The 'Bare' Sn^{2+} Ion. *X*-Ray Crystal Structure and Mössbauer Spectrum of $(Sn^{2+})(SbF_6^-)_2(AsF_3)_2$

Anthony J. Edwards* and Khalaf I. Khallow

Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B15 2TT, U.K.

The ^{119}Sn Mössbauer spectrum of the title compound shows the highest isomer shift, with no detectable quadrupole splitting, so far recorded for a tin(II) species and the crystal structure reveals a nine co-ordinate arrangement of fluorine atoms around the tin atom, with a distortion in geometry compatible with the presence of the lone pair of electrons.

High ^{119}Sn Mössbauer chemical isomer shifts have previously been correlated with the presence of 'bare' Sn^{2+} ions in compounds. Thus crown ether complexes using either[1] 18-crown-6 or[2] 15-crown-5, show isomer shifts in the range 4.44—4.59 mm s^{-1} and the compound $Sn(SbF_6)_2$ was reported[3] to have an isomer shift of 4.44 mm s^{-1}. In all these cases no quadrupole splitting could be detected and a symmetric environment for the 'bare' Sn^{2+} ion was assumed. In 3-Sn-1,2-$B_9C_2H_{11}$ a very high isomer shift[4] of 4.67 mm s^{-1}, with a large quadrupole splitting of 3.83 mm s^{-1} was assumed to arise from a 'bare' ion in an asymmetric environment, with all neighbouring atoms on one side of the tin atom. No crystallographic studies were reported on any of these compounds. We now report the structure determination of the title compound, which gives the highest isomer shift, with no quadrupole splitting, so far recorded, for a tin(II) species.

The previously reported[3] compound $Sn(SbF_6)_2$ was prepared by direct interaction of SnF_2 and SbF_5. The powdered product was dissolved in AsF_3 and when left, needle-like crystals were obtained. These were shown by *X*-ray crystallography to be the compound $Sn(SbF_6)_2(AsF_3)_2$. A ^{119}Sn Mössbauer spectrum was obtained on a powdered sample of the compound, contained in a Teflon holder, at liquid nitrogen temperature, using a $Ca^{119}SnO_3$ source. The spectrum showed a single peak at $+4.66 \pm 0.01$ mm s^{-1}, line width at half height 0.92 mm s^{-1} [compared with 1.21 mm s^{-1} for $Sn(SbF_6)_2$]. No quadrupole splitting could be detected.

Crystal data: $Sn(SbF_6)_2(AsF_3)_2$, $M = 854$, monoclinic, space group *Pc*, $a = 6.031(7)$, $b = 11.446(4)$, $c = 11.091(3)$ Å, $\beta = 90.39(7)°$, $U = 766$ Å^3, $Z = 2$, $D_c = 3.70$ g cm^{-3}. *X*-Ray data were collected using an Enraf–Nonius CAD4 diffractometer of the Crystallography Unit, Universities of Aston and

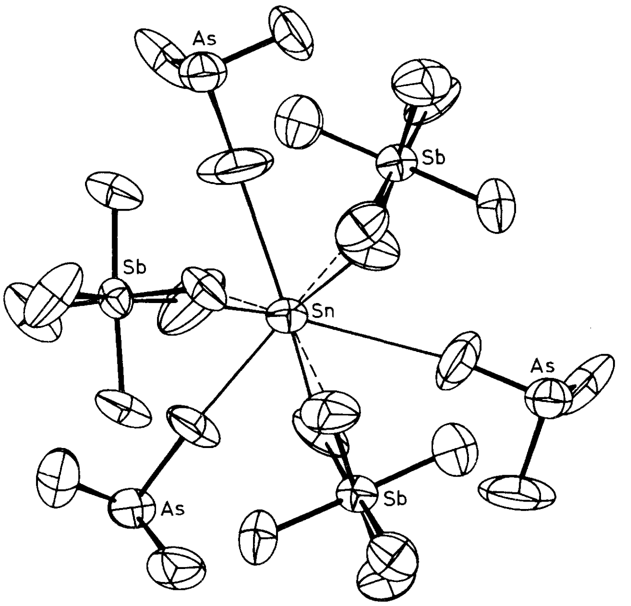

Figure 1. The structural arrangement in projection down the *a* axis. Three $[SbF_6]$ units lie directly under those shown.

Birmingham, and Mo-K_α radiation, with 1895 unique observed reflections $[I > 3\sigma(I)]$ having $2\theta \leqslant 55°$. The structure was solved by direct methods and refined by full-matrix least-squares to a current residual R of 0.054.†

The structural arrangement is shown in Figure 1, with the details of the co-ordination of the tin atom in Figure 2. The bond lengths and bond angles in the SbF_6^- and AsF_3 units are normal, and there is no significant lengthening of Sb–F or As–F distances for fluorine atoms in the tin co-ordination sphere. The tin atom is nine-co-ordinate, with six fluorine atoms from SbF_6^- units at the corners of a trigonal prism and three fluorine atoms from AsF_3 units capping the rectangular faces. These three fluorine atoms and the tin atom are coplanar to ± 0.07 Å. The fluorine atoms defining the three rectangular faces are also coplanar to ± 0.01, 0.08, and 0.06 Å.

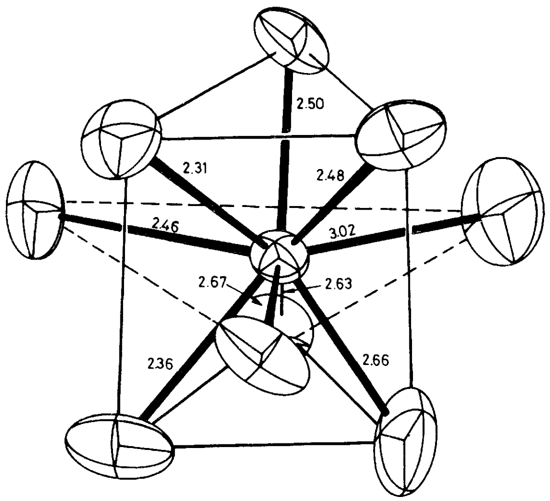

Figure 2. The nine-co-ordination of the tin atom. Distances in Å, e.s.d.s ± 0.02 Å.

The average Sn–F distance is 2.57 Å, compared with the sum of ionic radii of 2.48 Å, but there are significant differences in the individual Sn–F distances. We consider that the distortion in the geometry of the arrangement around the tin atom can be correlated with the presence of the lone pair of electrons, giving a non-spherical Sn^{2+} ion. Thus, the tin atom is equidistant (0.80 and 0.84 Å) from two of the rectangular faces, but further (1.01 Å) from the third face, and the fluorine atom capping this face is furthest from the tin atom, at 3.02 Å, suggesting that the lone pair lies along this direction. Significantly, the two shortest Sn–F distances of 2.31 and 2.36 Å are directly opposite this longest contact.

We thank Mr. J. Holden and Mr. C. Hallett for assistance with the Mössbauer measurements and Mosul University, Iraq for financial support (K. I. K.).

Received, 17th October 1983; Com. 1365

---

† The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Strasse 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.

References

1 R. H. Herber and A. E. Smelkinson, *Inorg. Chem.*, 1978, **17**, 1023.
2 R. H. Herber and G. Carrassquillo, *Inorg. Chem.*, 1981, **20**, 3693.
3 T. Birchall, P. A. W. Dean, and R. J. Gillespie, *J. Chem. Soc. A*, 1971, 1777.
4 R. W. Rudolph and V. Chowdhry, *Inorg. Chem.*, 1974 **13**, 248.