PO_2F_2 based on a comparison of the uv and esr spectra with the isoelectronic fluorosulfate free radical SO_3F.[14-17] The latter exhibits a complex uv absorption in the gas phase and its esr spectrum is a single broad line in both the liquid and gas phases. The failure to observe the fluorine hyperfine interaction in SO_3F is attributed to the large magnitude of the line width.[16] A similar argument can be made for the failure to observe the phosphorus and fluorine hyperfine interaction in PO_2F_2.

Other evidence strongly supports the formation of the PO_2F_2 radical in these systems. The persistent orange color observed in the reactions of XeF_2 with $HOPOF_2$ and $P_2O_3F_4$ and the isolation of a small amount of the orange material from the decomposition of $Xe(OPOF_2)_2$ are consistent with the formation of a reactive free radical. The apparent instability of PO_2F_2 in the presence of $HOPOF_2$ is also consistent with the failure to observe the radical by electrolysis of $HOPOF_2$.[18]

The formation of a PO_2F_2 free radical from the decomposition of $FXeOPOF_2$ and $Xe(OPOF_2)_2$ is quite reasonable based on the behavior of the xenon fluorosulfates. All of these including $FXeOSO_2F$,[2] $Xe(OSO_2F)_2$,[1,2] and F_5XeOSO_2F[5] form the peroxide $S_2O_6F_2$[19] on decomposition. These reactions probably involve an intermediate SO_3F radical. The difference between the xenon(II) difluorophosphates and fluorosulfates is that the dimer is stable in the latter case whereas PO_2F_2 is unstable and may be formed only as a minor decomposition product.

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Potassium, Rubidium, Cesium, and Barium Ferrates(VI). Preparations, Infrared Spectra, and Magnetic Susceptibilities

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Potassium, rubidium, and cesium ferrates(VI) have been prepared in high purity and good yield using the corresponding hypochlorite as the oxidizing agent and the corresponding hydroxide as the precipitation medium. Pure barium ferrate(VI) has been prepared by precipitation from a carbonate-free potassium ferrate(VI) solution. Potassium, rubidium, and cesium ferrates(VI) are all isostructural with β-potassium sulfate. The space group is *Pnma* and there are four molecules in the orthorhombic unit cell. The unit cell dimensions are $a = 0.7705$ nm, $b = 0.5863$ nm, $c = 1.0360$ nm for potassium ferrate(VI); $a = 0.8040$ nm, $b = 0.6052$ nm, $c = 1.0665$ nm for rubidium ferrate(VI); and $a = 0.8434$ nm, $b = 0.6289$ nm, $c = 1.1127$ nm for cesium ferrate(VI). The infrared spectra of the four ferrates(VI) have been measured. The temperature-dependent magnetic susceptibility measurements were obtained using the Faraday method over a temperature range of 85–303°K. The magnetic susceptibilities of the four ferrates(VI) were found to obey the Curie–Weiss law and to be field independent. Effective magnetic moments from the Curie–Weiss law were found to be $2.79\ (\pm 0.03) \times 10^{-23}$ A m^2, $2.70\ (\pm 0.03) \times 10^{-23}$ A m^2, $2.67\ (\pm 0.03) \times 10^{-23}$ A m^2, and $2.92\ (\pm 0.03) \times 10^{-23}$ A m^2 for potassium, rubidium, cesium, and barium ferrates(VI), respectively.

Introduction

The preparations of potassium ferrate(VI)[2-5] and barium ferrate(VI)[6-8] are well known. A simple procedure to obtain high-purity rubidium and cesium ferrate(VI)[9] has not, however, been previously reported. A general method for the preparation of the potassium, rubidium, and cesium salts is given below, along with the method used to obtain the barium salt.

The crystal system of K_2FeO_4[8,10] has been known for some time and the infrared spectra of Na_2FeO_4, K_2FeO_4, $SrFeO_4$, and $BaFeO_4$[11-14] have been previously reported. The magnetic susceptibilities of K_2FeO_4 and Cs_2FeO_4[2,15] have been determined by the Gouy method on samples containing ferric hydroxide impurities. The magnetic susceptibilities of K_2FeO_4, $SrFeO_4$, and $BaFeO_4$[16] have recently been determined using a torsion balance magnetometer. However, infrared spectra and adequate temperature-dependent magnetic

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susceptibility data on the pure rubidium and cesium ferrates(VI) were previously lacking. The infrared spectra and magnetic susceptibility determinations of K_2FeO_4, Rb_2FeO_4, Cs_2FeO_4, and $BaFeO_4$ are reported below. The unit cell dimensions of the potassium, rubidium, and cesium salts are also reported.

Throughout this paper the coherent SI units were employed.[17-20] Where the SI units used may be unfamiliar, the corresponding cgs units are reported in parentheses.

Experimental Procedures

Materials.—Reagent grade potassium hydroxide (Fischer), ferric nitrate (Fischer), chlorine (Matheson), rubidium and cesium hydroxides of purity 99% (Alfa), and barium chloride (Fischer) were used as supplied.

General Procedure for the Preparation of K_2FeO_4, Rb_2FeO_4, and Cs_2FeO_4.—To 10 cm^3 of distilled water, 0.10 mol of the appropriate hydroxide was added and the ensuing solution was constantly stirred while being cooled to 273°K in ice. With vigorous stirring, chlorine was slowly bubbled through this chilled solution until a total weight gain of 2.70 g was achieved. The solution temperature was kept below 278°K. The hypochlorite solution was then made strongly basic with the slow addition of 0.23–0.24 mol of the corresponding solid hydroxide. While the solution was constantly stirred, the solution temperature was allowed to rise to 295°K to aid the dissolving of the hydroxide. Finally, the reaction mixture was cooled to 255°K in an ice–sodium chloride bath, and the precipitated alkali metal chloride was removed by filtration through a 60-cm^3 coarse-porosity sintered-glass filter funnel.

While the hypochlorite solution was stirred and its temperature kept below 298°K, 5.0 mmol of pulverized ferric nitrate nonahydrate was added over a period of 15–30 min. The solution was then allowed to react further with an occasional stirring for a period of 1–2 hr at 295°K. Maintaining the temperature below 303°K, the stirred solution was made strongly basic with the addition of the corresponding solid hydroxide (approximately 0.18 mol of KOH, 0.15 mol of RbOH, or 0.20 mol of CsOH). Cooling the solution to below 298°K precipitated most of the ferrate(VI) salt, which was recovered by rapid filtration through a 60-cm^3 coarse-porosity sintered-glass filter funnel.

The precipitate was leached on the filter funnel with five 2-cm^3 portions of the corresponding alkali metal hydroxide solution (3 mol dm^{-3}) which were drawn through the filter into a 5-cm^3 volume of a chilled, saturated solution of the corresponding alkali metal hydroxide. A further 5 cm^3 of saturated alkali metal hydroxide solution was added. The suspension was stirred for 5 min and then rapidly filtered over a coarse-porosity filter funnel. Rapid filtration is important at this time if extensive decomposition of the ferrate(VI) is to be prevented.

The precipitate remaining on the filter funnel was washed with three 10-cm^3 portions of dry benzene in order to remove excess water and then washed with two or three 10-cm^3 portions of absolute methanol.

The removal of excess water with benzene as well as the use of dry methanol for the washings was absolutely essential to obtain a pure ferrate(VI) sample. Failure to remove the water results in the rapid oxidation of the methanol to formaldehyde[21,22] and the associated reduction of the ferrate(VI) ion.

The precipitate was subsequently transferred to 15-cm^3 centrifuge tubes and washed 15–20 times with 15-cm^3 portions of absolute methanol, centrifuging between each washing and decanting off the methanol which contained the dissolved hydroxide, chloride, and nitrate impurities and any suspended ferric hydroxide. Five further washings with 15-cm^3 portions of anhydrous ether were used to dry the precipitate and it was stored in a vacuum desiccator overnight. Twenty further 15-cm^3 washings with absolute methanol were carried out and the precipitate was again dried with five 15-cm^3 portions of anhydrous ether. The ferrate(VI) sample was stored in a vacuum desiccator. All three salts are dark purple.

K_2FeO_4 has been prepared using this method on scales as large as 100 times those described above.

Preparation of $BaFeO_4$.—In this preparation, special care was taken to avoid contact with CO_2 and the temperature was always kept near 273°K.

To 100 cm^3 of 1 mol dm^{-3} potassium hydroxide solution was added a sufficient amount of barium chloride dihydrate to precipitate completely any carbonate present. The barium carbonate formed was removed by filtration through a 60-cm^3 medium-porosity sintered-glass filter funnel. A further 4.2 mmol of barium chloride dihydrate was added and dissolved.

To 50 cm^3 of the barium chloride–potassium hydroxide solution was added 100-cm^3 of conductivity water. With constant stirring, 1.7 mmol of purified potassium ferrate(VI) obtained from the preceding preparation was added to 30 cm^3 of water. The resulting solution was rapidly filtered through a 15-cm^3 medium-porosity sintered-glass filter funnel to remove any trace of ferric hydroxide present. The filtered potassium ferrate(VI) solution was added over a 1–2 min period, with constant stirring, to the barium chloride–potassium hydroxide solution. Barium ferrate(VI) precipitated immediately. The solution was stirred for a further 5 min and rapidly filtered through a 60-cm^3 medium-porosity sintered-glass filter funnel. The precipitate was rapidly washed with eight 60-cm^3 portions of water. After removing as much of the water as possible from the precipitate on the filter funnel, the precipitate was transferred to a weighing bottle. The sample was dried in a vacuum desiccator using a dynamic vacuum for 24 hr. The barium ferrate(VI) recovered was mauve.

All of the ferrates(VI) must be stored in a vacuum desiccator to prevent slow decomposition due to traces of water.

Analysis.—Analyses of potassium, rubidium, cesium, and barium ferrates(VI) were done using the Schreyer, Thompson, and Ockerman[23] chromite method with a slight modification of their procedure. Only small quantities (0.8–1.0 g) of the rubidium and cesium ferrates(VI) were prepared due to the cost of the corresponding hydroxide reagents. The amount of sample used for analyses was approximately 0.05–0.06 g. Analysis required using a microburet (Fischer) of 10.00 ± 0.01 cm^3 capacity and reducing the amount of chromium(III) chloride solution used to 1–2 cm^3 instead of the 3–5 cm^3 recommended, as this large a volume tended to mask the end point of the titration. The above procedure was very reproducible and the average analyses obtained for the samples are in Table I.

TABLE I

	Purity, %	Theoret yield, %
K_2FeO_4	99.86 ± 0.20	50 ± 10
Rb_2FeO_4	99.85 ± 0.20	55 ± 10
Cs_2FeO_4	99.80 ± 0.20	60 ± 10
$BaFeO_4$	99.75 ± 0.20	

The purity of the barium ferrate(VI) was checked also by ir and C–H analysis. The sample was found to be free of carbonate and water.

X-Ray Crystal Structure Analysis of K_2FeO_4, Rb_2FeO_4, and Cs_2FeO_4.—The X-ray diffraction patterns of the potassium, rubidium, and cesium ferrate(VI) salts were obtained using a GE XRD-5 recording diffractometer equipped with an SPG spectrogoniometer and Geiger counter. An Mn-filtered CA8L high-intensity Fe radiation X-ray tube was used for all the diffraction patterns which were recorded from 25 to 75° 2θ with a 0.2°/min spectrogoniometer scanning speed and 1.0 in./min recorder speed.

Infrared Analysis of K_2FeO_4, Rb_2FeO_4, Cs_2FeO_4, and $BaFeO_4$.—Infrared spectra were obtained using a Beckman IR-12 spectrometer with a variable-expanded-scale attachment. The spectra of the four ferrates(VI) were measured using dilute samples in KBr disks.

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Magnetic Susceptibility Measurements of K_2FeO_4, Rb_2FeO_4, Cs_2FeO_4, and $BaFeO_4$.—The temperature-dependent magnetic susceptibility measurements of the four ferrate(VI) samples were determined using the Faraday method as adapted by Hatfield, *et al.*[24] The potassium, rubidium, and barium ferrate(VI) results were obtained using fields provided by a Varian V3703 6-in. electromagnet system with a V2200 regulating magnet power supply and constant force pole caps supplied by Varian Associates.[25] A Cahn RG recording electrobalance and a Sargent-Welch SRG strip chart recording potentiometer were used to make the weighings. The cesium ferrate(VI) results were obtained using fields provided by a Varian 4004 4-in. electromagnet system with constant force pole caps supplied by Varian Associates.[25] Weighings were made with a Cahn Gram electrobalance. The various fields were calibrated using $HgCo(SCN)_4$[26] as a standard.

The temperature range over which the magnetic measurements were made was 85–303°K. The sample temperature was maintained at a fixed value (±0.10°K) for 10–12 min before making a force measurement after a temperature change of approximately 10°K. The constant-temperature device was that of Figgis and Nyholm[27] as modified by Clark and O'Brien[28] and it employed a calibrated copper–constantan thermocouple within the cryostat tube. The thermocouple voltages developed were read from a Hewlett-Packard differential voltmeter for the cesium ferrate(VI) results. A Leeds-Northrup No. 7554 Type K-4 potentiometer and No. 9834 dc null detector were used for the potassium, rubidium, and barium ferrate(VI) results.

All of the measured susceptibilities were corrected for diamagnetism.[29] Using Pascal's constants for K^+, Rb^+, Cs^+, Ba^{2+}, and O^{2-} ions converted to SI units, values of -880×10^{-12} m^3 mol^{-1}, -1105×10^{-12} m^3 mol^{-1}, -1382×10^{-12} m^3 mol^{-1}, and -1005×10^{-12} m^3 mol^{-1} were calculated for the molar diamagnetic susceptibilities of the potassium, rubidium, cesium, and barium ferrates(VI), respectively.

Results and Discussion

Preparation of the Ferrates(VI).—The Thompson, Ockerman, and Schreyer[3] method of preparing 95–98% pure K_2FeO_4 has been widely employed in preparing various ferrate(VI) salts. Gump and Wagner,[9] with an adaption of this method, have been able to prepare samples of Rb_2FeO_4 and Cs_2FeO_4. However, this method of preparation tends to produce rather impure samples (93% Rb_2FeO_4 and 76% Cs_2FeO_4).

The precipitation of $BaFeO_4$ from a K_2FeO_4 solution has been accomplished by several authors.[6–8] However, in all cases the barium ferrate(VI) purity ranges from 81 to 97%, with various contaminants being present. The contaminants include $BaCO_3$, $Fe(OH)_3 \cdot H_2O$, and adsorbed water. Using an adaption of the method of Scholder, *et al.*,[7] Shinjo, *et al.*,[16] have produced samples of $BaFeO_4$. These authors confirmed the absence of any impurity phase using X-ray diffraction techniques, which would not be sensitive to amorphous impurities or 2–3% crystalline impurities. Since these authors used wet alcohol for washing their K_2FeO_4 and $BaFeO_4$, it is probable that their products were contaminated by ferric hydroxide.[21,22]

The preparative methods described in this paper result in much higher purities than reported for previous methods. All of our attempts at preparing pure strontium ferrate(VI) by the method reported by Shinjo, *et al.*,[16] have resulted in samples contaminated with ferric hydroxide.

Crystal Structures of the Alkali Metal Ferrates(VI).—The isomorphism of K_2FeO_4 with K_2SO_4 and K_2CrO_4 has been previously reported[8,10,30] and is confirmed in our studies on the crystal structures of K_2FeO_4, Rb_2FeO_4, and Cs_2FeO_4.

Analysis of the X-ray powder pattern data for the three ferrate(VI) salts is consistent with the ferrates(VI) crystallizing in the orthorhombic β-K_2SO_4 crystal system with the space group D_{2h}^{16} (*Pnma*). The calculated and observed densities are tabulated in Table II and are consistent with a tetramolecular unit cell. The cell parameters were calculated using a least-squares program[31] and are tabulated in Table II.

TABLE II

UNIT CELL DIMENSIONS OF POTASSIUM, RUBIDIUM AND CESIUM FERRATES

	K_2FeO_4	Rb_2FeO_4	Cs_2FeO_4
a, nm	0.7705 ± 0.0006	0.8040 ± 0.0006	0.8434 ± 0.0006
b, nm	0.5863 ± 0.0006	0.6052 ± 0.0003	0.6289 ± 0.0003
c, nm	1.0360 ± 0.0009	1.0665 ± 0.0006	1.1127 ± 0.0006
d_{calcd}, g cm^{-3}	2.81	3.72	4.36
d_{exptl}, g cm^{-3}	2.68	3.57	4.14

The crystal structures of these three ferrate(VI) salts are presently being further refined and will be reported in a subsequent paper.

Infrared Spectra of K_2FeO_4, Rb_2FeO_4, Cs_2FeO_4, and $BaFeO_4$.—The infrared spectra of Rb_2FeO_4 and Cs_2FeO_4 have not previously been investigated. A tetrahedral ferrate(VI) ion should show T_d symmetry, with the two triply degenerate vibrations being infrared active and giving rise to two fundamental bands (ν_3 and ν_4). The symmetric stretching frequencies (ν_1 and ν_2) should be infrared inactive. Due to the appearance of the ν_1 stretch frequency and due to the ν_3 stretch frequency being a triplet, Griffith[14] has suggested that in the case of K_2FeO_4, the site symmetry of the anion is lower than T_d. He suggested that the symmetry is closer to C_s. In their studies on K_2FeO_4 and $BaFeO_4$, Tarte and Nizet[12] came to the conclusion that the presence in their spectra of bands corresponding to absorption modes normally inactive (ν_1 and ν_2) and, in the case of the barium salt, the multiplicity of bands corresponding to the degenerate modes ν_3 and ν_4 suggested that the anions do not totally possess T_d symmetry in K_2FeO_4 and $BaFeO_4$. The deformation was stated to be most important in the $BaFeO_4$ case and of small importance in the K_2FeO_4 case. These authors did not report the ν_3 stretch for K_2FeO_4 to be a triplet but reported it as a singlet (809 cm^{-1}) with a small shoulder (825 cm^{-1}).

The expanded-scale infrared spectra of dilute K_2FeO_4, Rb_2FeO_4, Cs_2FeO_4, and $BaFeO_4$ in KBr disks are shown in Figure 1. The spectrum which we observed for K_2FeO_4 is essentially the same as reported by Tarte and Nizet.[12] In the spectrum of $BaFeO_4$ we did not observe the shoulder at ~790 cm^{-1} which Tarte and Nizet attributed to ν_1. Perhaps the ν_1 band is hidden under the ν_3 band at 777 cm^{-1}.

Tarte and Nizet[12] cautioned against using ν_1 as an indicator for distortion from true T_d symmetry, as their studies showed that these vibrations, in all likelihood, resulted from an antisymmetric coupling of the ν_1

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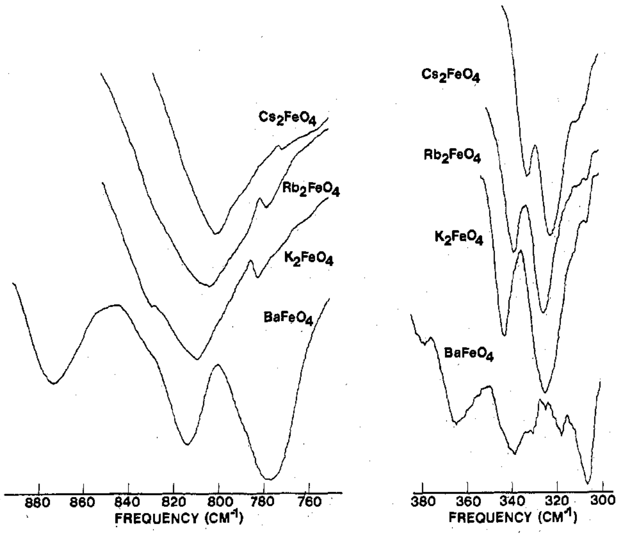

Figure 1.—Expanded-scale infrared spectra of the ferrate(VI) salts.

modes of several identical neighboring anions. The ν_3 and ν_4 stretch modes, therefore, provide a more reliable indicator for any distortion. As can be seen from Figure 1, the spectrum of Cs_2FeO_4 indicates that there is little distortion from T_d symmetry. ν_3 at 800 cm^{-1} is unsplit, ν_1 at 771 cm^{-1} is very weak, and ν_4 (and/or $\nu_4 + \nu_2$) at 310, 322, and 332 cm^{-1} shows the smallest splitting of the four compounds. The appearance of a shoulder on ν_3 for the potassium salt indicates that there is a small but increasing distortion of the ferrate(VI) ion proceeding from the cesium to the rubidium to the potassium salt. The increasing size of ν_1 suggests an increasingly stronger antisymmetric coupling. The barium ferrate(VI) spectrum indicates that the distortion from true T_d symmetry is most pronounced, thus removing the degeneracy of the ν_3 mode. These results are in agreement with those found by Tarte and Nizet.

Magnetic Susceptibilities of the Ferrates(VI).—The magnetic susceptibility of Rb_2FeO_4 has not been previously investigated. Both Hrostowski and Scott[2] and Klemm, *et al.*,[15] have measured the magnetic susceptibility of K_2FeO_4 (97%) containing a ferromagnetic impurity by the Gouy method. Using measurements involving an extrapolation to infinite magnetic field, Hrostowski and Scott[2] have reported an effective magnetic moment of $(2.84 \pm 0.1) \times 10^{-23}$ A m^2 (3.06 ± 0.1 BM) for K_2FeO_4 at room temperature. Klemm, *et al.*,[15] using 50% mixtures of K_2FeO_4 with KCl and K_2SO_4 and extrapolating to infinite magnetic field has found magnetic moments at $(2.55-2.81) \times 10^{-23}$ A m^2 (2.75–3.03 BM) at 90, 195, and 290°K. The magnetic susceptibility of K_2FeO_4 as a function of temperature from 2 to 300°K using a torsion balance magnetometer has been measured by Shinjo, *et al.*[12] They have reported an effective magnetic moment of $(2.76 \pm 0.09) \times 10^{-23}$ A m^2 (2.98 ± 0.1 BM) with a Weiss constant of −18°K and a Néel temperature of 5°K.

Cs_2FeO_4 containing some ferromagnetic impurity has been investigated by Klemm, *et al.*[15] The magnetic susceptibility of Cs_2FeO_4 at 90, 195, and 290°K showed a moment that corresponded to two unpaired electrons. The effective magnetic moment was found to be $(2.53-2.63) \times 10^{-23}$ A m^2 (2.73–2.84 BM). Klemm, *et al.*, reported that the Curie–Weiss law was, in general, obeyed and the cesium salt was found to have a Weiss constant of $\Theta = -25$°K.

$BaFeO_4$ has been recently reported by Shinjo, *et al.*,[16] to have a magnetic moment of $(3.20 \pm 0.09) \times 10^{-23}$ A m^2 (3.45 ± 0.1 BM) with a Weiss constant of −89°K. The magnetic moment for the $SrFeO_4$ prepared by these authors was reported to be $(3.01 \pm 0.09) \times 10^{-23}$ A m^2 (3.25 ± 0.1 BM) with a Weiss constant of −66°K.

We have investigated the magnetic susceptibility of high-purity K_2FeO_4, Rb_2FeO_4, Cs_2FeO_4, and $BaFeO_4$ by the Faraday method from liquid nitrogen temperature to room temperature. The experimental values of $1/\chi_M^{cor}$ for each determination were subjected to a least-squares analysis and the resulting least-squares equations along with their standard deviations are in Table III. The Weiss constants with their standard deviations and the effective magnetic moments calculated from the Curie–Weiss law are also in Table III.

The four ferrates(VI) were observed to follow the Curie–Weiss law of $\mu_{eff} = 7.397 \times 10^{-21}\sqrt{\chi_M^{cor}(T - \Theta)}$ m$^{1/2}$ A deg$^{-1/2}$ mol$^{1/2}$ over the temperature range of 85–303°K. Also, within the experimental error, the magnetic susceptibilities of the ferrates(VI) were found to be field independent.

Shinjo, *et al.*,[16,32] have shown, using Mössbauer and magnetic susceptibility techniques, that the potassium, barium, and strontium ferrate(VI) salts exhibit antiferromagnetic properties. However, Shinjo, *et al.*, have reported from their magnetic susceptibility experiments that the barium and strontium salts have unusually high magnetic moments and very large, negative Weiss constants. As well, all three salts examined indicated deviations from a straight line in the plot of $1/\chi_M^{cor}$ *vs.* T.

The experimental results reported in this paper have shown that, in all cases, when $1/\chi_M^{cor}$ was plotted *vs.* T for the K_2FeO_4, Rb_2FeO_4, Cs_2FeO_4, and $BaFeO_4$ salts, there was no apparent deviation from a straight line (Table III). However, compared to our purest samples, we have experimentally determined that in ferrate(VI) samples containing as little as 1% impurity (consisting of the hydroxide and Fe(III) probably from the decomposition of the ferrate(VI)), the effective magnetic moments were ~10% larger and Weiss constants decreased by ~10°K. As well, deviations from a straight line appeared in the plot of $1/\chi_M^{cor}$ *vs.* T. We suspect that the $BaFeO_4$ and $SrFeO_4$ samples of Shinjo, *et al.*,[16] were contaminated by paramagnetic iron(III) impurities.

Our results for K_2FeO_4 agree reasonably well with those of Shinjo, *et al.*[16] Their Weiss constant of −18°K is appreciably larger than our value (−6.5 to −8.8°K), but from Table III it is evident that Θ is somewhat field dependent and their field was undoubtedly greater than ours. Within experimental errors, our results for μ_{eff} agree with theirs. We find the agreement surprising, in that washing K_2FeO_4 with 95% alcohol, as was done by Shinjo, *et al.*, invariably results in appreciable

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[32] T. Shinjo, T. Ichida, and T. Takada, *J. Phys. Soc. Jap.*, **26**, 1547 (1969).

TABLE III

MAGNETIC SUSCEPTIBILITY DATA OF THE FERRATES(VI)

Compd	Temp range[a]	$\vec{H}(\partial\vec{H}/\partial x)$[b]	No. of observations	Least-squares eq[c]	Θ[d]	μ_{eff}[e]	μ_{eff}[f]
K_2FeO_4	94.3–294.3	1.524	22	$70.17\ (8)T + 619\ (17)$	-8.82 ± 0.24	2.79 ± 0.03	3.01
		1.093	21	$70.31\ (18)T + 512\ (36)$	-7.28 ± 0.51	2.79 ± 0.03	3.01
		0.775	21	$70.45\ (18)T + 457\ (37)$	-6.49 ± 0.52	2.79 ± 0.03	3.01
Rb_2FeO_4	94.8–295.8	1.524	20	$74.78\ (13)T + 288\ (26)$	-3.85 ± 0.35	2.70 ± 0.03	2.92
		1.093	20	$74.72\ (20)T + 269\ (42)$	-3.60 ± 0.56	2.70 ± 0.03	2.92
		0.775	20	$74.81\ (17)T + 270\ (34)$	-3.61 ± 0.46	2.70 ± 0.03	2.92
Cs_2FeO_4	91.4–303.4	3.739	24	$76.86\ (10)T + 470\ (20)$	-6.12 ± 0.26	2.67 ± 0.03	2.88
$BaFeO_4$	93.8–295.4	1.524	21	$64.59\ (6)T + 2339\ (13)$	-36.22 ± 0.21	2.91 ± 0.03	3.14
		1.093	21	$64.09\ (12)T + 2261\ (25)$	-35.27 ± 0.40	2.92 ± 0.03	3.15
		0.775	21	$63.46\ (8)T + 2240\ (16)$	-35.30 ± 0.26	2.94 ± 0.03	3.17

[a] All values are ±0.10°K. [b] Force in units of $10^9 \times (\mathrm{A\ m^{-1}})^2\ \mathrm{m^{-1}}$. [c] From the least-squares analyses of the values of $(\chi_M^{cor})^{-1} \times 10^{-3}$ in units of mol $\mathrm{m^{-3}}$. The standard deviations are in parentheses. [d] Determined from the least-squares analyses. Units are °K. [e] Calculated from the Curie–Weiss law. All values are $10^{-23} \times \mathrm{A\ m^2}$. [f] Units are BM.

reduction of ferrate(VI).[21,22] One possible explanation might be the presence of diamagnetic impurities (*e.g.*, KOH) in their samples which compensate for the presence of Fe(III).

To a first approximation, a $^3A_2$ ground state cannot have orbital contributions to the magnetic moment as the ligand field is able to quench fully the orbital angular momentum. Therefore, for the d^2 tetrahedral ferrate(VI) system the first-order Zeeman effect would predict a spin-only effective magnetic moment of 2.622×10^{-23} A m^2 (2.828 BM).

However, for the ferrate(VI) case, since there is a $^3T_2$ term of the same multiplicity at higher energy, there is a possibility for spin–orbit coupling occurring with the ground state. The effective magnetic moment would then be expressed by the formula[33]

$$\mu_{eff} = \mu_{spin\ only}\left(1 - \frac{4\lambda}{|10Dq|}\right)$$

where λ, the spin–orbit coupling constant, would be positive in sign and it has been estimated to be approximately 330 cm^{-1}.[34] The crystal field splitting energy, $10Dq$, is $-12{,}720$ cm^{-1}.[30,35]

Thus, if there was spin–orbit coupling, the effective magnetic moment would be reduced below the spin-only value by about 0.27×10^{-23} A m^2. The present experimental results show that in all cases the μ_{eff} is larger than, or almost equal to, the spin-only case. Therefore, the possibility of spin–orbit coupling is highly unlikely. This is contrary to what has been predicted by Figgis and Lewis.[36]

In their investigation of the esr spectrum of K_2FeO_4, Carrington, *et al.*,[30] stated that their experimental results indicate that the ground state of the ferrate(VI) ion "must be well isolated from its first excited state and that spin–orbit coupling is ineffective in mixing higher excited states into its ground state." They concluded that their "zero-field splittings observed were largely due to removal of the spin degeneracy by dipole–dipole interactions of the electron magnetic moments." Their experimental results supported the molecular orbital scheme proposed by Ballhausen and Liehr,[37] Viste and Gray,[38] and more recently De Michelis, *et al.*,[35] where the ground state of the ferrate(VI) ion was found to be $^3A_2$, with the first excited state being $^3T_2$ isolated from the ground state by 12,720 cm^{-1}. Thus, the present results are consistent with but not fully explained by those obtained from molecular orbital calculations and esr experiments.

As the effective magnetic moment is larger than the spin-only value, indicating that χ_M^{obsd} is larger than $\chi_M^{spin\ only}$, there is a possibility that there is a small temperature-independent paramagnetism present due to the second-order Zeeman effect. This has been predicted and observed for the magnetic behavior of ions possessing A and E ground states.[39]

The molar susceptibility for an A_2 ground state taking into account spin–orbit coupling, temperature-independent paramagnetism, and electron delocalization may be expressed as[40]

$$\chi_M = \chi_M^{spin\ only} - \frac{8k^2\lambda_0}{|10Dq|}\chi_M^{spin\ only} + \frac{32\pi k^2 N\beta^2}{|10Dq|}$$

Since the second term on the right-hand side is always numerically larger than the third term, a value of χ_M greater than $\chi_M^{spin\ only}$ cannot be accounted for. Therefore, other factors such as ligand field distortion, inaccurate diamagnetic corrections, antiferromagnetic interactions, ferromagnetic interactions, or e delocalization[41] may be contributing to χ_M^{obsd}.

We have made several attempts to prepare dilute mixed crystals of K_2FeO_4 in K_2SO_4. In all cases the ferrate(VI) partially decomposed. If a dilute solid solution of ferrate(VI) can be prepared, then the unusual magnetic results may be explained.

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(33) B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966, p 265.

(34) See ref 33, p 60.

(35) G. DeMichelis, L. Oleari, L. DiSipio, and E. Tondello, *Coord. Chem. Rev.*, **2**, 53 (1967).

(36) B. N. Figgis and J. Lewis, "Progress in Inorganic Chemistry," Vol. 6, Interscience, New York, N. Y., 1964, p 161.

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(38) A. Viste and H. B. Gray, *Inorg. Chem.*, **3**, 1113 (1964).

(39) See ref 36, pp 71–72, 116.

(40) See ref 33, pp 275–277.

(41) See ref 33, pp 196–200.