complexes a D_3 symmetry holds and the t_2 set of the d(π) orbitals is split into e(t_2) and a_1(t_2) orbitals. CT states come from e(t_2) → a_2(ψ) and e(t_2) → e(χ) orbital transitions and are of E symmetry.[15] In the $Ru(bpy)_2(biq)^{2+}$ case the trigonal symmetry lowers to digonal and the e(t_2) orbitals of the metal t_2 set further split. The energy separation of 400 cm^{-1} could originate from splitting of the relevant E state. This interpretation would explain the lack of similar energy separation in $Ru(biq)_3^{2+}$, where trigonal symmetry is present.

Photochemical Implications. It has long been known that the d(π) → d(σ*) MC excited states of d^6 octahedral complexes are inclined to undergo ligand dissociation.[38] A recent study by Durham et al.[25] has shown that this process is important for $Ru(bpy)_3^{2+}$ and that recoordination of the released bpy N atom reduces the quantum yield of photosubstitution products. Such a photodissociation reaction may be useful for preparative purposes, but it is harmful when $Ru(bpy)_3^{2+}$ is used as a photosensitizer. Our results (Table I, Figure 7) show that for $Ru(biq)_3^{2+}$ the photodissociative ^3MC excited state is easily populated at room temperature and it can be anticipated that this complex will undergo efficient photodissociation. By contrast, the lowest ^3MC excited state of $Ru(bpy)_2(biq)^{2+}$ is much less accessible because it is separated by about 5500 cm^{-1} from the lowest Ru → biq CT excited state (Figure 7). This suggests that $Ru(bpy)_2(biq)^{2+}$ could be less susceptible to photodissociation reactions. On the basis of the energy separation alone, one would also expect that $Ru(bpy)_2(biq)^{2+}$ is less susceptible to photodissociation than $Ru(bpy)_3^{2+}$. This would increase its interest as a photosensitizer for the water-splitting reaction.[20] For a definitive assessment of its stability toward irreversible photoreactions, the intrinsic reactivity of the ^3MC excited state has to be known, however.

Acknowledgment. This work was supported by the Italian National Research Council and Ministero della Pubblica Istruzione and by the Swiss National Science Foundation.

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Magnetic Properties of the Tetragonal Phase $K_xMn_xFe_{1-x}F_3$

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The tetragonal tungsten bronze-like system $K_xMn^{II}_xFe^{III}_{1-x}F_3$ was studied at compositions x = 0.40, 0.45, 0.50, 0.55, and 0.60. Chemical composition and high precision lattice dimensions verify the composition span is x = 0.40–0.60. The interlayer distances of $K_xMn_xFe_{1-x}F_3$, including that of $KMnF_3$, obey the linear relationship $c' = 0.682 \log x + 4.182$. Structural constraints on antiferromagnetic ordering result in canted spin arrangements that, in turn, give rise to parasitic ferromagnetic moments. The values of T_N for x = 0.40, 0.45, 0.50, 0.55, and 0.60 are 162, 154, 148, 139, and 130 K, respectively, which are 0.6 times the predicted T_N values if no constraints were present. The values of C_M and Θ decrease dramatically as x increases, which is a consequence of a decreased number of nearest-neighboring Fe^{3+} ions. This further supports the supposition that $K_xMn_xFe_{1-x}Fe_3$ is ionically ordered over its entire composition span.

Introduction

The crystal structure determination of $K_{0.54}Mn_{0.54}Fe_{0.46}Fe_3$ [space group $P4_2bc$ (C^8_{4v})] by Banks, Nakajima, and Williams[1] established the existence of M^{2+}–M^{3+} ionic ordering in this phase. Ordering of this type may not be universal in fluoride analogues of tetragonal tungsten bronze, nor may it exist over the entire theoretical composition range ($0.4 \leq x \leq 0.6$); however, from their magnetic properties, it is likely that this same ionic ordering pattern exists in $K_xV^{II}_xV^{III}_{1-x}F_3$[2,3] and $K_xMn^{II}_xCr^{III}_{1-x}F_3$.[4]

The phase $K_xMn_xFe_{1-x}F_3$ can be thought of as x mol of $KMnF_3$[5] (perovskite) combined with $1 - x$ mol of FeF_3[6] (distorted ReO_3). All three of the structures are perovskite-like. Octahedra are corner sharing with M–F–M bond angles approximately 180°. Another property shared by these three compounds is their cations (Mn^{2+} and Fe^{3+}) have the same electronic configuration (d^5). In the octahedral crystal field provided by fluoride ions, orbital magnetic moments should be totally quenched, making these magnetic systems "spin only". Both $KMnF_3$ (T_N = 88 K)[7] and FeF_3 (T_N = 394 K)[8] order antiferromagnetically, and one would expect $K_xMn_xFe_{1-x}Fe_3$ to demonstrate the same behavior.

One feature that sets the bronze structure apart from the other two is that it contains structural constraints on antiferromagnetic ordering. These constraints are a consequence of two nearest-neighboring magnetic ions having a common nearest neighbor, making it impossible for magnetic moments on all nearest neighbors to be ordered antiparallel. In the bronze structure, there are four constraints per every 10 magnetic cations. Figure 1, which illustrates M^{2+}–M^{3+} ionic ordering in $K_{0.50}Mn_{0.50}Fe_{0.50}F_3$, also shows one of the four constraints (solid circle). One possible consequence of this kind of constraint is that in the magnetically ordered state, spins are forced to be canted. This may give rise to a small spontaneous magnetic moment (parasitic ferromagnetism).

Another consequence of magnetic constraints is to lower the ordering temperature T_N. If in the triangular arrangement,

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Table I. Chemical Analyses of $K_xMn_xFe_{1-x}F_3$ Compounds

	%		formula	
element	found	calcd	exptl	theoret
K	12.31	12.21	$K_{0.41}Mn_{0.40}Fe_{0.60}F_{3.00}$	$K_{0.40}Mn_{0.40}Fe_{0.60}F_3$
Mn	17.13	17.15		
Fe	25.99	26.15		
F	44.36	44.49		
K	13.70	13.53	$K_{0.46}Mn_{0.45}Fe_{0.55}F_{2.98}$	$K_{0.45}Mn_{0.45}Fe_{0.55}F_3$
Mn	18.92	19.01		
Fe	23.76	23.62		
F	43.62	43.83		
K	15.01	14.82	$K_{0.51}Mn_{0.50}Fe_{0.50}F_{3.01}$	$K_{0.50}Mn_{0.50}Fe_{0.50}F_3$
Mn	20.64	20.82		
Fe	21.07	21.16		
F	43.07	43.20		
K	16.08	16.07	$K_{0.55}Mn_{0.55}Fe_{0.45}F_{2.98}$	$K_{0.55}Mn_{0.55}Fe_{0.45}F_3$
Mn	22.60	22.57		
Fe	18.87	18.78		
F	42.43	42.58		
K	17.24	17.28	$K_{0.60}Mn_{0.60}Fe_{0.40}F_{2.98}$	$K_{0.60}Mn_{0.60}Fe_{0.40}F_3$
Mn	24.31	24.28		
Fe	16.56	16.45		
F	41.85	41.98		

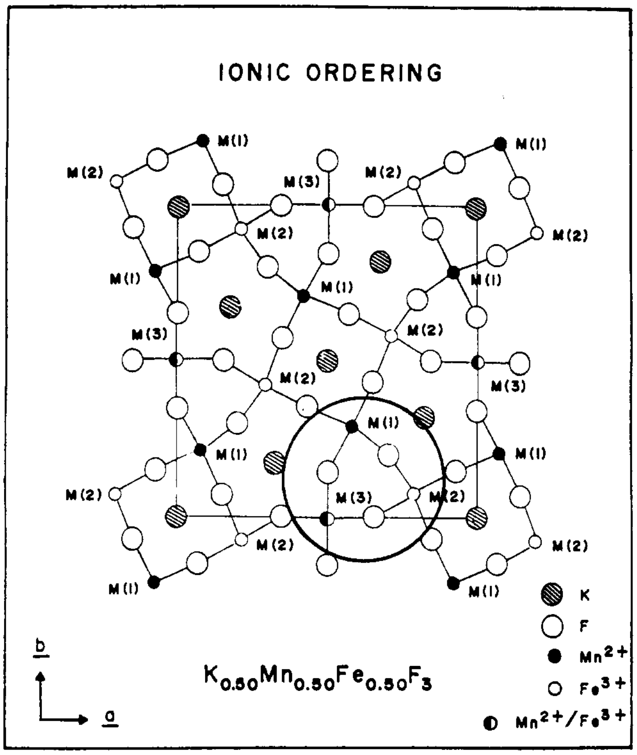

Figure 1. Ionic ordering and magnetic constraints in $K_{0.50}Mn_{0.50}Fe_{0.50}F_3$.

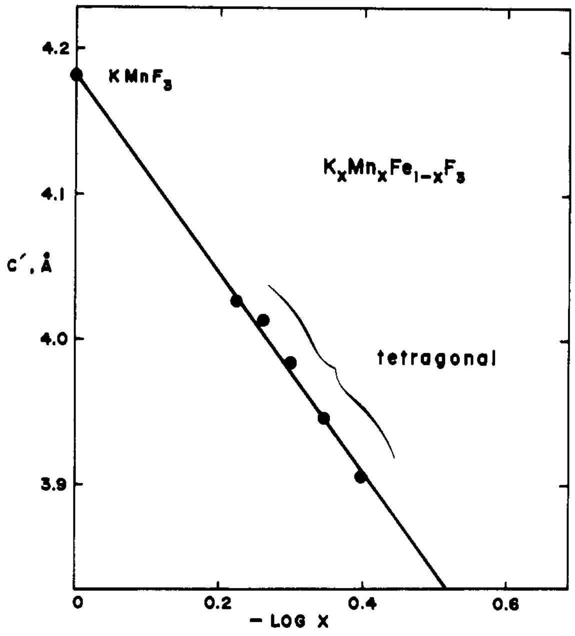

Figure 2. Linear plot of interlayer distances c' vs. $-\log x$ for $K_xMn_xFe_{1-x}F_3$ compounds.

the three nearest-neighboring cations have similar electronic configurations and all M–F–M antiferromagnetic interactions are approximately of the same strength, then the three M–F–M bonds involved will have the effect of neutralizing each other. In the bronze structure, for every 10 magnetic ions there are 30 M–F–M bonds. Each of the four constraints consist of three bonds; therefore, a total of 12 of the 30 magnetic interactions should be compromised. As a consequence, one would expect the magnitude of T_N for the tetragonal $K_xMn_xFe_{1-x}F_3$ phase to be reduced by approximately 12/30 = 0.4. Put another way, all other effects being equal, T_N should be 0.6 what it would be in the perovskite or ReO_3 structures.

This paper reports magnetic properties of the mixed-ion system $K_xMn_xFe_{1-x}F_3$. Conclusions relating magnetic ordering and other magnetic properties are correlated wherever possible to known ionic ordering.

Experimental Section

The samples were prepared by solid-state reaction of the simple fluorides in platinum capsules 8 mm in diameter and sealed under argon. All mixing and handling of the powder were done inside a drybox. The sealed capsules were fired in a tube furnace at 800 °C for 7 days with flowing argon as a protective atmosphere. Products were analyzed optically by steroscopic and polarized microscopy. Chemical analyses were done by Galbraith Laboratories. Potassium, manganese, and iron were determined by atomic absorption, and fluorine was determined by a specific-ion electrode. Samples were characterized by Guinier–Hagg X-ray techniques using Cu Kα_1 and Cr Kα_1 radiations. The X-ray data were reduced by computer using a least-squares program. Magnetic measurements were made from 4.2 to 300 K and between 0.14 and 10 kG with a Foner-type PAR vibrating-sample magnetometer equipped with a Janis liquid-helium Dewar, gallium arsenide thermometer, and temperature controller. Magnetic fields were measured with an F. W. Bell hall-probe gaussmeter, Model 8860. Magnetic data were corrected for core diamagnetism from ionic susceptibility tables of Mulay.[9]

Table II. Lattice and Magnetic Constants for Tetragonal $K_xMn_xFe_{1-x}F_3$

compd	lattice constants, Å (± 0.05%) Cu Kα	lattice constants, Å (± 0.05%) Cr $K\alpha_1$	T_N, K	Θ, K	C_M, cm³ deg mol⁻¹ obsd	C_M, cm³ deg mol⁻¹ calcd	σ_0, μ_B
$K_{0.40}Mn_{0.40}Fe_{0.60}F_3$	12.623 7.813	12.625 7.813	162	−1100	8.4	4.3	0.066
$K_{0.45}Mn_{0.45}Fe_{0.55}F_3$	12.674 7.889	12.679 7.898	154	−670	6.2	4.3	0.112
$K_{0.50}Mn_{0.50}Fe_{0.50}F_3$	12.720 7.965	12.726 7.971	148	−440	4.8	4.3	0.126
$K_{0.55}Mn_{0.55}Fe_{0.45}F_3$	12.787 8.024	12.789 8.031	139	−370	4.7	4.3	0.143
$K_{0.60}Mn_{0.60}Fe_{0.40}F_3$	12.826 8.053	12.828 8.054	130	−340	4.6	4.3	0.122

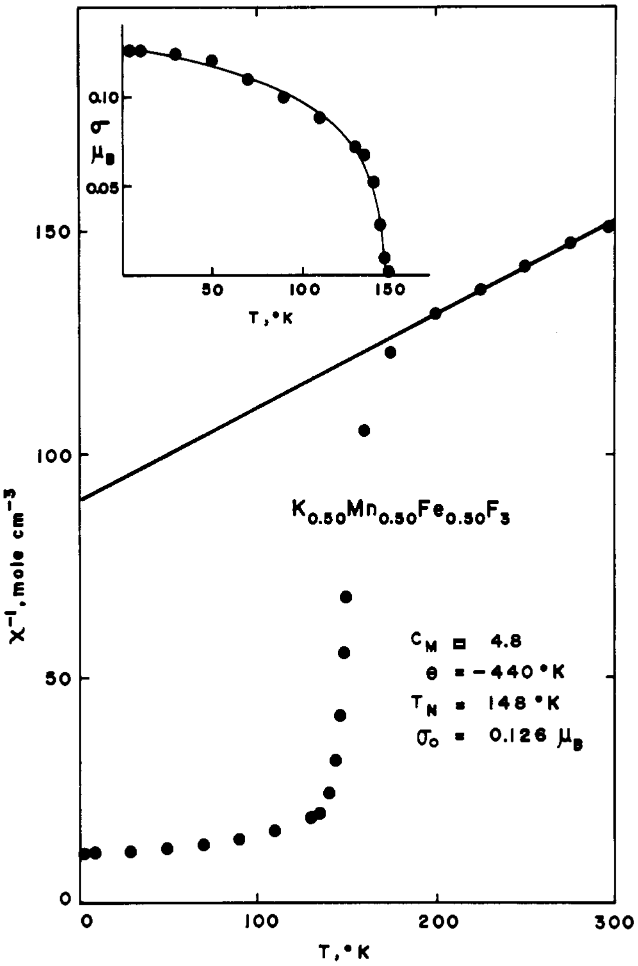

Figure 3. Inverse susceptibility vs. temperature, and magnetic moments extrapolated to zero field vs. temperature, for $K_{0.50}Mn_{0.50}Fe_{0.50}F_3$.

Results and Discussion

Chemical analyses shown in Table I indicate the experimental compositions are, within experimental error, identical with theoretical values. A summary of lattice dimensions of tetragonal $K_xMn_xFe_{1-x}F_3$ from Cu $K\alpha_1$ and Cr $K\alpha_1$ X radiation is shown in Table II. The lattice dimensions are composition dependent and, threfore, provide an independent method for checking composition. The tetragonal $K_xM^{II}_xM^{III}_{1-x}Fe_3$ phase is a layer structure, and the stacking of M–F–M–F atoms along the *c* direction is identical with that in cubic $KM^{II}F_3$. The empirical relationship between interlayer distance (c') and composition

$$c' = m \log x + a$$

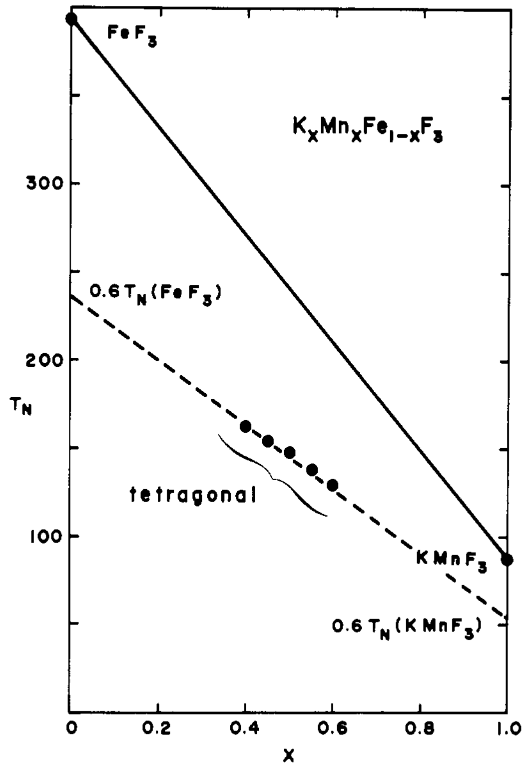

Figure 4. Nēel temperature (T_N) vs. *x* for $K_xMn_xFe_{1-x}F_3$ compounds including $KMnF_3$ and FeF_3.

(where *m* = slope and *a* is the lattice dimension of $KM^{II}F_3$) was established for $K_xV^{II}_xV^{III}_{1-x}F_3$[2,3] and $K_xMn^{II}_xCr^{III}_{1-x}F_3$.[4] Figure 2 is a plot of c' (from Table II, $c' = c/2$) vs. −log *x* for the system $K_xMn_xFe_{1-x}F_3$ including the value of $a = 4.182$ Å for $KMnF_3$.[5] Within experimental error, all points obey the linear relationship

$$c' = 0.682 \log x + 4.182$$

We conclude that the composition of $K_xMn_xFe_{1-x}F_3$ extends to the theoretically allowed limits $x = 0.40$–0.60.

A summary of magnetic constants is also given in Table II. The inverse susceptibility of $K_{0.50}Mn_{0.50}Fe_{0.50}F_3$ vs. *T* and its spontaneous moment vs. *T* (insert) of a random powder sample are shown in Figure 3. The small spontaneous moments, σ_0, present in every sample are believed to be a consequence of a canted spin arrangement caused by the magnetic contraints. The constraints are also believed to lower the T_N values to approximately 0.6 of their expected values were the constraints not present. Figure 4 is a plot of T_N from magnetic susceptibilities vs. *x*, including values for FeF_3 (T_N = 394 K)[8] and $KMnF_3$ (T_N = 88 K).[7] The solid line connects the T_N values of FeF_3 and $KMnF_3$, and the dashed line connects $0.6T_N$ of FeF_3 with $0.6T_N$ of $KMnF_3$. The fit of $K_xMn_xFe_{1-x}F_3$ T_N values to the dashed line is quite remarkable.

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The space-group symmetry of $K_{0.54}Mn_{0.54}Fe_{0.46}F_3$ is $P4_2bc$ (C_{4v}^8).[1] Important in the hypothesis by Banks et al.[1] is the structural feature that Mn^{2+} and Fe^{3+} ions occupy three distinct crystallographic sites. As seen in Figure 1, ions located on M(1) and M(2) sites are perfectly ordered. Ions located on M(3) sites are not ordered within the *a–b* plane, but for the ideal composition $x = 0.50$, they are most likely ordered (alternate Fe^{3+}–Mn^{2+}) along the *c* axis. All of these conditions minimize the number of Fe^{3+}–Fe^{3+} near neighbors as predicted by Pauling's fourth rule.[10] Along this same line of thought, one would expect the Fe^{3+}–Fe^{3+} near neighbors to be minimized over the entire composition range. This is easily seen to be the case if composition changes in Fe^{3+} and Mn^{2+} occur only on M(3) sites. This of course would mean the $K_xMn_xFe_{1-x}Fe_3$ phase belongs to space group $P4_2bc$ at all compositions. Then, the fractions of nearest neighbors which are Fe^{3+}–Fe^{3+} at the compositions studied are 0.200, 0.133, 0.067, 0.033, and 0.00 for $x = 0.40$, 0.45, 0.50, 0.55, and 0.60, respectively.

The calculated values for the molar Curie constants given in Table II are the same for all compositions since Mn^{2+} and Fe^{3+} both have $S = {}^5/_2$. The experimental values of C_M and Θ become surprisingly large at $x = 0.45$ and 0.40. From Figure 3, it is seen that these constants are approximated from χ^{-1} values between 200 and 300 K and are, therefore, not very accurate. It is obvious that better values of C_M and Θ could be obtained if measurements of χ were extended to higher temperatures. However, if the values of χ^{-1} between 200 and 300 K are asymptotic to a line extrapolated from higher temperatures, then the values of C_M and Θ would be still greater. There is little doubt, nevertheless, that the large values of C_M and Θ at $x = 0.45$ and 0.40 are related to the number of Fe^{3+}–Fe^{3+} nearest neighbors, or perhaps Fe^{3+} clusters.

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Registry No. FeF_3, 7783-50-8; $KMnF_3$, 13827-01-5.

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Cobalt(III) Complexes of Stereospecific Linear NSNN Tetradentate Ligands. 1. Synthesis of Ligands That Adopt the Cis-β Coordination Geometry

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The syntheses of four linear tetradentate ligands containing a sulfur atom and an amide nitrogen atom as internal donor atoms and either amine or pyridine terminal donor groups are reported. The ligands include geeH (*N*-[2-((2-aminoethyl)thio)ethyl]-2-aminoacetamide), pygeH (*N*-((2-pyridyl)methyl)-2-((2-aminoethyl)thio)acetamide), egeH (*N*-(2-aminoethyl)-2-((2-aminoethyl)thio)acetamide), and egpyH (*N*-(2-aminoethyl)-2-[((2-pyridyl)methyl)thio]acetamide). Co(III) complexes of these ligands were prepared, and chromatographic and spectroscopic evidence is presented which indicates that only one geometric isomer is formed. A single-crystal X-ray diffraction study of $Co(gee)(NO_2)_2{\cdot}H_2O$ ($C_6H_{14}CoN_5S{\cdot}H_2O$) was undertaken to establish its stereochemistry. The complex crystallized in space group $C2/c$ with $a = 20.832$ (6) Å, $b = 7.823$ (3) Å, $c = 15.570$ (4) Å, $\beta = 95.19$ (2)°, and $Z = 8$. The structure was solved by conventional Patterson and Fourier methods for 2786 independent reflections having $2\theta_{\mathrm{Mo}\,K\bar{\alpha}} = 58.7°$ and $I > 3\sigma(I)$. Full-matrix least-squares refinement led to a final R value of 0.033. The tetradentate gee ligand adopts the cis-β coordination geometry about the cobalt atom. Arguments based upon ligand structural similarities, spectroscopic techniques, and interconversion reactions of the complexes are presented which suggest that all four ligands bind to Co(III) stereospecifically in the cis-β geometry for all complexes prepared in this study.

Introduction

In recent years, the study of metal complexes containing flexible tetradentate ligands has been an area of active interest.[1-5] Investigations have involved evaluation of factors governing the overall geometry of the complexes, their reactions, and the stereochemistry of the reaction products.[1-5] Cobalt(III) complexes of such ligands have been found to promote hydrolysis of amino acid esters, peptides, and other carbonyl compounds.[3-6] In some cases, peptide formation has been observed.[7] In addition, since metal complexes of a particular stereochemistry may be optically active and chiral

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