Electron Spin Resonance and Electronic Spectra of Some Silver Hexafluorometallates(IV) and Metal(II) Tetrafluoroargentates(II)

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E.s.r. and diffuse-reflectance spectra have been obtained for the compounds $AgMF_6$ (M = Sn, Pb, Hf, or Zr) and $MAgF_4$ (M = Ba, Ca, Hg, or Sr). The data indicate that all the compounds studied contain the silver(II) ion in either an axially elongated tetragonal or a square-planar arrangement. Possible assignments for the electronic-absorption bands are discussed.

LIMITING formulations for the compounds $MAgF_4$ (M = Ba, Ca, Hg, or Sr) and $AgMF_6$ (M = Sn, Pb, Hf, or Zr) are possible in which either the silver atom has a formal oxidation state of II or two oxidation states are present in a Ag^I–Ag^{III} mixed-valence structure. The compounds $MAgF_4$ when originally prepared[1] were reported to be nearly black, and this led Robin and Day[2] to suggest they might be mixed-valence compounds. In any mixed-valence formulation however the Ag^{III} must have a high-spin configuration since all the compounds under consideration are strongly paramagnetic. More recent preparations of the $MAgF_4$ compounds[3] show that they are in fact violet, whereas the $AgMF_6$ compounds are various shades of blue, ranging from pale blue for Sn to dark blue for the very similar compounds of Zr and Hf. Such colourations might, by analogy with various mixed-valence compounds of Fe and Sb, indicate the presence of intervalence transfer bands in the visible and near-i.r. spectral regions. Nevertheless it is possible that the internal *d–d* transitions of a single-valence silver(II) compound might occur in this region also, and this argument is given some substance by the fact that most copper(II) fluoride compounds have $10Dq$ values[4] in the range 8 800—9 200 cm^{-1} and an energy increase of *ca.* 50% generally occurs for the second transition series.

Powder *X*-ray data are available for both sets of compounds.[3,5] The results for the $AgMF_6$ compounds are complicated and have not yet been fully interpreted, while $MAgF_4$ are shown to be isomorphous with $KBrF_4$. In this structure[6] (Figure 1) all the silver sites are equivalent and have a square-planar co-ordination. It should be remembered, however, that $Cs_2Sb^{III,V}Cl_6$ is isomorphous with $K_2Pt^{IV}Cl_6$, and it may not be possible to detect the fine splitting of lines in powder spectra which would indicate the presence of a superlattice. It is possible that discrete sites exist within the structure with somewhat different Ag–F bond lengths, but nevertheless square-planar stereochemistry is unusual for Ag^I, and Ag^{III} would be expected to be present in a low-spin configuration. In this work, reflectance and e.s.r. spectra are presented and discussed for both series of compounds. The interpretation of these spectra in the light of the available magnetic and *X*-ray structural data is most readily achieved using a single-valence model.

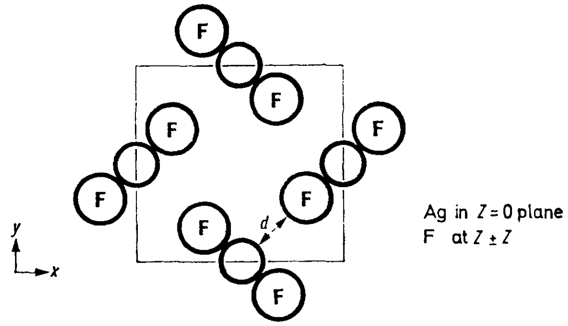

FIGURE 1 The environment of the silver atoms with respect to the fluorine atoms in $MAgF_4$ compounds

EXPERIMENTAL

Samples of the pure compounds were provided by Professor R. Hoppe, University of Giessen, West Germany, and were prepared according to methods already described.[3,5] The compounds were sealed *in vacuo* in silica cells. For reflectance measurements the cells were mounted in a polystyrene block over the sample port of a Beckman DK-2A spectroreflectometer. The intensities are expressed in terms of the Kubelka–Munk function, F_R, defined in equation (1), where $R_{\text{diff.}} = I/I_{\text{std.}}$ is the relative diffuse

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[1] R. Hoppe, *Z. anorg. Chem.*, 1957, **292**, 28.

[2] M. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 361.

[3] R. Hoppe and R.-H. Odenthal, *Naturwiss.*, 1970, **57**, 305.

[4] D. Oelkrug, *Structure and Bonding*, 1971, **9**, 1.

[5] R. Hoppe and B. Müller, *Naturwiss.*, 1966, **56**, 89.

[6] W. G. Sly and R. E. Marsh, *Acta Cryst.*, 1957, **10**, 378.

reflectance referred to a non-absorbing standard, k is the absorption coefficient defined by $I = I_0 e^{-ks}$, and s is the

$$F_R = (1 - R_{\text{diff.}})^2/2R_{\text{diff.}} = k/s \qquad (1)$$

scattering coefficient for the substance in question. Care was taken in each run to ensure that the sample beam shone centrally on the flat face of the silica cell, and also that this face was perpendicular to the beam so that light reflected by the silica returned directly along the path of the beam. Magnesium oxide was used as a standard for the reference beam, either contained in a similar silica cell or in an open Teflon mounting. The former technique has the advantage that it compensates for direct reflection from the silica, giving more reasonable base-line positions, but the use of a silica sample cell in the reference beam reduces its intensity and thus restricts the possible spectral range and resolution. However, since it was usually possible to infer the position of the base line without too much difficulty, the open mounting technique was preferred.

For e.s.r. spectroscopy the cells were inverted and the sample introduced into the stem, which was then inserted into the sample cavity of a Varian E9 e.s.r. spectrometer (9-in magnet). A small sample of powdered diphenylpicrylhydrazyl (dpph) in a silica tube was introduced into the reference cavity and this served as a standard.

RESULTS AND DISCUSSION

Reflectance Data for the Series $AgMF_6$ (M = Sn, Pb, Hf, *or* Zr).—The reflectance spectra recorded for the compounds $AgMF_6$ (M = Sn, Pb, or Hf) are illustrated in Figure 2. The spectrum obtained for the zirconium compound was essentially the same as that obtained for $AgHfF_6$. The overall intensities of the spectra in the visible and near-i.r. covered a wide range, as might be expected from the variation in the depth of colouration of the samples. The degree of resolution and structure shown in the spectra would be unusual for mixed-valence transitions, which are usually broad and featureless, and the splitting between components was too large to arise from exciton transitions.

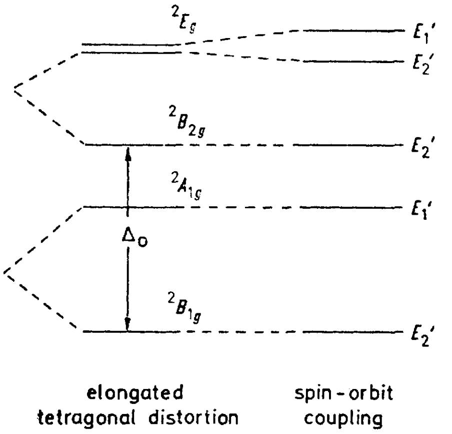

FIGURE 2 Crystal-field energy levels of Ag^{2+} in elongated tetragonal symmetry

The low-energy transitions at 8 000—10 000 cm^{-1} could be due to intervalence transfer, and the higher-energy bands assigned to internal transitions of Ag^{III}, but if the compounds are assumed to contain only Ag^{II} relatively simple assignments can be made in terms of *d–d* transitions for a d^9 system. Octahedral d^9 compounds are generally found to be subject to substantial Jahn–Teller distortion, and the most common stereochemistries for the copper(II) and silver(II) ions are square planar and axially elongated tetragonal.

The crystal-field model for the tetragonally distorted d^9 system including spin–orbit interactions is well established. Strong- and weak-field descriptions are possible. The strong-field matrix elements derived by Liehr [7] but written according to the more recent sign convention for Ds and Dt [8] are given below:

$$\begin{array}{c} \begin{array}{cc} {}^2T_{2g} & {}^2E_g \end{array} \\ \left| \begin{array}{cc} -\dfrac{\lambda}{2} - 4Dq + Ds - 4Dt - E & \left(\dfrac{3\lambda}{2}\right)^{\frac{1}{2}} \\ \left(\dfrac{3\lambda}{2}\right)^{\frac{1}{2}} & 6Dq + Ds + 6Dt - E \end{array} \right| = 0 \end{array}$$

$$\begin{array}{c} \begin{array}{ccc} {}^2T_{2g} & {}^2T_{2g} & {}^2E_g \end{array} \\ \left| \begin{array}{ccc} \lambda - 4Dq - \dfrac{7}{3}Dt - E & \left(\dfrac{2}{3}\right)^{\frac{1}{2}}(5Dt - 3Ds) & 0 \\ \left(\dfrac{2}{3}\right)^{\frac{1}{2}}(5Dt - 3Ds) & -\dfrac{\lambda}{2} - 4Dq - Ds - \dfrac{3}{2}Dt - E & \left(\dfrac{3\lambda}{2}\right)^{\frac{1}{2}} \\ 0 & \left(\dfrac{3\lambda}{2}\right)^{\frac{1}{2}} & 6Dq - 2Ds + Dt - E \end{array} \right| = 0 \end{array}$$

The value and sign of both Ds and Dt will depend on the size and nature of the distortion, but here Ds and Dt increase with increasing axial field. The energy levels of an axially elongated octahedron are shown in Figure 2. The compressed and elongated forms have different ground states and can be distinguished using e.s.r. spectroscopy.

In the elongated tetragonal form the d^9 configuration gives rise to three transitions, $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$, and $^2B_{1g} \rightarrow {}^2E_g$. The $^2B_{1g} \rightarrow {}^2E_g$ transition would be expected to show some splitting by virtue of spin–orbit effects. In the spectrum of $AgSnF_6$ (Figure 3) three bands are readily discernible. The band occurring at *ca.* 12 600 cm^{-1} can be assigned quite readily to the $^2B_{1g} \rightarrow {}^2B_{2g}$ transition, the energy of which is, to a first approximation, $10Dq$. The spectrum of $AgPbF_6$ showed predominantly the same features as that of $AgSnF_6$ and can be similarly assigned. The spectra of $AgHfF_6$ and $AgZrF_6$ on the other hand showed marked differences from those containing the non-transition elements Sn and Pb, which may be related to increased tetragonal distortion or a reduction in symmetry below D_{4h}.

E.S.R. Data for the Series $AgMF_6$ (M = Sn, Pb, *or* Hf).—The room-temperature e.s.r. spectra of the compounds studied are illustrated in Figure 4. *X*-Band

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[7] A. D. Liehr, *J. Phys. Chem.*, 1960, **64**, 43.

[8] R. Krishnamurthy, W. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, 1967, **6**, 1338.

radiation was used and reference resonances are marked in the Figure. In all the spectra the signal was strongly anisotropic with distinctly differing values for $g_{\parallel}$ and $g_{\perp}$. Values for $g_{\parallel}$ and $g_{\perp}$ can be deduced from powder spectra in a semi-empirical manner [9] and these are listed in Table 1. Using these values it is possible to establish the structural configuration of the silver(II) ion. For the elongated form, $g_{\parallel} = 2 - \frac{8\lambda}{E}(^2B_{1g}\rightarrow{}^2B_{2g})$, and $g_{\perp} = 2 - \frac{2\lambda}{E}(^2B_{1g}\rightarrow{}^2E_g)$ while for the compressed form: $g_{\parallel} = 2$ and $g_{\perp} = 2 - \frac{6\lambda}{E}(^2A_{1g}\rightarrow{}^2E_g)$. The g values obtained are in all cases in accord with a tetragonally distorted silver(II) species, and the values obtained for the $g_{\perp}$ components indicate a $d_{x^2-y^2}(^2B_{1g})$ ground state consistent with this structure.

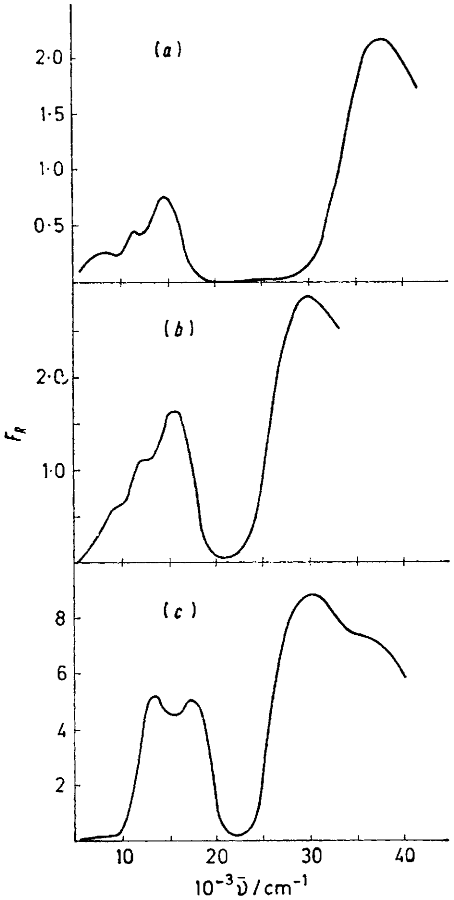

FIGURE 3 Diffuse-reflectance spectra of (*a*) AgSnF$_6$, (*b*) AgPbF$_6$, and (*c*) AgHfF$_6$

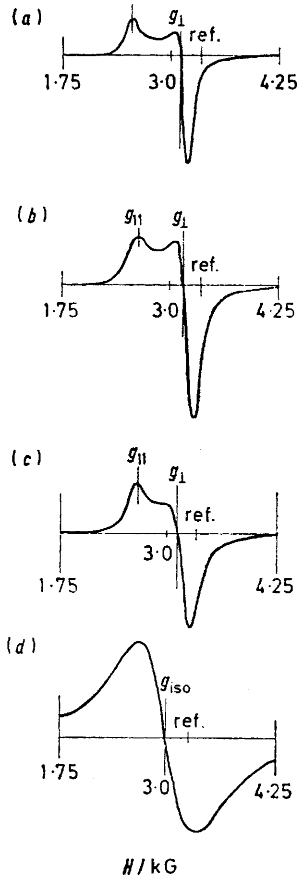

FIGURE 4 E.s.r. spectra of (polycrystalline) samples of (*a*) AgSnF$_6$, (*b*) AgPbF$_6$, (*c*) AgHfF$_6$, and (*d*) AgBaF$_4$

Crystal-field Parameters for the Series AgMF$_6$ (M = Sn, Pb, *or* Hf).—The energies of the *d–d* transitions can be expressed in terms of three crystal-field and one spin–orbit parameter: *Dq*, *Ds*, *Dt*, and λ. Estimation of these parameters would be possible if the spectra could be resolved into component bands, and preliminary results from calculations of this sort have already been published.[10] The spectra were resolved

TABLE 1

g Values, analyzed *d–d* transition energies, and calculated crystal-field parameters

	Electronic transition (10^3 cm^{-1})				Principle *g* values			*Dq*	*Ds*	*Dt*	λ
Compound	$^2B_{1g}\rightarrow{}^2A_{1g}$	$^2B_{1g}\rightarrow{}^2B_{2g}$	$^2B_{1g}\rightarrow{}^2E_g$	$^2B_{1g}\rightarrow{}^2E_g$	$g_{\parallel}$	$g_{\perp}$	*G*	cm^{-1}			
AgHfF$_6$ and AgZrF$_6$	8.34	13.08	15.23	17.34	2.519	2.143	3.6	−1 308	1 650	350	−2 110
AgSnF$_6$	8.05	11.70	13.70	15.30	2.610	2.153	4.0	−1 170	1 550	370	−1 500
AgPbF$_6$	9.14	12.28	14.35	16.00	2.548	2.132	4.1	−1 258	1 677	486	−1 650

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[9] B. J. Hathaway and D. E. Billing, *Co-ordination Chem. Rev.*, 1970, **5**, 143.

[10] G. C. Allen, R. F. McMeeking, R. Hoppe, and B. Müller, *J.C.S. Chem. Comm.*, 1972, 291.

by a computerized curve-fitting technique,[11] and crystal-field parameters calculated using Watanabe's energy eigenvalues for quadrate fields,[12] assuming a first-order splitting for the degenerate ^2E_g level due to spin–orbit effects. A more complete treatment shows that the various fittings obtained for the spectra are by no means unique and a fairly broad range of possible analyses give satisfactory results. Indeed, a detailed analysis of the spectrum of $AgSnF_6$ shows that in order to obtain a unique fit a rather sophisticated model for the chromophore system is required. Such a model must take into account the relative intensities of the various transitions for particular sets of band positions, which involves the calculation of eigenvectors of all the component states and to be realistic must allow for the possible reduction in the symmetry of the system to C_{2v}, either by a static or a vibronic mechanism. Here, account must be taken of possible *d–p* or *d*–(charge transfer) mixing. Such a procedure is hardly justifiable for the kind of spectral information available from reflectance studies. Moreover, the detailed analysis shows that even when definite values are assumed for the component transition energies unambiguous fits for the crystal-field parameters may not be possible. This problem does not arise with the simplified method using Watanabe's matrix elements where it is necessary only to solve four simultaneous equations in four unknowns. A rigorous analysis requires the use of Liehr's 'complete' matrix elements[7] and an optimizational method which varies the crystal-field parameters until agreement is reached between experimental and calculated transition energies. Problems may arise, however, because, although increasing the spin–orbit parameter, λ increases the splitting of the ($^2B_{1g}\rightarrow{}^2E_g$) transition; spin–orbit effects also mix the lower component of the ^2E_g with the $^2B_{2g}$ level, tending therefore to decrease the splitting of the ($^2B_{1g}\rightarrow{}^2E_g$) transition. Thus it may happen that a small splitting of the ^2E_g level can be associated with either a large or a small value of λ.

Table 1 lists the analyzed band positions and crystal-field parameters for $AgSnF_6$, $AgPbF_6$, and $AgHfF_6$. These represent good compromise values. A selection of possible fits for $AgPbF_6$ and $AgHfF_6$ are listed in Table 2 and illustrated in Figure 5. Because of its relatively weak intensity, the position of the low-energy band in the spectrum of $AgHfF_6$ should be treated with caution. It is possible that in a number of analyses the appearance of this particular feature in its exact position reflects the deviation of higher-energy transitions from the band shape used for spectral analysis rather than the nature of any low-energy band present. There remains the possibility that the lowest transition actually present in the spectrum is in the region of 13 000 cm^{-1}. If this were so there is a likelihood of inversion or near coincidence of the $^2A_{1g}$ and $^2B_{2g}$ levels. Such behaviour would indicate a very large tetragonal distortion, approaching the limiting case of square-planar stereochemistry.

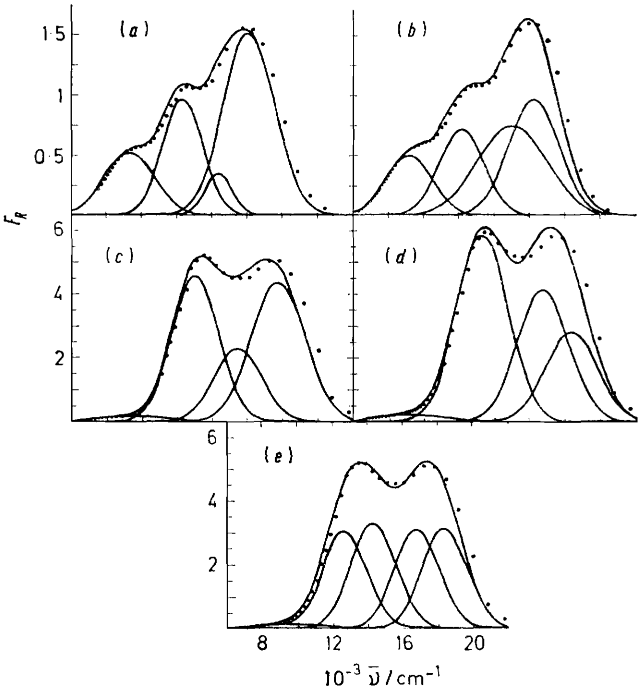

FIGURE 5 Deconvolution of spectrum of $AgPbF_6$ [(*a*) and (*b*)] and of $AgHfF_6$ [(*c*)—(*e*)] using the parameters listed in Table 2

TABLE 2

		Analysed transition energies (10^3 cm^{-1}) *				*Dq*	*Ds*	*Dt*	λ
Compound	Figure	$^2B_{1g}\rightarrow{}^2A_{1g}$	$^2B_{1g}\rightarrow{}^2B_{2g}$	$^2B_{1g}\rightarrow{}^2E_g$	$^2B_{1g}\rightarrow{}^2E_g$	cm^{-1}			
$AgPbF_6$	5 (*a*)	9.14 (9.17)	12.28 (12.20)	14.35 (14.65)	16.00 (15.81)	−1 251	1 620	592	−1 408
	5 (*b*)	8.96 (8.96)	12.02 (12.00)	14.77 (14.79)	16.10 (16.10)	−1 232	1 628	551	−1 590
$AgHfF_6$	5 (*c*)	9.14 (9.14)	12.91 (12.88)	15.34 (15.96)	17.61 (17.37)	−1 319	1 694	530	−1 737
	5 (*d*)	8.90 (8.92)	13.14 (13.11)	16.63 (16.68)	18.26 (18.21)	−1 322	1 781	402	−1 716
	5 (*e*)	14.2 (14.2)	12.5 (12.5)	16.7 (16.7)	18.3 (18.3)	−1 245	2 733	751	−1 216

* Obtained by curve analysis; the figures in parentheses were calculated using crystal-field parameters.

Diffuse-reflectance and E.S.R. Spectra of Compounds $MAgF_4$ (M = Ba, Ca, Hg, *and* Sr).—The diffuse-reflectance and e.s.r. spectra of $BaAgF_4$ are illustrated in Figures 4(*d*) and 6 respectively. The spectra of the remaining compounds are very similar, but the reflectance spectrum of the barium complexes showed the best resolution. Spectral details of all the compounds are presented in Table 3. As Figure 6 shows, there is some resemblance

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[11] G. C. Allen and R. F. McMeeking, unpublished work.

[12] H. Watanabe, 'Operator Methods in Ligand Field Theory,' Prentice-Hall, Englewood Cliffs, New Jersey, 1966, p. 100.

between the spectra of these compounds and those recorded for the series $AgMF_6$ (M = Hf or Zr), but there is, however, a marked difference in the e.s.r. spectra obtained for compounds of the respective series. The e.s.r. spectra recorded for the compounds $MAgF_4$ appear to be almost completely isotropic, an observation which at first is rather surprising for a silver(II) species having an essentially square-planar structure. However, it should be remembered that the unit cell contains groups with their principal axes close to 90° to each other and under these conditions exchange effects between groups might be expected to destroy the anisotropic nature of the e.s.r. signal.[13] Moreover, the g values observed are very similar to $g_{av.}$ for the $AgMF_6$ series, where $g_{av.} = [(g_{\parallel}^2 + 2g_{\perp}^2)/3]^{\frac{1}{2}}$. Thus both X-ray and spectroscopic evidence indicates a single-valence formulation for the silver species in these compounds.

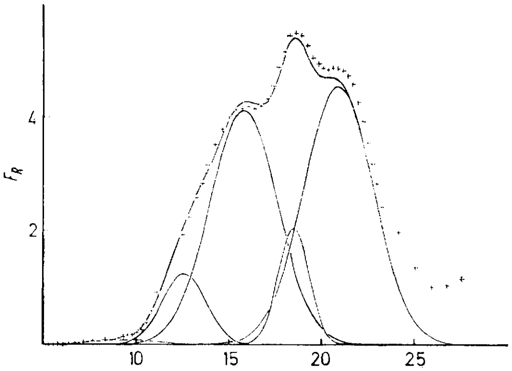

FIGURE 6 Diffuse-reflectance spectrum of $BaAgF_4$

TABLE 3

Compound	Reflectance spectra, peak positions (10^3 cm^{-1})					E.s.r. g value
$BaAgF_4$	15.9,	18.6,	20.9,		36.2	2.30
$SrAgF_4$	15.4,	18.8 (sh),	20.3,		35.8	2.30
$CaAgF_4$	14.9,	18.8 (sh),	19.19	24.5 (sh),	35.5	2.30
$HgAgF_4$	14.6,	19.15,			29.3	2.30

There are a number of possible assignments for the reflectance spectrum of $BaAgF_4$. If the crystal-field splitting of a square-planar compound is considered the bands at 15 900, 18 600, and 20 800 cm^{-1} might be taken to represent the transitions ($^2B_{1g}\rightarrow{}^2B_{2g}$), ($^2B_{1g}\rightarrow{}^2A_{1g}$), and ($^2B_{1g}\rightarrow{}^2E_g$). On this simple model the separation between bands is unrealistically low, but compression of the lattice will tend to increase the co-ordination number of the silver to eight, producing, in the limiting case, a cubic stereochemistry. As a consequence the simple crystal-field energy relation for square-planar stereochemistry will be destroyed. If the position parameters for the various atoms and the unit-cell constants are known, it is possible to calculate the second nearest-neighbour F distances shown as d in Figure 1 provided that an estimate can be made of the Ag–F bond distance in the planar $[AgF_4]^{2-}$ ion. Using the data of Hoppe and Odenthal, and assuming a value of 2.05 Å for the Ag–F distance, the following values can be derived: d = 3.16 for $BaAgF_4$ and 2.77 Å for $CdAgF_4$. Of the compounds studied, these represent those with the largest and smallest unit cells respectively. The distances appear to be rather large to produce a significant crystal-field effect, rendering somewhat untenable a theoretical interpretation based on cubic stereochemistry. Moreover, in practice it is doubtful if a simple crystal-field evaluation of energy levels is of much use even in a nearly square-planar situation where the energy levels are probably described more accurately by molecular-orbital theory. It is not so surprising therefore that judged by these standards the separation of the spectral bands is non-ideal.

By virtue of its position at the end of the second transition series, the spin–orbit coupling constant for the silver(II) ion is relatively large and should not be ignored when assigning and fitting spectra. Accordingly, it is possible that the three bands represent the transitions ($^2B_{1g}\rightarrow{}^2A_{1g}$) and ($^2B_{1g}\rightarrow{}^2E_g$) where the second transition is split by spin–orbit interactions. At first sight this seems improbable since, ignoring parity restrictions, the ($^2B_{1g}\rightarrow{}^2B_{2g}$) transition is allowed by the selection rules (z-polarized) whereas the $^2B_{1g}\rightarrow{}^2A_{1g}$ transition is not. However, spin–orbit interactions could allow mixing between the $^2A_{1g}$ level and one of the components of the ^2E_g level, and if this assignment is correct the observed d–d transitions could gain intensity by mixing with metal–fluorine transitions or possibly, after Fedder,[14] through transitions to F_2 groupings. The higher-energy d–d transitions might be expected to gain intensity from this mechanism due to close proximity with the metal–fluorine transitions. Even so there can be no direct d–d mixing with parity-allowed charge-transfer transitions since the silver atom occupies a centrosymmetric site (D_{2h}). To account for the high intensity of the d–d spectra in this way it is necessary to invoke a vibronic or related mechanism.

It is also possible that the three bands represent charge transfer from non-centrosymmetric F p_π molecular orbitals. For a square-planar model, and assuming the F–F distances to be sufficiently large for Fedder's model not to apply, the out-of-plane p_π orbitals are A_{2u}, E_g, and B_{2u} and the in-plane orbitals are B_{2g}, E_u, and A_{2g}. Thus for a square-planar arrangement there will be two fully allowed charge-transfer ($B_{1g}\rightarrow E_u$ and $B_{1g}\rightarrow B_{2u}$) transitions with a possible extra band appearing either through the $B_{1g}\rightarrow A_{2u}$ transition becoming allowed or by the $B_{1g}\rightarrow E_u$ bands splitting on reduction of the site symmetry to D_{2h}. One problem with this interpretation is that the observed bands might have been expected to be more intense. Also, if this model holds, similar transitions would be expected in the $AgMF_6$ series of compounds which is not the case if the assignments given earlier are accepted.

Conclusions.—There remains some uncertainty as to

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[13] I. M. Procter, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc.* (*A*), 1968, 1678.

[14] R. C. Fedder, *Phys. Rev.*, 1970, **2**, 32.

the precise values of the appropriate crystal-field parameters, but all the spectra discussed above show certain common features suggesting that the energy levels are similarly disposed in these compounds. Of the series $AgMF_6$, the measurements made for the compounds $AgZrF_6$ and $AgHfF_6$ are the most difficult to rationalize, but if the spectra of the compounds $AgHfF_6$ and $BaAgF_4$ are taken together a close relation is apparent if the assignment involving spin–orbit splitting of the $^2B_{1g}\rightarrow {}^2E_g$ transition is accepted. Here the low-energy band for $AgHfF_6$ is assumed to be at *ca.* 13 000 cm^{-1}. The relation can be illustrated by reference to Figures 5(*e*) and 6. If this assignment is correct the results indicate a positive correlation between the degree of tetragonal distortion and the magnitude of $10Dq$. From a simple crystal-field viewpoint, however, the transition $^2B_{1g}\rightarrow {}^2B_{2g}$ is independent of Ds and Dt, yielding $10Dq$ only. Clearly this ionic model is an oversimplification and if due allowance is made for increased equatorial covalency when the axial crystal field is reduced a corresponding increase in the $^2B_{1g}\rightarrow {}^2B_{2g}$ separation is not unexpected.

The isotropic e.s.r. spectrum observed for the $MAgF_4$ compounds may be taken to indicate exchange coupling between crystallographically non-equivalent ions and interactions of this type could provide a mechanism for the intensification of *d–d* transitions in these centrosymmetric chromophores.

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