (*a*) T. B. Brill, G. E. Parris, G. G. Long, and L. H. Bowen, *Inorg. Chem.*, 1973, **12**, 1888; (*b*) L. H. Bowen, G. G. Long, J. G. Stevens, N. C. Campbell, and T. B. Brill, *Inorg. Chem.*, 1974, **13**, 1787; (*c*) L. H. Bowen, J. G. Stevens, and G. G. Long, *J. Chem. Phys.*, 1969, **51**, 2010; (*d*) C. L. Raston and A. H. White, *J.C.S. Dalton*, 1976, 791.

[20] P. J. H. A. M. van de Leemput, J. A. Cras, and J. Willemse, *Rec. Trav. chim.*, 1977, **96**, 288.

[21] G. D. Thorn and R. A. Ludwig, 'The Dithiocarbamates and Related Compounds,' Elsevier, Amsterdam, 1962.

[22] J. A. Cras and J. Willemse, *Rec. Trav. chim.*, 1978, **97**, 28.

[23] T. P. Das and E. L. Hahn, *Solid State Physics Suppl.* 1, 1958, 196.

[24] S. Ogawa, *J. Phys. Soc. Japan*, 1958, **13**, 618.

[25] R. Bally, *Compt. rend.*, 1970, **C271**, 1436.

[26] J. A. Cras, P. J. H. A. M. van de Leemput, J. Willemse, and W. P. Bosman, *Rec. Trav. chim.*, 1977, **96**, 78.