Contribution from the Department of Chemistry,
Tulane University, New Orleans, Louisiana 70118

Preparation and Solid-State Properties of $CsVI_3$, $CsCrI_3$, and $CsMnI_3$

G. L. McPHERSON,* L. J. SINDEL, H. F. QUARLS, C. B. FREDERICK, and C. J. DOUMIT

Received June 19, 1974 AIC40392X

The salts $CsVI_3$, $CsCrI_3$, and $CsMnI_3$ crystallize in hexagonal lattices in which the most prominent structural feature is a parallel array of linear chains of octahedra sharing faces. The magnetic susceptibilities of these materials indicate that the salts are all antiferromagnetic. The magnetic exchange interactions in $CsVI_3$ are effective even at room temperature. The electronic spectra of the salts show the general features expected of octahedral complexes of these transition metal ions. The polarized crystal spectrum of $CsMnI_3$ shows that the intensities of the normally spin-forbidden transitions are enormously enhanced by the antiferromagnetic exchange interactions. The crystal spectrum also indicates the presence of a significant trigonal component to the ligand field.

Introduction

There has been considerable interest in transition metal salts of the general formula $M^IM^{II}X_3$ (where M^I is a large univalent cation, M^{II} a divalent transition metal ion, and X a halide). These materials often crystallize in hexagonal lattices in which the most prominent structural feature is a parallel array of infinite, linear chains of octahedra sharing faces. The chains run parallel to the crystallographic *c* axis with the transition metal ions at the centers and the halide ions at the corners of the octahedra. The magnetic properties of these types of salts approach those of a one-dimensional system of interacting spins. This paper presents the preparation and characterization of the salts $CsVI_3$, $CsCrI_3$, and $CsMnI_3$. The spectroscopic and magnetic properties of these iodides are of interest because the materials adopt the linear-chain structure. The vanadium and chromium salts are especially interesting since very little is known about the complex iodides of V(II) or Cr(II).[1]

Experimental Section

Preparation of Materials. Anhydrous VI_2 and CrI_2 were prepared by reaction of iodine with the pure metals at high temperatures. Stoichiometric mixtures of iodine and metallic chromium or vanadium were sealed in evacuated Vycor tubes and heated in a tube furnace. The chromium–iodine mixtures were heated to approximately 700° while the vanadium–iodine mixtures were heated to 850°. After heating of the full length of a tube for a few days, one end was allowed to extend outside the furnace. Crystals of the anhydrous iodides then grew on the cooler portion of the Vycor containers. The iodides were collected, resealed in evacuated Vycor tubes, and resublimed for purification.

Anhydrous MnI_2 was prepared by the reaction of iodine and manganese metal in diethyl ether. The ether was distilled off and the product was heated to 150° under vacuum. The MnI_2 was then sublimed at 750° in evacuated Vycor tubes.

The cesium metal triiodides $CsVI_3$, $CsCrI_3$, and $CsMnI_3$ were prepared by fusing equimolar mixtures of CsI and the appropriate metal iodide. $CsVI_3$ is a red-brown solid which tends to crystallize as long needles. $CsCrI_3$ is a dark brown, almost black, material, while $CsMnI_3$ is a red crystalline solid. All of the $CsMI_3$ salts as well as the anhydrous metal iodides are extremely hygroscopic and all manipulations of these materials were carried out in a dry nitrogen-filled glove box. Anal. Calcd for $CsVI_3$: V, 9.02; I, 67.4. Found: V, 8.92; I, 66.7. Calcd for $CsCrI_3$: Cr, 9.19; Cs, 23.5; I, 67.3. Found: Cr, 9.63; Cs, 23.0; I, 65.7. Calcd for $CsMnI_3$: Mn, 9.69; I, 67.0. Found: Mn, 9.70; I, 66.6.

Chemical Analyses. The iodide contents of the $CsMI_3$ salts were determined gravimetrically. Weighed samples were dissolved in dilute aqueous ammonia. The resulting solutions were filtered to remove the insoluble metal hydroxides (i.e., $Cr(OH)_3$). The iodide was then precipitated as AgI by slowly adding 0.05 *N* $AgNO_3$ solution. The transition metals were determined colorimetrically. Weighed samples of $CsVI_3$ were dissolved in dilute HNO_3. The solutions were boiled until all the iodine was driven from solution and the vanadium was oxidized to V(V). Sulfuric acid was then added and the solution was boiled until all the HNO_3 was driven off. After cooling, the solution was diluted to a known volume (less than 0.1 mg of V/ml) and the vanadium concentration was determined by the hydrogen peroxide method.[2] Reagent grade NH_4VO_3 was used as a standard. Weighed samples of $CsCrI_3$ were dissolved in boiling dilute HNO_3. After all of the iodine was expelled, KIO_4 was added and the boiling was continued until the Cr(III) was oxidized to Cr(VI). The solution was made basic with aqueous ammonia and diluted to a known volume. The chromium was determined spectrophotometrically as CrO_4^{2-}. Reagent grade $K_2Cr_2O_7$ was used as a standard. Manganese in $CsMnI_3$ was analyzed in a similar fashion, using KIO_4 to oxidize the manganese to MnO_4^-; however, the spectrophotometric determination of MnO_4^- was made in acidic rather than basic solution. Reagent grade $KMnO_4$ was used as a standard. The cesium content of $CsCrI_3$ was determined gravimetrically as the tetraphenylborate salt. A sample of $CsCrI_3$ was dissolved in water. The chromium was precipitated as $Cr(OH)_3$ by adding dilute NaOH and the resulting mixture was filtered. Aqueous HCl was added to the filtered solution until the concentration of acid was 0.05 *N*. The cesium was then precipitated with sodium tetraphenylborate.

Crystal Growth. Crystalline samples of the $CsMI_3$ salts were grown from the melt by the Bridgman method. Samples were sealed in evacuated Vycor ampoules. The ampoules were lowered through a tube furnace (12 in. long, 1.75-in. inside diameter) at the rate of 0.5 cm/hr. The temperature at the center of the furnace was maintained at 900° for $CsVI_3$, 750° for $CsCrI_3$, and 650° for $CsMnI_3$.

Crystallographic Studies. Single crystals of $CsMnI_3$ suitable for X-ray studies were cleaved from larger crystals grown from the melt by the Bridgman method. The crystals were sealed in 0.3-mm glass capillaries. Precession photographs of the $hk0$, $hk1$, hhl, and $h(h+1)l$ zones were taken using filtered Mo Kα radiation.

Magnetic Susceptibility Measurements. The magnetic susceptibilities of powdered samples of the cesium transition metal triiodides were determined by the Gouy method. The apparatus and procedure have been described previously.[3] The absolute accuracy of the susceptibility values is probably only ±5% due to packing errors, but the internal accuracy of measurements for the same compound should be considerably better.

Electronic Spectra. The mull spectra of $CsVI_3$, $CsCrI_3$, and $CsMnI_3$ were studied at room and liquid nitrogen temperatures using a Cary 14 spectrophotometer. The mulls were prepared with Kel-F grease and were supported between glass plates. A mull of $CaCO_3$ was used as a scattering reference. In the case of $CsMnI_3$, it was possible to cleave single crystals into plates thin enough to study crystal spectra. The $CsMX_3$ salts tend to cleave on the $[11\bar{2}0]$ face. The polarized crystal spectrum of $CsMnI_3$ was studied in the 15,000–25,000-cm^{-1} region at room and liquid nitrogen temperatures. The absorptions of the crystals above 25,000 cm^{-1} were too intense to be measured. The procedure for recording the spectra and determining oscillator strengths has been previously described.[4] Due to the many possible errors involved in the determination, the oscillator strengths are only expected to be accurate within ±25%.

Results and Discussion

Crystallography. Diffraction studies of $CsVI_3$ and $CsCrI_3$ have already been reported.[5] The X-ray photographs of $CsMnI_3$ show that the material crystallizes in the same type of hexagonal lattice as the $CsVI_3$ and $CsCrI_3$ salts. A summary of the diffraction data for the three salts is given in Table I. It is likely that $CsVI_3$ and $CsMnI_3$ are isostructural with $CsNiCl_3$,[6] $CsMgCl_3$,[7] $CsCoCl_3$,[8] and $CsMnBr_3$[9] (space group *P*6_3/*mmc*). The chromium salt is probably similar in structure to $CsCrCl_3$[4] and $CsCrBr_3$.[10] Although the structures of

Table I. Crystallographic Data

Crystal system: hexagonal
Extinctions: *hhl*, $l \neq 2n$
Space group: $P6_3/mmc$, $P6_3/mc$, or $P\bar{6}2c$
Molecules/unit cell: $Z = 2$
Lattice constants
$CsVI_3$[a]
$a = 8.21$ Å, $c = 6.81$ Å
$CsCrI_3$[a]
$a = 8.12$ Å, $c = 6.85$ Å
$CsMnI_3$
$a = 8.18$ Å, $c = 6.95$ Å

[a] Reference 5.

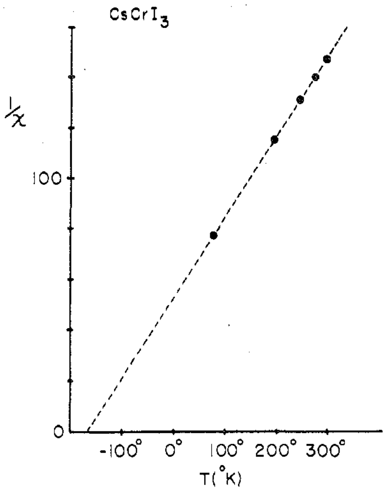

Figure 1. Plot of the reciprocal of the molar susceptibility of $CsCrI_3$ vs. the absolute temperature.

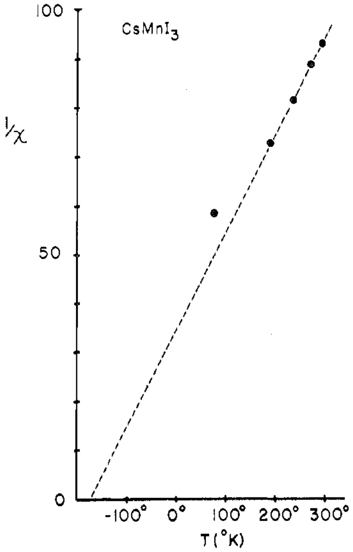

Figure 2. Plot of the reciprocal of the molar susceptibility of $CsVI_3$ vs. the absolute temperature.

$CsCrCl_3$ and $CsCrBr_3$ are somewhat different from those of $CsNiCl_3$ and $CsMgCl_3$, the basic feature of linear chains of octahedra sharing faces is present in both structures.

Magnetic Susceptibilities. Plots of the reciprocal molar susceptibilities of $CsCrI_3$ and $CsMnI_3$ vs. the absolute temperature are shown in Figures 1 and 2. The susceptibility of $CsCrI_3$ in the 300–77°K region obeys the Curie–Weiss law with a Θ value of −163°. An effective magnetic moment of 4.98 BM can be calculated from the expression

$$\mu_{\text{eff}} = 2.84[\chi(T - \Theta)]^{1/2}$$

This value is typical of a d^4 system. The large negative Weiss constant (Θ) is indicative of antiferromagnetic coupling. The susceptibility of $CsMnI_3$ exhibits Curie–Weiss law behavior above 195°K but deviates significantly at 77°K. A magnetic moment of 6.30 BM can be calculated from the high-temperature portion of the susceptibility data. This value is somewhat higher than would be expected for a d^5 system, but we do not attach any special significance to this result. The negative Weiss constant and the behavior of the susceptibility at low temperatures strongly suggest that $CsMnI_3$, like $CsCrI_3$, is antiferromagnetic. The magnetic properties of $CsCrI_3$ and $CsMnI_3$ are quite similar to those reported for $CsNiI_3$.[11]

Table II. Magnetic Susceptibilities[a]

Compd	Temp, °K	$10^6\chi$, esu/mol	$1/\chi$, mol/esu
$CsVI_3$	295	2,220	450
	195	2,360	425
	77	2,330	432
$CsCrI_3$	295	6,800	147
	273	7,130	140
	244	7,630	131
	195	8,690	115
	77	12,980	77
$CsMnI_3$	295	10,750	93
	273	11,350	88
	239	12,260	82
	195	13,760	73
	77	17,170	58

[a] Curie-Weiss law: $\chi = c/(T - \Theta)$; $\mu_{\text{eff}} = 2.84[\chi(T - \Theta)]^{1/2}$. $CsCrI_3$: $\Theta = -163 \pm 5°$; $\mu_{\text{eff}} = 4.98$ BM. $CsMnI_3$: $\Theta = -165 \pm 10°$; $\mu_{\text{eff}} = 6.30$ BM.

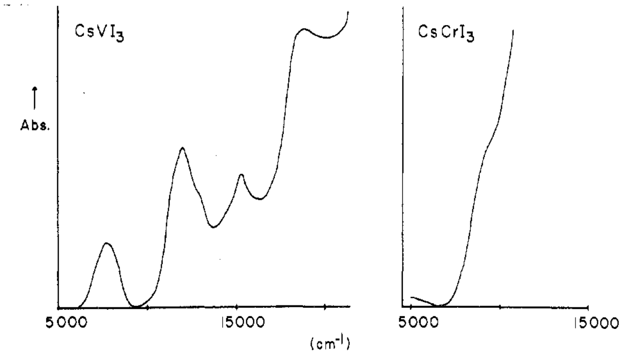

Figure 3. Mull spectra of $CsVI_3$ and $CsCrI_3$ at 77°K.

The vanadium salt, $CsVI_3$, exhibits a rather small susceptibility which is nearly independent of temperature. Apparently the antiferromagnetic interactions in this salt are operative even at room temperature. The strength of the exchange interactions must be considerably stronger in $CsVI_3$ than in $CsCrI_3$ or $CsMnI_3$. Table II contains a summary of the magnetic susceptibility data for all three salts.

Electronic Spectra. The electronic spectra of $CsVI_3$, $CsCrI_3$, and $CsMnI_3$ are shown in Figures 3 and 4. The spectrum of $CsVI_3$ shows a series of bands in the 5000–20,000-cm^{-1} range which can be ascribed to ligand field (d–d) transitions. The band assignments presuming an octahedral ligand field are given in Table III. The calculated energies of the quartet states were obtained from the energy matricies for a d^3 system in an octahedral field given by Tanabe and Sugano.[12] The values of *Dq* and *B* were varied until a reasonable fit between the observed and calculated transition energies was obtained. These crystal field parameters are very close to those reported by Smith from an analysis of the crystal spectrum of VI_2.[13]

The spectrum of $CsCrI_3$ consists only of an intense absorption edge with a weak shoulder at approximately 9000 cm^{-1}. The material absorbs strongly throughout the visible region. The intense absorption presumably results from charge-transfer transitions. The shoulder at 9000 cm^{-1} has been tentatively assigned to the $^5E \rightarrow {}^5T_2$ ligand field transition. Unfortunately, the analytical data indicate that the $CsCrI_3$ prepared by our procedure is somewhat impure. It

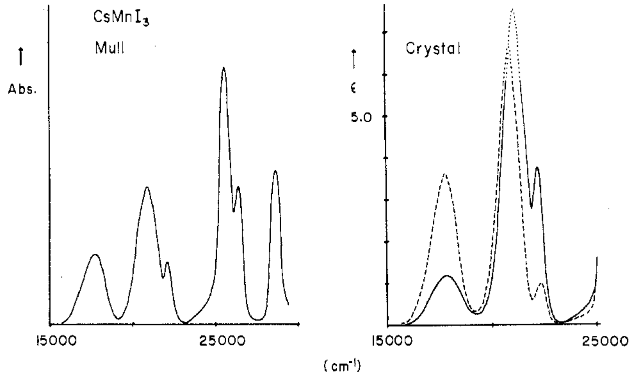

Figure 4. Mull and crystal spectra of $CsMnI_3$ at 77°K. In the crystal spectrum, the solid line represents the spectrum obtained with $\vec{E}$ polarized parallel to the *c* axis while the dashed line represents the spectrum obtained when $\vec{E}$ is perpendicular to *c*. The dotted lines correspond to regions where the absorption exceeded the limits of the spectrometer.

Table III. Spectroscopic Assignments and Transition Energies[a]

Compd	Band assignment	Energy, cm⁻¹	
		Obsd[b]	Calcd
$CsVI_3$	$^4A_2 \rightarrow {}^4T_2$	7,700	7,700
	$\rightarrow {}^4T_1(F)$	12,000	11,960
		13,000 sh	
	$\rightarrow {}^2T_2$[c]	15,300	
	$\rightarrow {}^4T_1$ (P)	18,700	18,860
$CsCrI_3$	$^5E \rightarrow {}^5T_2$	9,000 sh	9,000
$CsMnI_3$	$^6A_1 \rightarrow {}^4T_1(G)$	17,800	17,820
	$\rightarrow {}^4T_2(G)$	20,900	20,970
	$\rightarrow {}^4E, {}^4A_1(G)$	22,100	21,150
	$\rightarrow {}^4T_2(D)$	25,500	26,390
	$\rightarrow {}^4E(D)$	26,400	27,820
	$\rightarrow {}^4T_2(P)$	28,600	29,130

[a] $CsVI_3$: $Dq = 770$ cm⁻¹; $B = 515$ cm⁻¹. $CsCrI_3$: $Dq = 900$ cm⁻¹. $CsMnI_3$: $Dq = 610$ cm⁻¹; $B = 810$ cm⁻¹; $C/B = 3.47$. sh = shoulder. [b] The transition energies are taken from the mull spectra recorded at 77°K. [c] Based on the spectroscopic analysis in ref 13.

is possible that the sample is contaminated with chromium(III) (there is an excess of Cr with respect to Cs). The intense charge-transfer absorption could then result from Cr(III) rather than Cr(II). It should be pointed out that the percent compositions of Cr, Cs, and I do not add up to 100% which indicates the presence of a small amount of some other element. The only suggestion we have is that the $CsCrI_3$ samples may contain some oxygen (as oxide).

The spectrum of $CsMnI_3$ contains a number of absorptions which can be assigned to ligand field transitions. The general appearance of the spectrum is quite similar to those reported for $CsMnBr_3$[3] and $(CH_3)_4NMnCl_3$.[14,15] The band assignments and the calculated and observed transition energies are presented in Table III. The calculated energies were determined from the Tanabe and Sugano matrices using the procedure outlined in ref 3. The interelectronic repulsion parameter, *B*, of 810 cm⁻¹ found for $CsMnI_3$ can be compared with the value of 845 cm⁻¹ obtained for $CsMnBr_3$. The smaller *B* value presumably reflects the greater covalent character of the iodide lattice when compared with the bromide lattice. The *Dq* value of $CsMnI_3$ is smaller than that of $CsMnBr_3$ (610 cm⁻¹ compared with 680 cm⁻¹) which is consistent with the positions of the two halides in the spectrochemical series.

The spectra of compounds containing manganese(II) have been of considerable interest, since all the ligand field transitions of a high-spin d^5 system are spin forbidden. The intensities of these spin-forbidden transitions are usually smaller by a factor of 10^2–10^3 than those of spin-allowed transitions. However, it has been well documented that exchange interactions can enhance the intensities of spin-forbidden transitions. Compounds that contain manganese(II) ions bridged by common ligands have significantly more intense spectra than those which contain only "isolated" manganese(II) ions.[16] Oscillator strengths on the order of 10^{-7} are typical of the spectra of manganese(II) compounds in which there are no significant exchange interactions. The spectrum of $CsMnI_3$ indicates an enormous enhancement of the intensities due to the exchange interactions. The oscillator strengths reported in Table IV for the three lowest energy bands in the $CsMnI_3$ spectrum are as large as those usually observed for spin-allowed transitions of octahedral complexes ($f = 10^{-5}$–10^{-4}). The band intensities are more than twice as large as those of the corresponding bands in the spectrum of $CsMnBr_3$. It is clear that the antiferromagnetic exchange interactions in $CsMnI_3$ are extremely effective in relaxing the spin-selection rule.

Table IV. Oscillator Strengths of the Spectrum of $CsMnI_3$

Temp, °K	Band assignment	Polarizn[a]	$10^6 f$	Energy, cm⁻¹
295	$^6A_1 \rightarrow {}^4T_1(G)$	∥	14	18,000
		⊥	22	17,900
	$^6A_1 \rightarrow {}^4T_2(G)$	∥	60	21,500
	$^6A_1 \rightarrow {}^4E, {}^4A(G)$	⊥	29	21,000
77	$^6A_1 \rightarrow {}^4T_1(G)$	∥	9	17,900
		⊥	23	17,800
	$^6A_1 \rightarrow {}^4T_2(G)$	∥	43	21,100
		⊥	35	20,800
	$^6A_1 \rightarrow {}^4E, {}^4A_1(G)$	∥	8	22,200
		⊥	2	22,400

[a] ∥ denotes $\vec{E}$ parallel to *c* axis; ⊥ denotes $\vec{E}$ perpendicular to *c* axis.

The available crystallographic data on the $CsMX_3$ salts indicate that the coordination sphere of the metal ion (M) deviates somewhat from octahedral geometry.[6–9] The deviation can be described as a trigonal elongation of the octahedron directed along the threefold axis which runs the length of the MX_3^- anionic chain (the crystallographic *c* axis).[7] Although a complete structural analysis of $CsMnI_3$ has not been reported, it is reasonable to assume that the coordination sphere of the manganese ion has a similar trigonal distortion. The crystal spectrum of $CsMnI_3$ does indicate the presence of a low-symmetry component to the ligand field. There are noticeable differences between the band energies in the parallel spectrum and the energies of the corresponding bands in the perpendicular spectrum (see Table IV). Electron paramagnetic resonance studies of manganese(II) doped into $CsMgI_3$ (isomorphous with $CsMnI_3$) show the presence of large zero-field splittings in the ground state due to the axial (trigonal) component of the ligand field.[17]

Conclusions

The metal triiodides that have been studied adopt linear-chain $M^IM^{II}X_3$ type structures. Like the analogous chloride and bromide salts, the iodides are antiferromagnetic. The electronic spectra contain the expected d–d transitions. The band intensities of the spin-forbidden transitions in the spectrum of $CsMnI_3$ are abnormally large which suggests that the magnetic-exchange interactions are effective in relaxing the spin-selection rule. The $CsMX_3$ salts are a unique series of compounds in that the same basic structure is retained with a wide variety of transition metals and halogens.

Acknowledgment. We wish to acknowledge Tulane University, especially the Department of Chemistry, for the support of this work.

Registry No. $CsVI_3$, 43047-24-1; $CsCrI_3$, 43138-25-6; $CsMnI_3$, 54985-97-6.

References and Notes

(1) R. Colton and J. H. Canterford, "Halides of the First Row Transition Metals", Wiley-Interscience, New York, N.Y., 1969, pp 137, 189.

(2) A. I. Vogel, "Textbook of Quantitative Inorganic Analysis", 3rd ed, Longmans, Green and Co., London, 1961, p 790.
(3) G. L. McPherson, H. S. Aldrich, and J. R. Chang, *J. Chem. Phys.*, **60**, 534 (1974).
(4) G. L. McPherson, T. J. Kistenmacher, J. B. Folkers, and G. D. Stucky, *J. Chem. Phys.*, **57**, 3771 (1972).
(5) T. Li, G. D. Stucky, and G. L. McPherson, *Acta Crystallogr., Sect. B*, **29**, 1330 (1973).
(6) G. N. Tishcenko, *Tr. Inst. Kristallogr. Akad. Nauk SSSR*, **11**, 93 (1955).
(7) G. L. McPherson, T. J. Kistenmacher, and G. D. Stucky, *J. Chem. Phys.*, **52**, 815 (1970).
(8) H. Soling, *Acta Chem. Scand.*, **22**, 2793 (1968).
(9) J. Goodyear and D. J. Kennedy, *Acta Crystallogr., Sect. B*, **28**, 1640 (1972).
(10) T. Li and G. D. Stucky, *Acta Crystallogr., Sect. B*, **29**, 1529 (1973).
(11) G. L. McPherson, J. E. Wall, Jr., and A. M. Hermann, *Inorg. Chem.*, **13**, 2230 (1974).
(12) Y. Tanabe and S. Sugano, *J. Phys. Soc. Jpn.*, **9**, 753 (1954).
(13) W. E. Smith, *J. Chem. Soc., Dalton Trans.*, 1634 (1972).
(14) K. E. Lawson, *J. Chem. Phys.*, **47**, 3627 (1967).
(15) R. Dingle, M. E. Lines, and S. L. Holt, *Phys. Rev.*, **187**, 643 (1969).
(16) L. L. Lohr and D. S. McClure, *J. Chem. Phys.*, **49**, 3516 (1968).
(17) G. L. McPherson, R. C. Koch, and G. D. Stucky, *J. Chem. Phys.*, **60**, 1424 (1974).

Contribution from the Institute for Solid State Physics,
The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

Changes of the Electronic State and the Electrical Resistance of Some Iron Compounds at High Pressures

YOJI HARA,* ICHIMIN SHIROTANI, and SHIGERU MINOMURA

Received December 13, 1974 AIC40831S

The electrical resistance of some iron compounds has been measured at high pressures. In Fe(III) compounds, the resistance decreases with increasing pressure, by means of electron transfer from Fe(II), which is formed from Fe(III) under pressure, to Fe(III). A pressure-induced chemical reaction was observed for potassium ferricyanide and ferric oxalate. The resistance vs. pressure curve for these two compounds has a resistance minimum. The pressure-induced spin changes observed in Fe(II) compounds make only a small contribution to a decrease in resistance.

Introduction

A great deal of knowledge on a pressure-induced electronic transition of iron compounds has been accumulated from measurements of Mössbauer effect and optical absorption.[1] Champion et al.[2] first observed that the electronic transitions involving the reduction of ferric ions or the spin flip of ferrous ions are induced with various iron compounds by applying a wide range of pressures.

In a previous paper,[3] the effect of pressures up to 50 kbars was measured on the absorption spectra in some ferric and ferrous compounds by the authors, who observed pressure-induced bands at the lower energy side of the original one in both ferric and ferrous compounds. It was thought that such bands might decrease the electrical resistance. These bands are due to the thermal occupation of the excited states, which leads to a formation of new oxidation and spin states.

In this paper, the results presented will be divided into three sections: (1) the resistance and the Fe(III) → Fe(II) reduction in five ferric compounds with oxygen ligands at high pressures, (2) the resistance and the chemical reaction in two ferric compounds at high pressures, and (3) the resistance and the changes of the spin states in three ferrous compounds at high pressures. All the phenomena mentioned above involve electronic transitions and therefore electrical resistance surveys will be helpful to get some information concerning the electron-transport mechanism.

Experimental Section

In order to eliminate the difficulties in the near-ultraviolet region involved in a high-pressure diamond optical cell, a new apparatus was made, using a single crystal of sapphire instead of diamond. This sapphire single crystal is transparent up to ~350 nm (~28 kK). In the present experiments, the authors used it without a gasketing device; they simply placed the sample in a KBr disk between two sapphire windows, compressed it axially, and then clamped pressure up to ~15 kbars by screwing the bolt up until it did not rotate any more. The quasihydrostatic pressures were generated by means of a high-pressure optical bomb using a NaCl medium up to 50 kbars.[4] The infrared spectra of the samples were observed in a KBr disk. These optical measurements were performed with a Bausch–Lomb grating spectrometer, with a Shimazu double-beam spectrometer and with a Nihonbunko IR-S Type infrared spectrometer.

Table I. Materials Studied

Compd	Formula
Ferric phosphate hydrate (FPH)	$FePO_4 \cdot nH_2O$
Ferric acetylacetonate (FAA)	$Fe(C_5H_7O_2)_3$
Ferric citrate (FCT)	$Fe(C_6H_5O_7) \cdot 3H_2O$
Ferric oxide (FOD)	Fe_2O_3
Basic ferric acetate (BFA)	$Fe_3(CH_3CO_2)_6(OH)_2 \cdot CH_3CO_2 \cdot H_2O$
Potassium ferricyanide (PFIC)	$K_3Fe(CN)_6$
Ferric oxalate (FIOL)	$Fe_2(C_2O_4)_3 \cdot 5H_2O$
Ferrous oxalate (FOOL)	$FeC_2O_4 \cdot 2H_2O$
Potassium ferrocyanide (PFOC)	$K_4Fe(CN)_6$
Ferrous chloride hydrate (FCH)	$FeCl_2 \cdot nH_2O$
Ferrous phosphate (FP)	$Fe_3(PO_4)_2$

Table II. Fraction of Fe(II) Formed under Pressure

	Pressure, kbars				
Compd	25	50	75	100	125
FPH	22[a]	32	39	43	46
FAA	0	10	17	24	31
BFA	0	5	6	7	8
FCT	35	46	50	54	56

[a] Expressed in percent.

The electrical resistance has been measured as a function of pressure up to 130 kbars at room temperature, using a supported-taper piston apparatus.[5] The resistance was observed by the two-probe method. The pellet of the sample was made by the compression of about 5 kbars and was set between two Cu electrodes.

In this study, seven ferric and three ferrous complexes were studied. Ferric acetylacetonate was prepared as described in the literature.[6] The other materials used were all of a commercially available reagent grade quality. Ferric oxalate was handled in the dark to prevent photoreduction.

The materials studied are listed in Table I.

Results and Discussion

Resistance and Fe(III) → Fe(II) Reduction. In Figure 1, the resistances of various ferric compounds are shown as a function of pressure. The five compounds in Figure 1 are FPH, FAA, FCT, FOD, and BFA, in all of which Fe(III) is sur-