

## $^{121}\text{Sb}$ Mössbauer Spectra for Crown Ether Adducts of Antimony(III) Chloride and Molecular Structure of $\text{SbCl}_3 \cdot 12\text{-crown-4}$

Masashi Takahashi,\* Takafumi Kitazawa and Masuo Takeda

Department of Chemistry, Faculty of Science, Toho University, Miyama, Funabashi, Chiba 274, Japan

The  $^{121}\text{Sb}$  Mössbauer spectra for the crown ether (12-crown-4, 15-crown-5 and 18-crown-6) adducts of antimony(III) chloride at 20 K show that the stereochemical activity of the lone pair of the  $\text{Sb}^{\text{III}}$  atom varies with the antimony-crown ether interaction, which is strongest in the 12-crown-4 adduct having the shortest average Sb–O distance of 2.81(7) Å.

Recently, X-ray crystal structures have been reported for two crown ether adducts of antimony(III) chlorides; 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5)<sup>1</sup> and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) adducts.<sup>2</sup> They have similar structures in which the pyramidal  $\text{SbCl}_3$  molecule is capped with the crown ether and the lone pair of the antimony(III) atom is approximately directed to the centre of the crown ether. The bond distances between the oxygen atoms of the crown ether and the antimony(III) atom are significantly different in the two adducts; the average Sb–O distance is 3.18 Å for  $\text{SbCl}_3 \cdot 18\text{-crown-6}$  and 2.90 Å for  $\text{SbCl}_3 \cdot 15\text{-crown-5}$  suggesting that this is the origin of the difference in stereochemical activity<sup>3</sup> of the lone pair of the antimony(III) atom in the two adducts. We have thus carried out a  $^{121}\text{Sb}$  Mössbauer spectroscopic study on the two adducts and the freshly prepared  $\text{SbCl}_3 \cdot 12\text{-crown-4}$ . In the course of the study we have noted the  $^{121}\text{Sb}$  Mössbauer data by Schäfer *et al.* for  $\text{SbX}_3 \cdot 15\text{-crown-5}$  (X = F, Cl, Br, I).<sup>4</sup>

Fig. 1 shows the  $^{121}\text{Sb}$  Mössbauer spectra of the crown ether adducts and solid  $\text{SbCl}_3$  measured at 20 K with a  $\text{Ca}^{121\text{m}}\text{SnO}_3$  source (16 MBq) using an Austin S-600 Mössbauer spectrometer and a Seiko 7800 multichannel analyser.<sup>5</sup> The isomer shift provides a measure of the 5s electron density on the antimony nucleus. Since  $\Delta R/R$  for  $^{121}\text{Sb}$  is negative, the decrease in the isomer shift means an increase in s electron density. The values of isomer shift ( $\delta$ ; relative to  $\text{InSb}$  at 20 K) for  $\text{SbCl}_3 \cdot 15\text{-crown-5}$  ( $-8.57 \text{ mm s}^{-1}$ ) and  $\text{SbCl}_3 \cdot 18\text{-crown-6}$

( $-6.51 \text{ mm s}^{-1}$ ) are more negative than that for crystalline  $\text{SbCl}_3$  ( $-5.90 \text{ mm s}^{-1}$ ), implying larger 5s electron density for the crown adducts. Since the isomer shifts for  $\text{Sb}^{\text{III}}$  compounds are dominated by the s character of the lone pair, the observed decrease in the isomer shift indicates that adduct formation causes an increase in the s character; *i.e.* a decrease in the stereochemical activity of the lone pair.

The magnitude of the quadrupole coupling interaction is another measure of the stereochemical activity of the lone pair because the electric field gradients of the  $\text{Sb}^{\text{III}}$  compounds are dominated by 5p electrons localized in the lone pair. The values of  $e^2qQ$  for  $\text{SbCl}_3 \cdot 15\text{-crown-5}$  ( $10.2 \text{ mm s}^{-1}$ , which agrees with the reported value<sup>4</sup>) and  $\text{SbCl}_3 \cdot 18\text{-crown-6}$  ( $12.7 \text{ mm s}^{-1}$ ) are smaller than that for solid  $\text{SbCl}_3$  ( $13.1 \text{ mm s}^{-1}$ ), suggesting a reduction in the stereochemical activity of the adducts.

In order to gain further knowledge of the lone pair in the crown ether adducts we prepared a new adduct,  $\text{SbCl}_3 \cdot 12\text{-crown-4}$ .<sup>†</sup> The Mössbauer spectrum for  $\text{SbCl}_3 \cdot 12\text{-crown-4}$  (*d* in Fig. 1) shows a rather symmetric absorption at the most negative velocity. The Mössbauer parameters are  $\delta = -9.10 \text{ mm s}^{-1}$ ,  $e^2qQ = 6.2 \text{ mm s}^{-1}$  and an asymmetry parameter,  $\eta =$

<sup>†</sup> Addition of a dichloromethane solution of purified  $\text{SbCl}_3$  (10 mmol) to an acetonitrile solution of 12-crown-4 (10 mmol, Merck) at 0 °C gave white crystals.

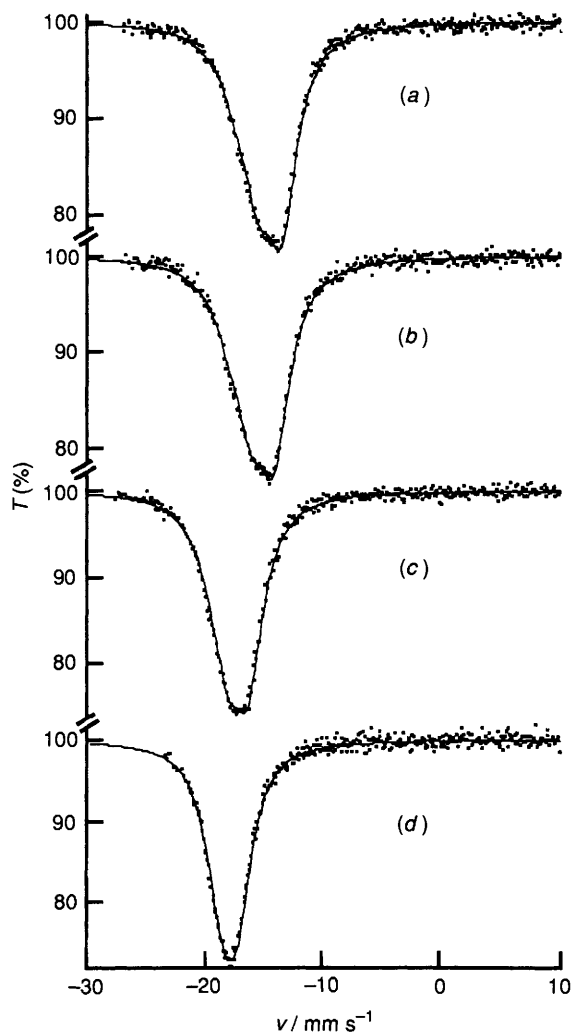


Fig. 1  $^{121}\text{Sb}$  Mössbauer spectra at 20 K for  $\text{SbCl}_3$  and its adducts: (a) crystalline  $\text{SbCl}_3$ , (b)  $\text{SbCl}_3 \cdot 18\text{-crown-6}$ , (c)  $\text{SbCl}_3 \cdot 15\text{-crown-5}$ , (d)  $\text{SbCl}_3 \cdot 12\text{-crown-4}$

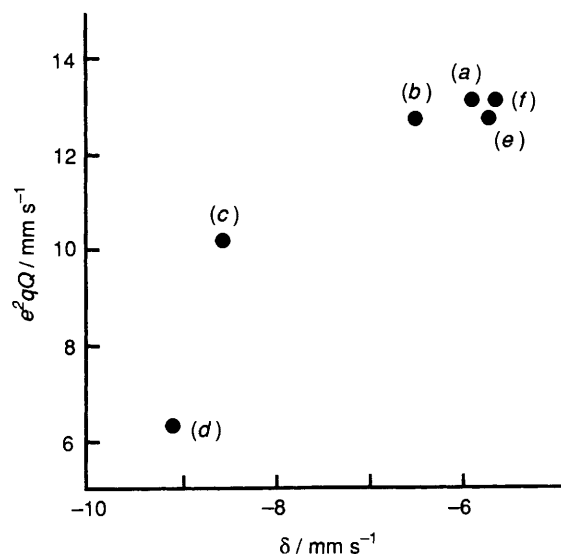


Fig. 2 Plot of  $e^2qQ$  against  $\delta$  for  $\text{SbCl}_3$  compounds: (a) crystalline  $\text{SbCl}_3$ , (b)  $\text{SbCl}_3 \cdot 18\text{-crown-6}$ , (c)  $\text{SbCl}_3 \cdot 15\text{-crown-5}$ , (d)  $\text{SbCl}_3 \cdot 12\text{-crown-4}$ , (e) cumene frozen solution of  $\text{SbCl}_3$ , (f) 1,2-dichloroethane frozen solution of  $\text{SbCl}_3$

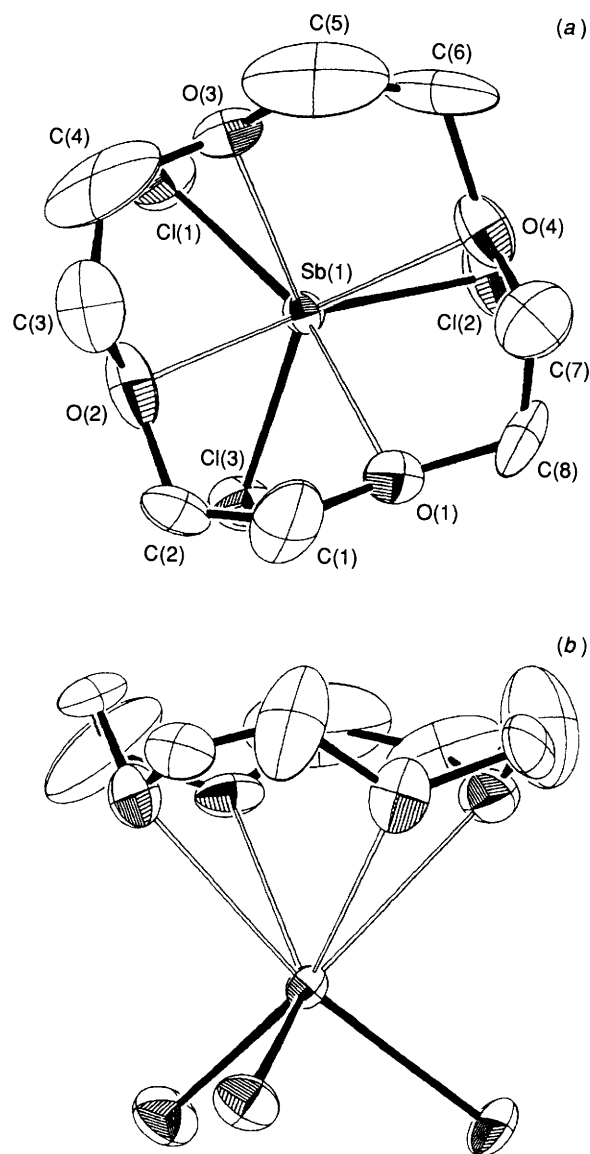


Fig. 3 Molecular structure of  $\text{SbCl}_3 \cdot 12\text{-crown-4}$ : (a) viewed along the direction normal to the mean  $O_4$  plane, (b) viewed along the direction parallel to the mean  $O_4$  plane. Hydrogen atoms are omitted for clarity. **1** is shown. **2** has an equivalent geometry. Principal mean distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) are: Sb-Cl 2.41(2), Sb-O 2.80(5), Cl-Sb-Cl 92.8(3), O-Sb-O(*trans*) 91.0 for **1**; Sb-Cl 2.42(3), Sb-O 2.81(9), Cl-Sb-Sl 92(2), O-Sb-O(*trans*) 90.7 for **2**.

0.66. The values of both  $\delta$  and  $e^2qQ$  are much smaller than those of the 15-crown-5 adduct and are among the smallest values of more than sixty  $\text{Sb}^{\text{III}}$  compounds we have measured, being close to those $\ddagger$  of the octahedral  $[\text{SbCl}_6]^{3-}$  anions with a stereochemically inactive lone pair.<sup>6,7</sup> The present observation suggests the stereochemical activity of the lone pair is considerably decreased in the 12-crown-4 adduct. Interestingly, the value of  $\eta$  becomes larger with the reduction of the stereochemical activity of the lone pair:  $\eta$  values are 0.33, 0.27, 0.53 and 0.66 for crystalline  $\text{SbCl}_3$ ,  $\text{SbCl}_3 \cdot 18\text{-crown-6}$ ,  $\text{SbCl}_3 \cdot 15\text{-crown-5}$  and  $\text{SbCl}_3 \cdot 12\text{-crown-4}$ , respectively. This implies that the electric field gradient is not dominated uniquely by the lone pair.

Fig. 2 is a plot showing a correlation between the values of the isomer shift and the quadrupole coupling constant. We

$\ddagger$  Values for  $[\text{SbCl}_6]^{3-}$  are:  $\delta = -11.06 \text{ mm s}^{-1}$ ,  $e^2qQ = 0.4 \text{ mm s}^{-1}$  for  $[\text{Co}(\text{NH}_3)_6]^{3+}$  salt and  $\delta = -10.25 \text{ mm s}^{-1}$ ,  $e^2qQ = 5.2 \text{ mm s}^{-1}$  for potassium salt.

have already demonstrated that there is a linear relationship between the values of  $\delta$  and  $e^2qQ$  for a large number of antimony(III) compounds,<sup>3</sup> this also holds for the crown ether adducts studied. It is worth noting that the variation of the Mössbauer parameters on adduct formation are quite large compared with those on dissolution of  $\text{SbCl}_3$  in some non-coordinating solvents,<sup>8</sup> which would release intermolecular Sb–Cl interactions in the solid state.<sup>9</sup> This implies that the Sb–O interactions are much more direct and stronger than the intermolecular Sb–Cl interactions and that the Sb–O interactions depend strongly on the capping crown ethers.

An X-ray analysis§ for  $\text{SbCl}_3 \cdot 12\text{-crown-4}$  shows that there are two crystallographically independent molecules (designated as **1** and **2**) having an equivalent geometry. The structural feature of the adduct bears a strong resemblance to those of other  $\text{SbCl}_3$  adducts,<sup>1,2</sup>  $\text{SbF}_3 \cdot 15\text{-crown-5}$ <sup>4</sup> and  $\text{BiCl}_3 \cdot 12\text{-crown-4}$ <sup>10</sup> as shown in Fig. 3. Although the atomic coordinates of the carbon and oxygen atoms of the crown ethers cannot be determined with a large degree of accuracy owing to the thermal motion of the crown ethers, four oxygen atoms are in a plane (mean deviation from the plane: 0.02 Å for molecules **1** and **2**) which is parallel to that containing the three chlorine atoms (dihedral angles between the planes: 176.2° for **1**, 176.3° for **2**). The  $\text{SbCl}_3$  pyramids have very similar dimensions to those in other adducts; Sb–Cl =

2.387(7)–2.425(6) Å, Cl–Sb–Cl = 92.6(3)–93.1(3)° for **1** and Sb–Cl = 2.397(6)–2.461(7) Å, Cl–Sb–Cl = 90.4(2)–94.7(2)° for **2**. In contrast, the Sb–O bond lengths [2.73(2)–2.85(1) Å for **1**, 2.72(1)–2.92(2) Å for **2**; average 2.81(7) Å] are obviously shorter than those of the 15-crown-5 adduct, indicating the stronger Sb–crown ether interactions, which would cause the smaller stereochemical activity of the lone pair. Consequently, the X-ray structure supports the conclusions based on the <sup>121</sup>Sb Mössbauer spectra.

This work was supported in part by a Grant-in-Aid for Scientific Research (No. 04217234) from the Ministry of the Education, Science and Culture of the Japanese Government.

Received, 8th July 1993; Com. 3/03971D

## References

- 1 E. Hough, D. G. Nicholson and A. K. Vasudevan, *J. Chem. Soc., Dalton Trans.*, 1987, 427.
- 2 N. W. Alcock, M. Ravindran, S. M. Roe and G. R. Willey, *Inorg. Chim. Acta*, 1990, **167**, 115.
- 3 M. Takeda, M. Takahashi, R. Ohyama and I. Nakai, *Hyperfine Interactions*, 1986, **28**, 741. The authors have noted that the Mössbauer parameters cited should be slightly larger owing to calibration using an iron foil at 20 K rather than room temp.
- 4 M. Schäfer, J. Pebler, B. Borgsen, F. Weller and K. Dehnicke, *Z. Naturforsch., Teil B*, 1990, **45**, 1243.
- 5 M. Takeda, *Radioisotopes*, 1985, **24**, 628.
- 6 T. Birchall, B. Della Valle, E. Martineau and J. B. Milne, *J. Chem. Soc. (A)*, 1971, 1855.
- 7 J. D. Donaldson, M. J. Tricker and B. W. Dale, *J. Chem. Soc., Dalton Trans.*, 1972, 893.
- 8 M. Yanaga, K. Endo, H. Nakahara, S. Ikuta, T. Miura, M. Takahashi and M. Takeda, *Hyperfine Interactions*, 1989, **52**, 147. The Mössbauer parameters for  $\text{SbCl}_3$  in the frozen solutions were remeasured. The results are:  $\delta = -5.65 \text{ mm s}^{-1}$ ,  $e^2qQ = 13.1 \text{ mm s}^{-1}$ ,  $\eta = 0.16$  for 1,2-dichloroethane and  $\delta = -5.72 \text{ mm s}^{-1}$ ,  $e^2qQ = 12.7 \text{ mm s}^{-1}$ ,  $\eta = 0.16$  for cumene frozen solution.
- 9 A. Lipka, *Acta Crystallogr., Sect. B*, 1979, **35**, 3020.
- 10 N. W. Alcock, M. Ravindran and G. R. Willey, *J. Chem. Soc., Chem. Commun.*, 1989, 1063.

§ Crystal data:  $\text{SbCl}_3 \cdot \text{C}_8\text{H}_{16}\text{O}_4$ ,  $M = 404.32$ , monoclinic, space group  $Pc$  (No. 17),  $a = 12.053(2)$ ,  $b = 7.965(1)$ ,  $c = 15.020(2)$  Å,  $\beta = 90.39(1)^\circ$ ,  $U = 1442.1(6)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.862 \text{ g cm}^{-3}$ ,  $\lambda = 0.71069$  Å,  $\mu(\text{Mo-K}\alpha) = 24.81 \text{ cm}^{-1}$ ,  $F(000) = 792$ ,  $R = 0.027$ ,  $R_w = 0.026$  and goodness of fit = 1.75 for 2478 reflections with  $I > 3\sigma(I)$ . 3546 Unique reflections were collected at room temp. on a Rigaku AFC5S diffractometer in an  $\omega$ -2 $\theta$  scan. The structure was solved by direct methods (MITHRIL) and refined by full-matrix least-squares analysis using a TEXSAN program package. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed at calculated positions. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.