Evidence for Tetragonally Distorted Silver(II) in Complex Fluorides

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Summary Electron spin resonance and diffuse reflectance measurements indicate an elongated tetragonally distorted $[AgF_6]^{4-}$ unit in complex fluorides of type $AgM^{IV}F_6$ (M = Sn, Pb, Zr or Hf).

The tetragonally distorted silver(II) ion doped in various crystal lattices has been known for several years.[1,2,3] We report here the first silver(II) compounds with the fluoride ligands which show a similar arrangement. The analogous copper(II) compounds are well established and are known to exhibit distorted arrangements in which the observed structure appears to be a balance between the electrostatic energy of the arrangement and the repulsion of the ligands which are squeezed together by the distortion.

A series of compounds having the general formula $AgM^{IV}F_6$ (M = Sn, Pb, Zr or Hf) have been prepared by heating Ag_2SO_4 and a complex hexahalide of M^{IV} in a stream of fluorine at 480 °C.[4] For the spectroscopic measurements the air sensitive compounds were sealed under vacuum in silica cells.

For silver(II) complexes in D_{4h} symmetry the octahedral states ^2E_g and $^2T_{2g}$ are split: $^2E_g \rightarrow {}^2A_{1g} + {}^2B_{1g}$ and $^2T_{2g} \rightarrow E_g + {}^2B_{2g}$ and the ^2E_g level will be further split into two Kramer's doublets by spin–orbit interactions. The operation of the Jahn–Teller effect on regular octahedral complexes can give rise to elongated ($^2B_{1g}$ ground state) or compressed ($^2A_{1g}$ ground state) tetragonal arrangements. The nature of the distortion for the complexes considered here can be elucidated from the e.s.r. data[5]. For the elongated form $g_{\parallel} = 2 - 8\lambda/E(^2B_{1g} \rightarrow {}^2B_{2g})$, $g_{\perp} = 2 - 2\lambda/E(^2B_{1g} \rightarrow {}^2E_g)$. For the compressed form $g_{\parallel} = 2$, $g_{\perp} = 2 - 6\lambda/E(^2A_{1g} \rightarrow {}^2E_g)$. The Table lists the principle g values calculated for polycrystalline samples at room temperature. For all the compounds studied the results are consistent with an elongated tetragonal distortion.

Diffuse reflectance spectra of the $AgM^{IV}F_6$ complexes can also be interpreted on the basis of an elongated tetragonally distorted $[AgF_6]^{4-}$ unit. The absorption maxima obtained by computorised curve analyses of the room temperature spectra together with their assignments are listed in the

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	Electronic transition (10^3 cm^{-1})				Principle g-values						
	$^2B_{1g} \rightarrow {}^2A_{1g}$	$^2B_{1g} \rightarrow {}^2B_{2g}$	$^2B_{1g} \rightarrow {}^2E_g$	$^2B_{1g} \rightarrow {}^2E_g$	$g_{\parallel}$	$g_{\perp}$	G (cm^{-1})	Dq (cm^{-1})	Bs (cm^{-1})	Ft (cm^{-1})	λ (cm^{-1})
$AgHfF_6$ and $AgZrF_6$	8·34	13·08	15·23	17·34	2·519	2·143	3·6	−1308	1650	350	−2110
$AgSnF_6$	8·05	11·70	13·70	15·30	2·610	2·153	4·0	−1170	1550	370	−1500
$AgPbF_6$	9·14	12·28	14·35	16·00	2·548	2·132	4·1	−1258	1677	486	−1650

Table. The transition $^2B_{1g} \rightarrow {}^2B_{2g}$ corresponds to 10 Dq. Tetragonal copper(II) fluoride complexes have values of 10 Dq in the range 8·8—9·2 kK[6] and since the crystal field splitting energy would be expected to increase by roughly 50% in the second transition series this transition can be attributed to the second band in all of the compounds. The high energy $^2B_{1g} \rightarrow {}^2E_g$ transition is split into two components by the linear effect of the spin-orbit interaction. The crystal field parameters derived by fitting the absorption maxima to Watanabe's energy eigenvalues for quadrate fields[7] are also included in the Table.

A precise correlation of the extent of distortion in the various compounds studied is complicated by the absence of detailed structural information. However, a number of interesting features emerge. For example, the Sn and Pb complexes are pale blue while the Zr and Hf complexes are dark blue-violet in colour. The intensity of the $^2B_{1g} \rightarrow {}^2B_{2g}$ transition measured in F_R units increases in the order Sn (0·59) < Pb (1·33) < Hf and Zr (6·67). In D_{4h} symmetry *d–d* transitions are parity forbidden but may become allowed through vibronic interactions or by the application of a static distortion which destroys the centre of inversion. It seems likely that the large increase in band intensity on going to the Zr and Hf compounds derives from such a static distortion. An equality in axial bond lengths, reducing the symmetry to C_{4v}, removes the centre of inversion, but is not expected to alter greatly the electronic energy states from those expected for D_{4h}. In fact, the same energy matrices are appropriate for both environments. However, rhombic or similar distortions will allow mixing between many of the D_{4h} states leading to a greater splitting of the ^2E_g level than is possible through spin-orbit interactions. This could explain the unrealistically high value for the spin-orbit coupling constant λ calculated for the Zr and Hf complexes using quadrate field matrix elements.

The degree of rhombic distortion is not sufficiently large for the three principle g-values to be discernible from the e.s.r. signal[8] (Figure), but as the Table shows, further differences between the Zr and Hf compounds and the Sn and Pb compounds are apparent from the values for $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$. The low values ($G < 4$) together with the absence of ^{107}Ag and ^{109}Ag hyperfine structure in the e.s.r. spectra indicate the presence of substantial exchange coupling between Ag^{II} ions in crystallographically non-equivalent sites[9] for the Zr and Hf compounds. This results in a lower and a higher value of g respectively compared to an isolated $[AgF_6]^{4-}$ unit. The Sn and Pb compounds on the other hand, do not have sufficiently high G-values for such interactions to be excluded, but they are clearly less important. The magnitude of such exchange effects is probably closely related to the degree of rhombic distortion and the associated misalignment of the principle axes of the various $[AgF_6]^{4-}$ units in the lattice.

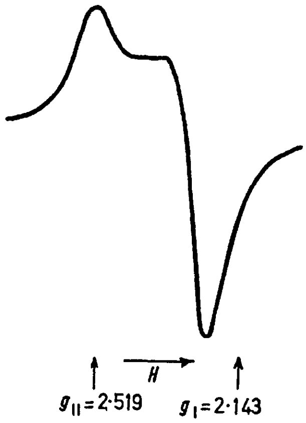

FIGURE. *The room temperature e.s.r. spectrum of (polycrystalline)* $AgZrF_6$

The degree of distortion may simply be related to the size of the counter ion but Zr and Hf are known to have co-ordination numbers greater than six in a number of fluoride lattices[10] and this characteristic could apply to the present compounds.

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