The Crystal Structure of $Cs_3Fe_2Cl_9$ *and of* $Cs_3Sb_2Cl_9$

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A successful attempt has been made to obtain a new double chloride of cesium and ferric iron, which was expected to be isomorphous with $Cs_3Sb_2Cl_9$, and this compound as well as $Cs_3Sb_2Cl_9$ has been found to have the $Cs_3As_2Cl_9$ type of structure.

The double chloride $Cs_3Fe_2Cl_9$ was prepared by mixing solutions of cesium chloride and ferric chloride both in concentrated hydrochloric acid. The crystal of this compound was found under the microscope to be shaped like hexagonal plates and brownish orange in color, the larger crystals looking dark red to the naked eye. Under the polarizing microscope the crystal was found to be uniaxial. The crystal is stable if kept dry, but on exposure to moist air it is readily converted into the known double chloride $Cs_2FeCl_5 \cdot H_2O$ Accordingly, the accurate determination of density of this compound was not successful, but it was confirmed that this compound has a density higher than that of bromoform, 2. 9.

It is known that the three arrangements $A_3B_2X_9$ are those typified by $Cs_3As_2Cl_9$,[1] $Cs_3Tl_2Cl_9$[2] and $Cs_3W_2Cl_9$[3]. Powder photographs of these three compounds as well as those of $Cs_3Fe_2Cl_9$ and $Cs_3Sb_2Cl_9$ were prepared, Cu K_α radiation ($\lambda=1.542$Å) being used except in the case of $Cs_3Fe_2Cl_9$ in which Fe K_α radiation ($\lambda=1.937$Å) was used. In order to avoid decomposition by atmospheric moisture during the preparation of the photograph, $Cs_3Fe_2Cl_9$ crystals were ground under the mother liquor, sealed together with the liquor in a thinwalled capillary of borosilicate glass of diameter 0. 5mm., and then immersed in an X-ray beam. The similarity of $Cs_3Fe_2Cl_9$ and $Cs_3Sb_2Cl_9$ in the diffraction pattern suggested that the structure of these compounds belongs to the same type.

The cell dimensions derived are:

	a	*c*
$Cs_3Fe_2Cl_9$	7. 28±0. 05Å	8. 90±0. 05Å
$Cs_3Sb_2Cl_9$	7. 61±0. 05Å	9. 32±0. 05Å

The calculated densities are 3. 37 and 3. 41 respectively, with one formula unit per unit cell in each case. The observed intensities of reflection of $Cs_3Fe_2Cl_9$ and $Cs_3Sb_2Cl_9$ are well accounted for by means of the space group $D_{3d}^3-P\bar{3}m1$, if the atomic positions are assumed as follows:

1Cs(1) in 1(*a*) : 000
2Cs(2) in 2(*d*) : 1/3 2/3 *z*, etc.
with $z=0.333$
2Fe(or Sb) in 2(*d*) : 1/3 2/3 *z*, etc.
with $z=-0.167$
3Cl(1) in 3(*e*) : 1/2 0 0, etc.
6Cl(2) in 6(*i*) : *xxz*, etc.
with $x=0.167$
$z=-0.333$

As was shown by Hoard and Goldstein[1] in their study on the structure of $Cs_3As_2Cl_9$, a slight distortion from the ideal structure adopted here would cause no essential change in the calculated intensities, but improve the agreement between the observed and calculated values a little.

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