A Note on the Alleged Tetravalency of Antimony

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The black diamagnetic [1-3] double salts of tetravalent antimony: $(NH_4)_2SbBr_6$ and Rb_2SbBr_6 which K. A. Jensen [2] found to be cubic, are only pseudocubic. Using a 19 cm Bradley-Jay powder camera, and CoKα X-radiation, we have found that some of the lines which Jensen registered as singlets are in reality doublets. Powder photographs of $(NH_4)_2SbBr_6$, Rb_2SbBr_6 and Cs_2SbBr_6 can be indexed on the basis of a tetragonal lattice with $c/a = 1.43$. In an ideally cubic lattice $c/a = \sqrt{2} = 1.414$, hence the deviation from cubic symmetry, is about 1 % in the tetragonal salts. Rb_2SbCl_6 is strictly cubic. Its diagram, however, shows an abnormally rapid decrease in intensity with increase in glancing angle.

It has been found possible to prepare the following compounds which likewise have a cubic structure: $K_4FeSbCl_{12}$, $(NH_4)_4FeSbCl_{12}$, $Rb_4FeSbCl_{12}$ and $Cs_4FeSbCl_{12}$, all of which are yellow, and $(NH_4)_4InSbCl_{12}$ and $(NH)_4TlSbCl_{12}$, which are white or slightly violet.

After ageing for some years, the strictly cubic lattice of $(NH_4)_4FeSbCl_{12}$ is deformed into a tetragonal one with the axial ratio of $c/a = 1.40$. The atoms of this compound can be arranged in the space group $P4/mmm$ and the lattice change interpreted as being due to a transformation from a somewhat disordered arrangement of the Fe and Sb atoms to an ordered arrangement. With a primitive lattice, reflections are theoretically possible for any values of (h, k, l) but $h + k + l$ was found to be even for all the reflections observed except the one with the indices 102. A calculation of the intensities was carried out with the parameters chosen so that all metal-chlorine distances were set equal to 2.40 Å. The calculation showed that for such an arrangement the reflections with $(h+k+l)$ even would generally be of observable magnitude, while the 102 reflection would be the only one with an odd index sum strong enough to be found. It could be called a superlattice line of an I_4/mmm lattice.

It seems reasonable on the basis of the crystallographic data to ascribe the formula $Me_4Sb^{III}Sb^{V}X_{12}$ to the formally tetravalent black antimony compounds. In the tetragonal salts we assume an ordered arrangement of the trivalent and of the pentavalent antimony atoms, in Rb_2SbCl_6 a somewhat disordered arrangement.

Ephraim and Weinberg [4] have prepared a black cubic compound to which they ascribe the curious formula $9NH_4Cl$, $2FeCl_3$, $3SbCl_4$. Their compound is in reality a mixed crystal of a black salt, $Me_4Sb^{III}Sb^{V}X_{12}$ with a yellow salt of our new type $Me_4Fe^{III}Sb^{V}X_{12}$.

Jensen's theory [5] for the black colour of the tetravalent antimony compounds depicts a crystal of the salts as a single resonating system. This theory seems untenable in its present form since it assumes all antimony atoms in a crystal to be structurally equivalent, which in fact, they are not.

The following lattice constants have been found:

Cubic salts.

$K_4FeSbCl_{12}$	$a = 9.931$ Å
$(NH_4)_4FeSbCl_{12}$	$a = 10.01$ Å
$Rb_4FeSbCl_{12}$	$a = 10.18$ Å
$Cs_4FeSbCl_{12}$	$a = 10.22$ Å
$(NH_4)_4InSbCl_{12}$	$a = 10.09$ Å
$(NH_4)_4TlSbCl_{12}$	$a = 10.12$ Å
Rb_2SbCl_6	$a = 10.14$ Å

Tetragonal salts.

$(NH_4)_4FeSbCl_{12}$	$a = 7.098$ Å	$c = 9.915$ Å,	$c/a = 1.397$
$(NH_4)_2SbBr_6$	$a = 7.538$ Å	$c = 10.760$ Å,	$c/a = 1.427$
Rb_2SbBr_6	$a = 7.565$ Å	$c = 10.839$ Å,	$c/a = 1.433$
Cs_2SbBr_6	$a = 7.675$ Å	$c = 10.985$ Å,	$c/a = 1.431$
			$\sqrt{2} = 1.414$

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