Anal. Calcd. for $[PdC_{16}H_{20}N_2S_2](ClO_4)_2$: C, 31.5; H, 3.3; Pd, 17.5. Found: C, 31.1; H, 3.3; Pd, 17.4.

[1,8-Bis-(2′-pyridyl)-3,6-dithiaoctane]-αα′-bipyridine Ruthenium(II) Perchlorate-4-hydrate (XXI).—A solution of XIX (0.08 g.) in ethanol (5 ml.) was added to a solution of ammonium tetrachloro-αα′-bipyridine ruthenate(III) (0.11 g.) in hot water (10 ml.) and the mixture heated on a water-bath for several hours. The color changed gradually from deep-green to light orange brown. Addition of sodium perchlorate then caused separation of the light-brown crystalline complex perchlorate. It was washed with cold water and recrystallized from ethanol–ether.

Anal. Calcd. for $[RuC_{26}H_{28}N_4S_2](ClO_4)_2 \cdot 4H_2O$: C, 37.5; H, 4.4; Ru, 12.2. Found: C, 37.8; H, 4.2; Ru, 12.0.

2,2′-Bis-(2″-pyridylmethylamino)-biphenyl (XXIII).—A solution of pyridine-2-aldehyde (10.7 g.) in ethanol (5 ml.) was gradually added to a vigorously stirred hot solution of 2,2′-diaminobiphenyl (9.2 g.) in ethanol (200 ml.) and glacial acetic acid (100 ml.) in which zinc dust (100 g.) was dissolving. Further additions of ethanol, acetic acid and zinc dust were made during the course of 3 hr. The hot solution was then filtered rapidly and ethanol and excess acetic acid removed by repeated dilution with water and evaporation under reduced pressure. Some crystalline zinc acetate was also removed. Eventually, excess of cold concentrated sodium hydroxide solution was added. The heavy oil which separated was induced to crystallize by the addition of ether. It was recrystallized from ethanol as colorless prisms, m.p. 137°.

Anal. Calcd. for $C_{24}H_{22}N_4$: C, 78.7; H, 6.1. Found: C, 78.3; H, 6.1.

2,2′-Bis-(2″-pyridylmethylamino)-biphenyl Palladium(II) Perchlorate (XXIVa).—A solution of potassium tetrachloropalladate(II) (0.33 g.) in water (15 ml.) was stirred into a solution of XXIII (0.37 g.) in hot ethanol (5 ml.). The bright orange solution obtained was heated to boiling and filtered. Sodium perchlorate was added to the filtrate which was then cooled. The light orange crystals which separated were collected, washed with cold water and dried *in vacuo*.

Anal. Calcd. for $[PdC_{24}H_{22}N_4](ClO_4)_2$: C, 42.9; H, 3.3. Found: C, 42.5; H, 3.4.

2,2′-Bis-(2″-pyridylmethylamino)-biphenyl Copper(II) Chloride-1-hydrate (XXIVb).—A solution of copper(II) chloride-2-hydrate (0.34 g.) in ethanol (8 ml.) was gradually stirred into a solution of XXIII (0.74 g.) in hot ethanol (12 ml.). A deep green solution was obtained from which green crystals deposited on cooling. These were collected, washed with ethanol and dried *in vacuo*.

Anal. Calcd. for $[CuC_{24}H_{22}N_4]Cl_2 \cdot H_2O$: C, 55.5; H, 4.7. Found: C, 55.8; H, 4.6.

2,2′-Bis-(2″-pyridylmethylamino)-biphenyl Copper(II) Perchlorate-2-hydrate (XXIVc).—Sodium perchlorate was added to a warm aqueous solution of XXIVb. Dark green crystals separated. They were collected, washed with water and dried *in vacuo*. When tested they were found to be quite free from chloride ion.

Anal. Calcd. for $[CuC_{24}H_{22}N_4](ClO_4)_2 \cdot 2H_2O$: C, 43.3; H, 3.9. Found: C, 43.3; H, 3.6.

{2,2′-Bis-(2″-pyridylmethylamino)-biphenyl}-α,α′-bipyridine Ruthenium(II) Perchlorate (XXV).—A solution of XXIII (0.37 g.) in ethanol (5 ml.) was added to a solution of ammonium α,α′-bipyridine tetrachlororuthenate(III) (0.42 g.) in hot water (15 ml.). An intense red-violet color quickly developed. The mixture was heated on a water-bath for 1 hr., the color gradually changing to a deep orange-brown. Addition of sodium perchlorate and cooling caused separation of a crystalline precipitate. This was recrystallized from methanol and dried *in vacuo*.

Anal. Calcd. for $[RuC_{34}H_{30}N_6](ClO_4)_2$: C, 49.6; H, 3.7. Found: C, 49.7; H, 3.8.

2,2′-Bis-(8″-quinolylmethyleneamino)-biphenyl (XXVI).—Hot solutions in ethanol of quinoline-8-aldehyde[12] (6 g. in 10 ml.) and 2,2′-diaminobiphenyl (3.5 g. in 10 ml.) were mixed and gently boiled for a few minutes. The product crystallized on cooling. Recrystallized from much ethanol it had m.p. 187°.

Anal. Calcd. for $C_{32}H_{22}N_4$: C, 83.1; H, 4.8. Found: C, 82.5; H, 4.8.

2,2′-Bis-(8″-quinolylmethyleneamino)-biphenyl Copper (II) Perchlorate (XXVII).—A solution of copper(II) perchlorate-6-hydrate (0.37 g.) in ethanol (5 ml.) was added to a hot solution of XXVI (0.46 g.) in ethanol (15 ml.). A deep brown solution resulted. On cooling and scratching the dark-brown crystalline complex perchlorate separated. It was washed with ethanol and dried *in vacuo*.

Anal. Calcd. for $[CuC_{32}H_{22}N_4](ClO_4)_2$: C, 53.0; H, 3.1. Found: C, 53.0; H, 3.5.

Acknowledgments.—The authors gratefully acknowledge the assistance of Miss B. Stevenson, M.Sc., for all the C, H and N analyses recorded in this paper; and, also, the help of Mr. D. StC. Black, B.Sc., in carrying out some of the preparations and measurements.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS]

Magnetic and Spectral Properties of the Spin-Free 3d⁶ Systems Iron(II) and Cobalt(III) in Cobalt(III) Hexafluoride Ion: Probable Observation of Dynamic Jahn–Teller Effects

BY F. A. COTTON AND M. D. MEYERS

RECEIVED MARCH 9, 1960

The electronic (d–d) absorption spectra of the 3d⁶ systems in several salts containing either $[Fe(H_2O)_6]^{+2}$ or $[CoF_6]^{-3}$ have been studied. In all cases this is a distorted or double absorption band contrary to what would be expected assuming Russell–Saunders coupling and ligand fields of regular octahedral symmetry. It is concluded that spin-orbit coupling effects are an order of magnitude too small to account for the observed splittings and that in only a few cases might the splittings be attributable to permanent, ground-state distortion of the octahedra. It is proposed that in most cases these splittings are due to a dynamic Jahn–Teller effect in the electronic excited states. The order of magnitude of the splittings agrees well with a prior theoretical estimate made by Liehr and Ballhausen. The magnetic behavior of Co(III) in K_3CoF_6 is shown to agree well with theoretical predictions contrary to the implication of earlier data.

Introduction

The electronic state and the consequent spectral and magnetic properties of the cobalt ion (Co^{3+}) when octahedrally coördinated and spin-free (*i.e.*, with four unpaired electrons) are of considerable interest. Such ions are known to occur in a few oxide systems. Thus, for example, in the spinels, $MnCo_2O_4$ and $ZnCo_2O_4$, Lotgering has concluded that 5.5 and 15.5%, respectively, of the cobaltic ions are in the spin-free state,[1] and Jonker and van Santen find spin-free cobaltic ions in the perovskite

[1] F. K. Lotgering, *Philips Research Rept.*, 11, 337 (1956).

system (La–Sr)CoO_3.[2] In such oxide systems magnetic interactions render it difficult to derive unequivocal information about the intrinsic magnetic properties of the ions themselves and in fact interpretation of the properties of the ions in these mixed metal oxides depends on prior knowledge or *a priori* assumptions about the intrinsic properties of the metal ions. For spin-free cobaltic ion, such knowledge has not heretofore been available in accurate and detailed form.

In order to study the magnetic and spectral properties of spin-free cobaltic ions, we have examined several salts of CoF_6^{-3} taking precautions to use pure and well-characterized samples.[3a] The CoF_6^{3-} ion is the only known simple complex ion containing spin-free Co^{+3}. In all other known octahedral complexes, including even $Co(H_2O)_6^{+3}$, studied by Freedman, *et al.*,[3b] the cobaltic ion is spin-paired and hence diamagnetic. We also have studied some compounds containing spin-free ferrous ion, a more common and important $3d^6$ system.

Before proceeding to describe and discuss our experimental work we shall summarize briefly the theoretical predictions which may be made about the electronic structure, as manifested in the spectral and magnetic properties, of $3d^6$ ions. The spin-free $3d^6$ configuration occurring in the Fe(II) and Co(III) ions may be treated in the approximation of Russell–Saunders coupling. The free ion ground state is ^5D (and there are no other quintuplet states) which splits into a $^5T_2$ ground state and a ^3E excited state in an octahedral ligand field. Further lowerings of the symmetry will have the effects indicated in the diagram.

$$\begin{array}{cccc} \text{Trigonal } (D_{3d})^{4} & \text{Octahedral } (O_h) & \text{Tetragonal } (D_{4h}) & \text{Rhombic } (D_{2h}) \\ \left.\begin{matrix} E \\ A_1 + E \end{matrix}\right\} \longleftarrow & \left\{\begin{matrix} E \\ T_2 \end{matrix}\right. \begin{matrix} \longrightarrow \\ \longrightarrow \end{matrix} & \begin{matrix} A_1 + B_1 \\ B_2 + E \end{matrix} \begin{matrix} \longrightarrow \\ \longrightarrow \end{matrix} & \begin{matrix} 2A \\ B_1 + B_2 + B_3 \end{matrix} \end{array}$$

Thus for these ions the portion of the electronic spectrum which is due to *d–d* transitions and occurs in the visible or near infrared should have these properties for each ligand field symmetry: for O_h symmetry, only one band; for a trigonally distorted octahedron, only one band; for a tetragonally distorted octahedron, two bands; for a rhombically distorted octahedron also two bands. This covers the effects expected from the static symmetry of the environment. There is, however, a second factor determining the nature of the spectrum in the case of regular octahedral symmetry for the ground state, namely, a possible dynamic Jahn–Teller effect. There is of course a Jahn–Teller effect for the T_2 ground state but. as Van Vleck observed many years ago,[5] this should be rather small. However, for the d^6 case the excited state is also orbitally degenerate, so that a splitting of the potential energy surface and hence a doubling of the absorption band is to be anticipated. Theoretical estimation of the magnitude of this splitting is a formidable task even when a number of approximations are made. Recently, however, Liehr and Ballhausen[6] have performed such a calculation which predicts the separation of the potential energy surfaces to be about 1800 cm.$^{-1}$.

The magnetic properties expected for the spin-free $3d^6$ system have been treated by several authors. For the case of regular octahedral symmetry, the work of Griffith[7] and Figgis[8] on Fe(II) is relevant here. By an extension of Kotani's method they have calculated that the magnetic moment at room temperature should be about 5.6 B.M. Figgis also reports upon the intrinsic temperature dependence of the moment.

Discussion

Magnetic Moments.—Hoppe[9a] previously has reported the Li, Na, K,[9b] Rb and Cs salts of CoF_6^{-3} to have magnetic moments in the range 5.1–5.3 B.M (temperature and limits of error not specified). Our data for K_3CoF_6 and $Ba_3(CoF_6)_2$ are presented in Table I. K_3CoF_6 has a moment of 5.60 ± 0.08 at 298°. The results at 298, 194 and 73° K. follow the Curie–Weiss law with $\mu = 5.63 \pm 0.05$ and $\theta = -10 \pm 2$°K. This concordance with the Curie–Weiss law may, however, be more apparent than real for Figgis' calculations predict some intrinsic variation of μ_{eff} in the range of our measurements if we assume that the spin-orbit coupling constant for Co(III) will be of the order of 100 cm.$^{-1}$. We believe that the results of Hoppe for K_3CoF_6 must be in error. Our moment at room temperature agrees well with

TABLE I

MAGNETIC DATA FOR TWO HEXAFLUOROCOBALTATES

Substances[a]	T (°K.)	$X_M^{corr.b}$ × 10^2	θ (°K.)[c]	μ (B.M.)[c]
K_3CoF_6 (1)	299	1.29	− 8	5.66
	194	1.98		
	73	4.83		
	296	1.31	− 8[d]	5.65
K_3CoF_6 (2)	298	1.25	−12	5.60
	194	1.88		
	73	4.55		
$Ba_3(CoF_6)_2$ (4)	302	2.03	−42	5.29
	194	2.88		
	74	5.90		
$Ba_3(CoF_6)_2$ (5)	301	2.03	−36	5.25
	194	2.96		
	73	6.13		

[a] The numbers in parentheses identify the samples according to the listing in Table I of ref. 3a. [b] Diamagnetic corrections: for K_3CoF_6, − 115 × 10^{-6} c.g.s. units per mole; for $Ba_3(CoF_6)_2$, − 248 c.g.s. units/mole. [c] Obtained, except as noted under (d), from graphical fit of the data to the Curie–Weiss equation, μ (B.M.) = 2.84 $[X_M^{corr.}(T - \theta)]^{1/2}$. [d] $\theta = -8$ assumed. This measurement was made on a separate packing several months after the first three measurements and gives evidence of the stability of the substance when stored in vacuum and of the reproducibility of the measurements.

---

(2) G. H. Jonker and J. H. van Santen, *Physica*, **19**, 120 (1953).

(3) (a) M. D. Meyers and F. A. Cotton, THIS JOURNAL, **82**, 5027 (1960); (b) H. L. Freedman, J. P. Hunt, R. A. Plane and H. Taube, *ibid.*, **73**, 4029 (1951).

(4) In going from O_h to D_{3d} by making one of the 3-fold axes of the octahedron the axis of uniquely high order, the entire set of reference axes is changed. Hence the E upper state in D_{3d} does not correspond directly to the E upper state in O_h.

(5) J. H. Van Vleck, *J. Chem. Phys.*, **7**, 72 (1939).

(6) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, **3**, 304 (1958).

(7) J. S. Griffith, *Trans. Faraday Soc.*, **54**, 1109 (1958).

(8) B. N. Figgis, *Nature*, **182**, 1568 (1958).

(9) R. Hoppe, *Rec. trav. chim.*, **75**, 569 (1956). (b) The value 4.26 B.M. reported by J. T. Grey (THIS JOURNAL, **68**, 605 (1946)) and, unfortunately often quoted, is evidently erroneous.

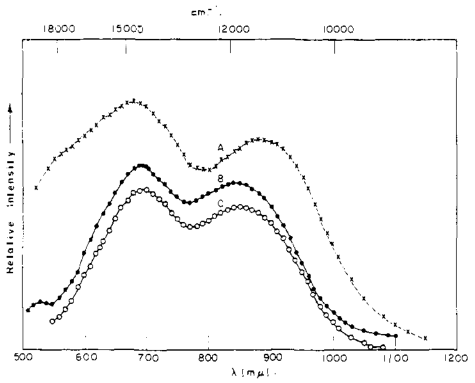

Fig. 1.—Electronic spectra, by reflectance, of Li_3CoF_6 (x-x-x-x-), K_2NaCoF_6 (●-●-●-●-●-●) and Na_3CoF_6 (o-o-o-o-o-).

the predicted[7,8] value (~5.6 B.M.) at room temperature assuming no significant distortion of the CoF_6^{-3} octahedron. X-Ray and infrared studies[3a] have suggested that in this salt there is little if any distortion

$Ba_3(CoF_6)_2$ also appears to follow the Curie–Weiss law with $\mu = 5.27 \pm 0.08$ B.M. and $\theta = -39 \pm 5$. The moment at 300°K. (calculated from the Curie law) is 4.97 B.M. It appears that the most reasonable way to interpret these data is to assume that there is considerable distortion of the octahedra, as evidenced in the X-ray and infrared data,[3a] and also appreciable interionic magnetic interactions as evidenced by the relatively large Weiss constant. If the splitting of the T_{2g} ground state by distortion of the octahedron is appreciable then a genuine Curie–Weiss law dependence may be expected.

Electronic Spectra.—The electronic (d–d) spectra of the Fe(II) complexes and CoF_6^{3-} salts are displayed in Figs. 1–3, and the numerical data are tabulated in Table II. For the spectra in Figs. 1 and 2 the maxima are so well resolved that their positions may be read directly from the curves. The curves in Fig. 3 may each be resolved (approximately) into two Gaussian curves, and it is the maxima for these component Gaussians which are quoted in Table II. The high energy tail on the spectrum of the Tutton salt (Fig. 3) presumably is spurious. Only translucent pressings (see Experimental section) were obtainable with this material, and scattering effects, tending to increase with increasing frequency, were not entirely eliminated.

TABLE II

OBSERVED MAXIMA IN THE ELECTRONIC (d–d) SPECTRA OF SOME Fe(II) AND CoF_6^{-3} COMPOUNDS

Compound	State	Band maxima (cm.⁻¹)		Separation (cm.⁻¹)
K_3CoF_6	Solid	14,500	11,400	3100
Na_3CoF_6	Solid	14,400	11,800	2600
K_2NaCoF_6	Solid	14,400	11,800	2600
Li_3CoF_6	Solid	14,600	11,200	3400
$Ba_3(CoF_6)_2$	Solid	16,700	10,200	6500
Fe^{2+} (aq.)	H_2O	10,400	8,300	2100
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	Solid	10,800	8,400	2400
$FeSiF_6 \cdot 6H_2O$	Solid	10,300	8,700	1600

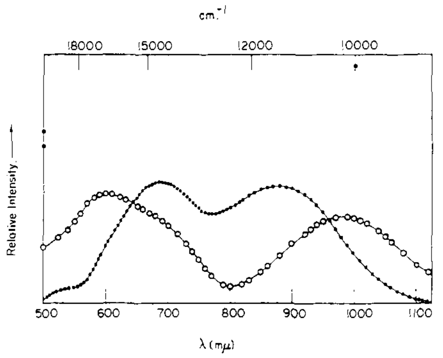

Fig. 2.—Electronic spectra, by reflectance, of K_3CoF_6 (●-●-●-●-) and $Ba_3[CoF_6]_2$ (o-o-o-o-).

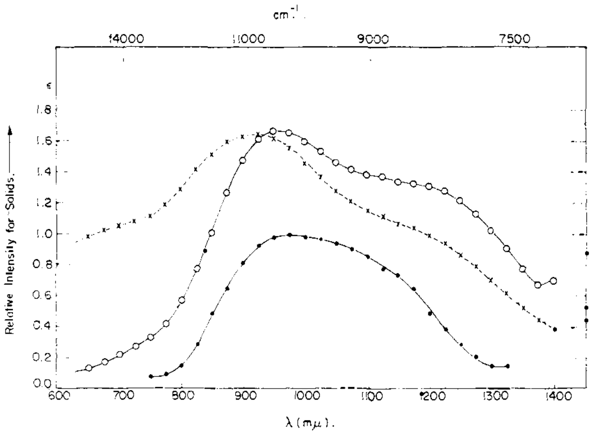

Fig. 3.—Electronic spectra of aqueous Fe^{+2} (o-o-o-o-o-) (to which the numerical values of ε apply), and of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (x-x-x-x-x) and $FeSiF_6 \cdot 6H_2O$ (●-●-●-●-●) for which the intensities (ordinates) are only relative.

As noted in the introduction, a d^6 system in a field of octahedral symmetry should have only one absorption band due to excitation of the d shell electrons, if no account is taken of (1) spin-orbit coupling, (2) static (*i.e.*, permanent, ground state) distortion of the octahedron and (3) Jahn–Teller effects. Since the observed spectra show marked departure from the simple exception of one symmetrical band, we must now consider how these departures may be explained in terms of one or more of the three complicating factors listed above.

We think spin-orbit coupling effects may be discounted for both the Fe(II) and Co(III) cases. For Fe(II) the spin-orbit coupling constant is only -100 cm.$^{-1}$ and it is likely to be of comparable magnitude in Co(III). The observed splittings are 20–30 times this magnitude.

It already has been mentioned that a dynamic Jahn–Teller effect could, according to the estimate of Liehr and Ballhausen,[6] produce a splitting of the right order of magnitude. So, however, could a sufficiently large permanent distortion of the octahedron, since tetragonal and rhombic distortions split the E_g excited state as noted in the introduction. It is necessary, therefore, to consider whether the observed splitting of the absorption bands can be accounted for by existing static distortions. We shall attempt to show that in most cases they cannot and that it must then be concluded that the dynamic Jahn–Teller effect has been observed.

We shall consider first the CoF_6^{-3} salts. K_2NaCoF_6 appears on the basis of X-ray and infrared studies,[3a] to have a rigorously cubic structure, and distortions in K_3CoF_6 cannot, on the same criteria,[3a] be more than slight. Hence, in these two cases there seems no alternative but to assume that the observed splitting is due to the dynamic Jahn–Teller effect. While Na_3CoF_6 appears to have a monoclinically distorted unit cell, this does not necessarily mean that the CoF_6^{-3} octahedra themselves need be appreciably distorted. The envelope of the electronic absorption is essentially identical with the envelopes for K_2NaCoF_6 and K_3CoF_6, and it seems likely that here again the splitting is attributable to the Jahn–Teller effect. Li_3CoF_6 is certainly not cubic and the infrared spectrum suggests that there is some distortion of the CoF_6^{-3} octahedron. As Fig. 2 shows, the envelope of the electronic absorption in Li_3CoF_6 is broader than that for K_2NaCoF_6, K_3CoF_6 and Na_3CoF_6. For $Ba_3(CoF_6)_2$ where the structure as a whole is not cubic and where the octahedra themselves appear to be so distorted that the T_{1u} Co–F stretching mode is actually split, the electronic spectrum is quite different from the spectra in the undistorted salts. It appears quite possible, though of course not completely certain, that the splitting of the electronic absorption in $Ba_3(CoF_6)_2$ may be due to a large static distortion of the octahedron. If the degeneracy of the upper electronic state is effectively removed by such a static distortion, then no Jahn–Teller effect need be considered. It would appear impossible to say with any certainty whether a permanent distortion or a Jahn–Teller effect causes the splitting in Li_3CoF_6.

The spectra of $[Fe(H_2O)_6]^{+2}$ in three different environments are shown in Fig. 3. For the ferrous ion in aqueous solution we know of no reason to expect a significant permanent, ground-state distortion of the octahedron and therefore conclude that the observed splitting is attributable to the dynamic Jahn–Teller effect.

$FeSiF_6 \cdot 6H_2O$ presents a particularly interesting case. X-Ray studies[10] have shown that the crystal is nearly cubic with a rhombohedral distortion, that it contains $[Fe(H_2O)_6]^{2+}$ octahedra which are trigonally distorted and detailed magnetic studies[11,12,13] have confirmed this quite conclusively. Now as noted in the Introduction, a trigonal distortion of the octahedron will leave the upper state degenerate, but again the absorption band is split. There appears then to be no explanation of the splitting except the dynamic Jahn–Teller effect. That the magnitude here is a little different from that in the other cases is not surprising.

The $[Fe(H_2O)_6]^{+2}$ octahedron in the Tutton salt $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ is known to have a distinct tetragonal and a slight rhombic distortion.[14,15] Fe–O distances are 2.14, 1.88 and 1.85 Å. Thus the splitting of the electronic absorption band in this case may be attributable entirely to the splitting of the excited state in this permanently distorted ligand field.

Experimental

The preparation and characterization of the CoF_6^{-3} salts are already described.[3a] Fisher reagent grade $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and Baker and Adamson reagent grade $FeSO_4 \cdot 7H_2O$ were used as obtained. The ferrous solution was prepared by bubbling prepurified nitrogen vigorously through a mixture of 5 g. $FeSO_4 \cdot 7H_2O$, 1 g. of Fisher electrolytic iron powder, 50 ml. distilled water and 5 drops of 36 *N* H_2SO_4. After five minutes the excess iron was removed by filtration. The solution gave no coloration on adding thiocyanate and the spectrum was taken immediately. The concentration was then determined accurately by titration with permanganate. $FeSiF_6 \cdot 6H_2O$ was prepared by dissolving 1.48 g. of Fisher electrolytic iron powder in 11 ml. of 30% H_2SiF_6 in a polyethylene beaker. The mixture was permitted to stand overnight, warmed 2 hr. on a steam-bath and the excess iron was then removed by filtration. On evaporation of the solvent in a desiccator at room temperature, 4.5 g. of pale blue-green crystals were obtained.

Anal. Fe, found, 18.20%; calcd., 18.19%.

Spectra were taken using a Beckman DK recording spectrophotometer and a Beckman DU spectrophotometer. Reflectance spectra were taken on the DU using the standard Beckman reflectance attachment with reagent $MgCO_3$ as a reference blank. Spectra of Fe(II) ion were also taken using the DK. The ferrous sulfate solution was run in the normal manner. The spectra of solid $FeSiF_6 \cdot 6H_2O$ and $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ were obtained by pressing the finely ground powder into thin plates. The fluorosilicate gave a fairly transparent pressing which was run with a comparably transparent pressing of KBr in the reference beam. The Tutton salt consistently gave translucent pressings and the best of these was run with a piece of Nujol-impregnated filter paper placed in each beam of the instrument.[16,17]

The bulk magnetic susceptibility measurements were made with a sensitive Gouy balance. Calibrations were made with Mohr's salt, using Jackson's values[18] and checked with $CuSO_4 \cdot 5H_2O$. The susceptibility values should be accurate to within 2%.

Acknowledgments.—We gratefully acknowledge financial support in the form of the Procter and Gamble Fellowship, 1957–1958, and a Summer NSF Fellowship to M. D. M., and from the U. S. Atomic Energy Commission under contract No. AT(30-1)-1965. We are also grateful to Professor Walter Thorson for informative discussions.

---

(10) R. W. G. Wyckoff, "Crystal Structures," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1953.

(11) L. C. Jackson, *Phil. Mag.*, Series 8, **4**, 269 (1959).

(12) T. Ohtsuka, *J. Phys. Soc. Japan*, **14**, 1245 (1959).

(13) D. Palumbo, *Nuovo Cimento*, Series 10, **8**, 271 (1958).

(14) W. Hückel, "Structural Chemistry of Inorganic Compounds," Vol. II, Elsevier Publishing Co., New York, N. Y., 1950, p. 920.

(15) K. D. Bowers and J. Owen, *Repts. Prog. Phys.*, **18**, 304 (1955).

(16) K. S. Shibata, A. A. Benson and M. Calvin, *Biochem. Biophys. Acta*, **15**, 461 (1954).

(17) D. S. McClure, *Phys. Chem. Solids*, **3**, 311 (1957).

(18) L. C. Jackson, *Phil. Trans. Roy. Soc. (London)*, **A224**, 1 (1923).