A Study of the Mixed-valency Compound Cs_2SbCl_6 by *X*-Ray Photoelectron Spectroscopy

By **Peter Burroughs, Andrew Hamnett,** and **Anthony F. Orchard,*** Inorganic Chemistry Laboratory, Oxford University, Oxford OX1 3QR

It is shown that the presence of distinct Sb^{III} and Sb^{V} atoms in the mixed-valency compound Cs_2SbCl_6 can be directly demonstrated by *X*-ray photoelectron spectroscopy. The surface purity of the material can be checked by supplementary studies using argon ion bombardment.

THE possibility of applying *X*-ray photoelectron spectroscopy (*X*-p.e. or ESCA) to the study of electron distributions in mixed-valency compounds[1] of the metallic elements has attracted much attention. However, much of the published work (reviewed recently[2]) is difficult to evaluate because of uncertainties regarding the *surface* purity of the solid samples.† It appears that for some systems (certain Fe^{II}/Fe^{III} compounds, for example) one can readily distinguish the two different oxidation states through a differential chemical shift effect, but often (Pb_3O_4 is a case in point) the technique apparently fails to confirm the presence of more than one oxidation state. It is not clear, in the latter cases, whether the *X*-p.e. data reflect a high degree of charge equalisation between the formally distinct oxidation states, or whether the expected resolution of core p.e. signals is prevented by a compensating difference in the Madelung potentials experienced by the two species of metal atom.‡ There is the further possibility that in many of these compounds there is a surface layer

---

† It is clear from a variety of different investigations (*e.g.* refs. 3 and 4) that the average sampling depth of *X*-p.e. spectroscopy is extremely small, typically of the order of 20 Å.

‡ In general, it will not be easy, even when separate core p.e. signals are observed (and one is confident of the surface purity), to gauge the relative importance of these effects. Furthermore, if the characteristic core p.e. band is indeed a doublet, one must examine the possibility that one of the components is due to some secondary process such as 'shake-up', especially if one component is distinctly less intense than the other.

[1] M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.

[2] S. Evans and A. F. Orchard, in 'Electronic Structure and Magnetism of Inorganic Compounds,' *Chem. Soc. Specialist Periodical Report*, 1973, **2**.

[3] C. R. Brundle, in 'Surface and Defect Properties of Solids,' *Chem. Soc. Specialist Periodical Report*, 1972, **1**.

[4] T. A. Carlson and G. E. McGuire, *J. Electron Spectroscopy*, 1972, **1**, 161.

in which one of the oxidation states predominates (perhaps PbO_2 in the case of Pb_3O_4, or Fe_2O_3 in the case of Fe_3O_4).

We report here an exploratory study of the Sb^{III}/Sb^V compound, Cs_2SbCl_6, a mixed-valency system of particular importance since its crystal structure approximates closely to the cubic K_2PtCl_6 structure.[5,6] In other words, the Sb^{III} and Sb^V atoms occupy crystallographically almost equivalent sites and should therefore experience virtually identical lattice potentials. Moreover, it will be shown that one can characterise the surface composition of this material by a careful study of the effects of argon ion bombardment.

The *X*-p.e. spectrum of Cs_2SbCl_6 was first measured by Jørgensen,[7] though only the ionisation energy data were reported. The antimony 3*d* region of the *X*-p.e. spectrum has also been studied by Hamnett and Orchard,[8] and by Thomas and his co-workers.[9] The spectrum obtained in Oxford was very similar to that recorded by Jørgensen, and showed two overlapping Sb 3*d* signals (each of these being a spin–orbit doublet with $3d_{3/2} - 3d_{5/2}$ separation 9·5 eV), the lower ionisation energy signal being distinctly the more intense. The spectrum reproduced by Tricker *et al.*,[9] measured under similar conditions using the same spectrometer model (the A.E.I. ES 100), is significantly different, however, exhibiting just one pair of broad $3d_{3/2}$ and $3d_{5/2}$ bands. The conflict of evidence is resolved by the present work.

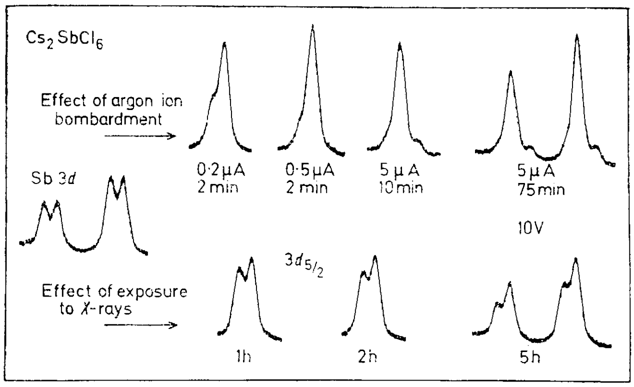

FIGURE 1 Antimony 3*d* region of the *X*-p.e. spectrum of the mixed valency compound Cs_2SbCl_6

EXPERIMENTAL

The *X*-p.e. spectra were obtained with Al-K_α exciting radiation (216 W generating power throughout) using an A.E.I. ES 200 spectrometer: the source region vacuum was always better than 5×10^{-9} Torr. The antimony compounds were studied in the form of pressed pellets clipped to one face of the copper sample probe. Fresh samples of Cs_2SbCl_6 and the Sb^V compound $CsSbCl_6$ were used,[10] and the pellets were made by compression between sheets of aluminium foil. Manufacture in an ordinary stainless steel die apparently resulted in partial reduction of Sb^V to Sb^{III} (see later), the pellets acquiring a yellow colouration due presumably to contamination of the surface by $FeCl_3$.

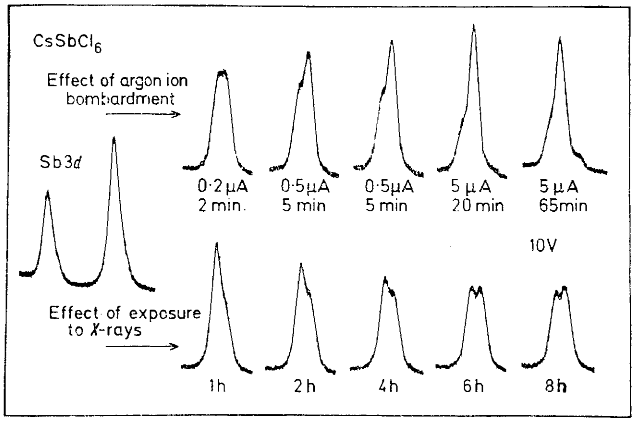

FIGURE 2 Antimony 3*d* region of the *X*-p.e. spectrum of the Sb^V compound $CsSbCl_6$

The signal strength for the antimony 3*d* ionisations was typically 2000—3000 counts s^{-1}. The $3d_{3/2}$ and $3d_{5/2}$ bands were always identical in appearance, indicating that there is no significant contamination of the samples by oxygen (the 1*s* signal of which would occur in the neighbourhood of the Sb $3d_{5/2}$ signal). Argon ion bombardment of the samples was carried out *in situ* with a Physical Electronics Industries Inc. Phi model 20–005 ion gun, operated at 5×10^{-5} Torr argon pressure with 700 V beam voltage. The ion current figures and duration times given in Figures 1—3 are successive, but the *X*-ray exposure times are cumulative.

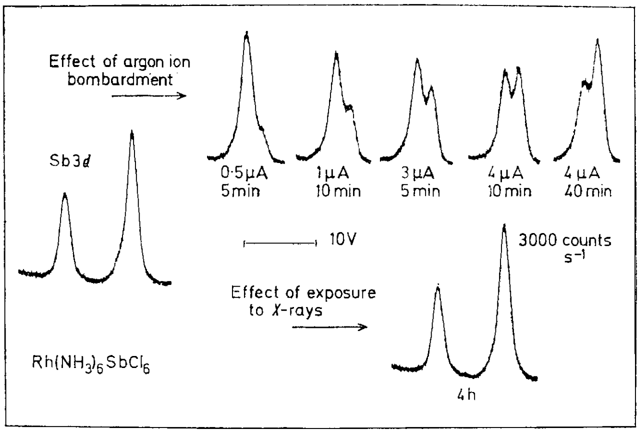

FIGURE 3 Antimony 3*d* region of the *X*-p.e. spectrum of the Sb^{III} compound $Rh(NH_3)_6SbCl_6$

RESULTS AND DISCUSSION

The antimony 3*d* region of the Cs_2SbCl_6 spectrum (Figure 1) shows two sets of $3d_{3/2}$, $3d_{5/2}$ bands having equal intensity and a separation of 1·80 (±0·05) eV.

---

[5] A. T. Jensen and S. E. Rasmussin, *Acta Chem. Scand.*, 1955, **9**, 708.

[6] K. A. Jensen, *Z. anorg. Chem.*, 1937, **232**, 193.

[7] C. K. Jørgensen, *Chimia* (*Switz.*), 1971, **25**, 213.

[8] A. Hamnett and A. F. Orchard, reproduced in ref. 2.

[9] M. J. Tricker, I. Adams, and J. M. Thomas, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 633.

[10] R. F. Weinland and H. Schmidt, *Ber.*, 1905, **38**, 1080.

The two signals must be identified with the chemically inequivalent Sb^{III} and Sb^{V} atoms, the latter presumably ionising at the higher energy. The total half-width (FWHM) of the overlapping bands ($3d_{3/2}$ or $3d_{5/2}$) is *ca.* 3·5 eV, which agrees well with the figure of 3·4 eV quoted by Tricker *et al.*[9] It thus appears that the Aberystwyth group simply failed to resolve the doublet structure reported here. The sample of Cs_2SbCl_6 investigated by Hamnett and Orchard clearly must have been partially reduced at the surface: the spectra obtained from pellets contaminated as a result of compression in a steel die gave similar *X*-p.e. spectra, with the Sb^{V} signal again much reduced relative to that of Sb^{III}.

The antimony 3*d* spectra of $CsSbCl_6$ (Figure 2) and the Sb^{III} compound $Rh(NH_3)_6SbCl_6$ (Figure 3) each show simple $3d_{3/2}$ and $3d_{5/2}$ signals with half widths of about 1·7 eV. These band widths would permit an adequate synthesis of the Cs_2SbCl_6 spectrum.

We have also studied the effects of controlled argon ion etching on the spectra of these compounds. As shown in Figure 1, mild ion bombardment rapidly reduces the surface of the mixed-valency compound to the Sb^{III} state, while prolonged etching at higher power produces an additional peak, presumably due to the formation of antimony metal, *ca.* 2·6 eV away on the low ionisation energy side of each of the $3d_{3/2}$ and $3d_{5/2}$ bands. Evidently the chlorine atoms sputter much more easily than the antimony atoms. The behaviour of $CsSbCl_6$ (Figure 2) and $Rh(NH_3)_6SbCl_6$ (Figure 3) presents a consistent picture. In the case of the Sb^{V} compound it appears that mild etching first produces a surface layer of the mixed-valency compound, though the individual Sb^{III} and Sb^{V} signals are not resolved. The $SbCl_6^{3-}$ salt is particularly sensitive to ion bombardment, and a strong additional Sb 3*d* signal (again probably due to surface antimony) is obtained after only mild etching.

Exposure to the *X*-rays also results in the reduction of Sb^{V} to Sb^{III}, though the photo-reduction proceeds rather slowly at the relatively low *X*-ray generating power that was used. There was no indication of further reduction to Sb^{0}. Notice, in the case of $CsSbCl_6$ (Figure 2), that the Sb^{III} and Sb^{V} signals are well resolved in the mixed-valency surface compound produced by limited *X*-irradiation. Similar *X*-ray photo-reduction of a wide variety of Pt^{IV} compounds has recently been observed.[11]

These additional experiments, in which argon ion bombardment or *X*-irradiation is used to effect a controlled surface reduction, leave us confident that we have a genuine spectrum of Cs_2SbCl_6. The ion etching technique can clearly be of considerable use in connection with *X*-p.e. spectroscopy, though there will be many pitfalls for the unwary, especially those who believe they are simply ' cleaning ' their samples.

We conclude that *X*-ray photoelectron spectroscopy provides direct, unequivocal evidence for the presence of mixed oxidation states in the antimony compound Cs_2SbCl_6. The resolution of the *X*-p.e. spectrum is admittedly less good than that of the ^{121}Sb Mössbauer spectrum, which shows two completely separated primary signals,[12-14] but *X*-p.e. spectroscopy has of course wider application than Mössbauer spectroscopy.

We are grateful to Dr. P. Day for samples [including the $Rh(NH_3)_6SbCl_6$ specimen used in the present work] and discussions, and to the S.R.C. for financial support.

[3/1889 *Received*, 13*th September*, 1973]

---

[11] P. Burroughs, A. Hamnett, J. F. McGilp, and A. F. Orchard, unpublished work.

[12] A. Y. Aleksandrov, S. P. Ionov, A. M. Pritchard, and V. I. Goldanski, *Soviet Physics J.E.T.P.*, 1971, **13**, 13.

[13] J. D. Donaldson, M. J. Tricker and B. W. Dale, *J.C.S. Dalton*, 1972, 893.

[14] T. Birchall, B. Della Valle, E. Martineau, and J. B. Milne, *J. Chem. Soc.* (*A*), 1971, 1855.