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Electron Paramagnetic Spectrum of Manganese(II)–Manganese(II) Pairs in Single Crystals of Cesium Cadmium Chloride. Electronic Structure of the $Mn_2Cl_9^{5-}$ Dimer[1]

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The EPR spectrum of $CsCdCl_3$ crystals doped with manganese(II) contains resonances from magnetically coupled Mn(II) pairs as well as from isolated Mn(II) ions. The host material adopts a hexagonal lattice in which there are two crystallographically distinct types of cadmium ions (Cd(1) and Cd(2)). An analysis of the pair resonances shows that the pairs are formed by Mn(II) ions entering two adjacent Cd(2) sites. This creates an $Mn_2Cl_9^{5-}$ dimer whose structure approximates that of two octahedra sharing a face. Resonances from spin states $\Sigma = 1$ through $\Sigma = 5$ have been identified and characterized. The temperature dependence of the spectrum indicates that the magnetic interaction within the dimer is antiferromagnetic. The zero-field splittings suggest that the Mn(II)–Mn(II) separation in the dimer is not constant but depends to some extent on the spin state. The magnitude of the magnetic dipole–dipole interaction indicates that there is a significant metal to ligand delocalization in the $Mn_2Cl_9^{5-}$ dimer.

Introduction

When crystallized from the melt $CsCdCl_3$ adopts a hexagonal lattice in which the cadmium ions occupy two crystallographically distinct sites.[2,3] In either case the cadmium ion is surrounded by an octahedron of chloride ions; however, the mode of halide bridging differentiates the two sites. As can be seen from Figure 1 the Cd(2) site contains both linear and bent Cd–Cl–Cd bridges while only linear Cd–Cl–Cd bridges are associated with the Cd(1) site. Since the $CsCdCl_3$ lattice contains octahedra sharing corners and faces, the structure of this material can be thought of as an intermediate between two structural extremes. These extremes would be represented by the linear-chain $CsNiCl_3$ structure which contains octahedra sharing only faces and the perovskite structure which consists entirely of octahedra sharing corners.

It has been previously reported that the EPR spectrum of $CsCdCl_3$ doped with Mn(II) contains resonances from two types of Mn(II) ions.[4] This indicates that Mn(II) enters both cadmium sites in the host lattice. In addition to the resonances from the two types of isolated Mn(II) ions, weak resonances arising from coupled pairs were also observed. Although the pair resonances were not analyzed in detail, it was established that the pairs resulted from the substitution of Mn(II) into two adjacent Cd(2) sites. This paper presents a detailed analysis of the pair resonances and a discussion of the spectroscopic and magnetic properties of the $Mn_2Cl_9^{5-}$ dimer system.

Experimental Section

Preparation of Materials. The salt, $CsCdCl_3$, was crystallized by slow evaporation of aqueous HCl solutions containing equimolar amounts of CsCl and hydrated $CdCl_2$. The white crystalline solid was dried at 120 °C and stored in a desiccator. The material is quite stable in air. Anal. Calcd for $CsCdCl_3$: Cd, 31.9; Cl, 30.3. Found: Cd, 32.1; Cl, 30.4.

The preparation of $CsMnCl_3$ has been described previously.[5]

Crystal Growth. Single crystals of $CsCdCl_3$ suitable for spectroscopic study were grown from the melt by the Bridgman method. Doped crystals were prepared by adding small amounts (between 0.1 and 2.0 mol %) of $CsMnCl_3$ to the $CsCdCl_3$. The apparatus and procedure has been described previously.[6] It was found that crystals with approximately 0.5 mol % of Mn(II) gave the optimum results. The EPR resonances were noticeably broadened at Mn(II) concentrations of greater than 1.0 mol %.

EPR Measurements. The crystals of $CsCdCl_3$ have no prominent cleavage planes, which makes mounting somewhat difficult. The samples were oriented with the aid of a polarizing microscope. In most cases, the crystals were mounted so that the magnetic field can be parallel and perpendicular to the crystallographic *c* axis. The spectra were recorded at room and liquid nitrogen temperatures on Varian E-3 X-band and E-12 Q-band spectrometers using 100-kHz field modulation. The field strength was calibrated with a Perkin-Elmer gaussmeter using ^7Li and ^1H NMR frequencies. The *g* values were determined by using polycrystalline diphenylpicrylhydrazyl ($g = 2.0036$) as a reference.

Results and Discussion

Dimeric systems of paramagnetic ions have been known and studied for some time. The electronic structure of such a system may differ considerably from that of the individual paramagnetic ions due to the magnetic interactions between the two ions. The magnitudes of these interactions depend on the distance between paramagnetic centers and the nature and geometrical arrangement of the intervening ligands. Numerous investigations have been carried out in order to elucidate the electronic structures of various dimeric systems. Electron paramagnetic resonance has proved to be an especially valuable experimental tool for studying magnetic interactions in dimers. Single crystals are especially amenable to EPR study since a maximum amount of information is obtained when the spectrum can be studied as a function of the orientation of the dimeric species. Bleaney and Bowers' early study of copper(II) acetate monohydrate is a classic example of the elucidation of the electronic structure of a dimeric system by EPR techniques.[7]

Ionic crystals which have been doped with paramagnetic impurities may contain dimeric species which come about when two paramagnetic ions occupy nearby lattice sites. Dimeric systems of this type are often called "pairs". Generally, the impurity ions are present in low concentration and are randomly distributed throughout the crystal. Thus, the probability of forming pairs may be quite small. The EPR resonances from pairs are usually orders of magnitude less intense than those from the isolated paramagnetic ions. In spite of the low concentration, a number of detailed analyses of pair resonances have been reported. The situation is quite favorable in the case of the Mn(II)–Mn(II) pairs in $CsCdCl_3$ crystals. The resonances from the isolated Mn(II) ions do not cover a wide range of magnetic field since the zero-field splittings of these isolated ions are quite small.[4] Thus, the portion of the pair spectrum that is obscured by the isolated ion resonances is minimized. The pairs have axial symmetry and are aligned parallel to the crystallographic *c* axis which greatly simplifies the interpretation of the spectrum.

It has already been established that the pair resonances observed in the EPR spectrum of $CsCdCl_3$ doped with Mn(II) arise from a dimeric system formed by the occupation of two

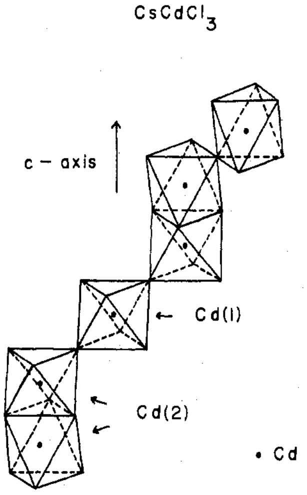

Figure 1. Perspective drawing of the $CsCdCl_3$ lattice. The corners of the octahedra are occupied by chloride ions. The cesium ions have been omitted.

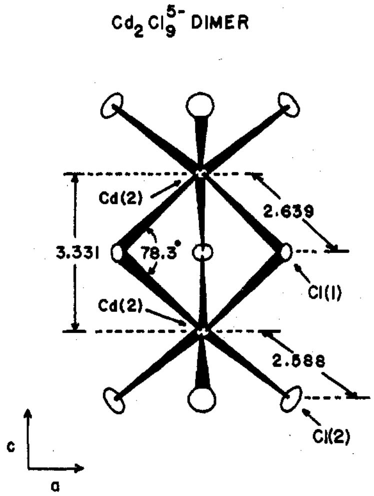

Figure 2. Perspective drawing of the $(Cd(2))_2Cl_9{}^{5-}$ portion of the $CsCdCl_3$ structure. The distances and angles are from ref 3.

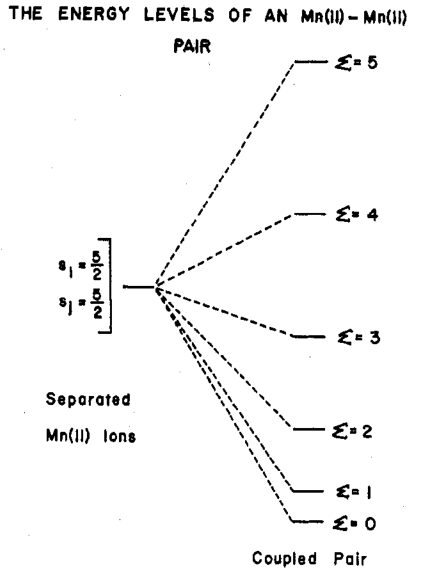

Figure 3. Energy level diagram for a hypothetical Mn(II)–Mn(II) dimer. Energy is assumed to increase in the vertical direction.

adjacent Cd(2) sites. Figure 2 shows a perspective drawing of the $(Cd(2))_2Cl_9{}^{5-}$ portion of the $CsCdCl_3$ structure. Although the replacement of two cadmium ions with manganese ions will undoubtedly cause some localized lattice distortion, the structure of the $Mn_2Cl_9{}^{5-}$ dimer must still be fairly similar to that of the host lattice. The structure of this system can be approximated as a pair of octahedra sharing a face; however, there are noticeable deviations from true octahedral geometry. Presumably, the electrostatic repulsion between the positively charged cadmium ions causes the Cd(2)–Cl(1) distances to lengthen relative to the Cd(2)–Cl(2) distances. This also causes the Cd(2)–Cl–Cd(2) angle to open up to 78.3° which is significantly larger than the angle of 70.5° required for an idealized octahedral structure.

The theoretical treatments for dimeric systems of paramagnetic ions have been discussed in a number of papers and reviews.[8-11] The spin Hamiltonian for a dimer must include terms describing the exchange and dipolar interactions between the two paramagnetic ions as well as the usual Zeeman, hyperfine, and zero-field terms. Such a Hamiltonian may be quite complex and difficult to solve. When the exchange interaction between ions is very large or very small, certain simplifying approximations may be used. In the case of the $Mn_2Cl_9{}^{5-}$ dimer, the exchange interaction would be expected to be relatively large since the Mn(II) ions are fairly close and are connected by three bridging chloride ions.

When two paramagnetic ions interact to form a magnetically coupled dimer, the spins on each ion combine as vectors to produce a manifold of spin states each characterized by a total spin quantum number, Σ. The degeneracy of these spin states is lifted by the exchange interaction. In the case of d^5 ions such as Mn(II) a dimeric system will produce a manifold of six spin states. These states are characterized by total spin quantum numbers of $\Sigma = 0$ through $\Sigma = 5$. Figure 3 shows an energy level diagram of a hypothetical Mn(II) dimer. All of the spin states except the $\Sigma = 0$ state may give rise to EPR resonances. If the exchange energies which separate these spin states are large compared with the Zeeman energies, the resonances from each spin state can be analyzed independently. Thus, a spin Hamiltonian can be written for each state. Using the formalism described by Owen[8,9] the following axial spin Hamiltonian can be derived to describe the resonances of the $Mn_2Cl_9{}^{5-}$ dimer in the crystals of $CsCdCl_3$

$$\mathcal{H} = \beta\vec{H}\cdot g\cdot\hat{\Sigma} + \hat{\Sigma}\cdot A\cdot(\hat{I}_1 + \hat{I}_2) + D_{\Sigma}\,[\hat{\Sigma}_z{}^2 - (1/3)\Sigma(\Sigma + 1)]$$

The first term describes the electron Zeeman interaction, while the second term describes the nuclear hyperfine interaction. The symbol, $\hat{\Sigma}$, represents the electron spin operator for the dimeric system, while $\hat{I}_1$ and $\hat{I}_2$ refer to the nuclear spin operators for the individual ^{55}Mn nuclei. Naturally occurring manganese consists entirely of the ^{55}Mn isotope which has a nuclear spin of $^5/_2$. Two equivalent nuclei having spins of $^5/_2$ will produce an 11-line hyperfine structure with an intensity pattern of 1:2:3:4:5:6:5:4:3:2:1. The coupling constant, A, would be expected to be half of that of an isolated Mn(II) ion. The third term in the Hamiltonian is the zero-field term which gives rise to the fine structure. The zero-field splitting parameter, D_Σ, will be different for each spin state. The spectrum of an Mn(II)–Mn(II) dimer may be very complicated since each spin state will have a fine structure containing 2Σ components and each of these components will exhibit an 11-line hyperfine structure.

As anticipated, the spectrum of the $Mn_2Cl_9{}^{5-}$ dimer has a very complex appearance. There is extensive overlap of the hyperfine structures of the resonances from the different spin states in certain regions of the spectrum. In some crystal orientations a few of the components are separated sufficiently so that the 11-line hyperfine structure may be observed. Figure

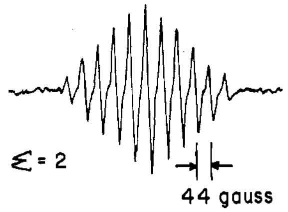

Figure 4. Hyperfine structure of one of the $\Sigma = 2$ resonances recorded at 77 K using Q-band frequency.

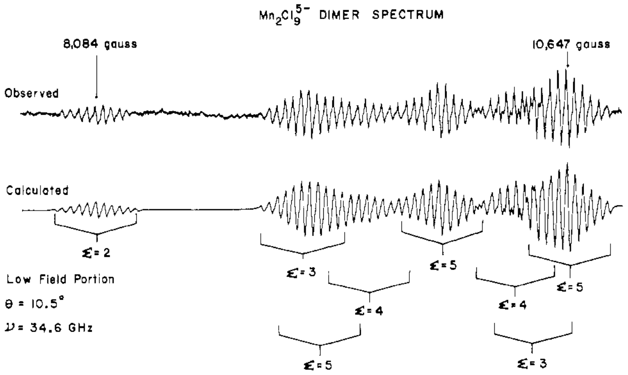

Figure 5. Portion of the observed and calculated spectra recorded at room temperature using Q-band frequency.

Table I. Spin-Hamiltonian Parameters[a] of the $Mn_2Cl_9^{5-}$ Dimer ($g = 2.00$ (1); $A = 0.0041$ (1) cm^{-1})

Σ	$\lvert D_\Sigma \rvert$, cm^{-1}	Σ	$\lvert D_\Sigma \rvert$, cm^{-1}
1	0.623 (3)	4	0.0388 (6)
2	0.139 (2)	5	0.0334 (5)
3	0.0609 (8)		

[a] The numbers in parentheses indicate the estimated error in the last decimal place of the reported parameter.

4 shows the hyperfine structure of one of the resonances from the $\Sigma = 2$ state. The coupling constant (44 G) is very close to half that of the isolated ions.[4] In spite of the complexity of the spectrum, resonances from spin states $\Sigma = 1$ through $\Sigma = 5$ can be identified and characterized. The resonances from some of the spin states can be observed at only certain crystal orientations. The $\Sigma = 1$ state, for example, gives observable resonances only when the magnetic field is perpendicular to the crystallographic *c* axis.

The **g** and **A** tensors appear to be isotropic and are the same for all the spin states. The zero-field parameters were obtained from the spectra recorded with the field either perpendicular or approximately parallel to the *c* axis. The spin-Hamiltonian parameters are given in Table I. Figure 5 shows a portion of the $Mn_2Cl_9^{5-}$ spectrum recorded at Q-band frequency with the field approximately parallel to the *c* axis ($\theta = 10.5°$). The computer simulation is based on line positions calculated from the parameters in Table I. The relative intensities of the hyperfine lines of each fine structure component was fixed at the theoretical ratio of 1:2:3:4:5:6:5:4:3:2:1. All of the lines were given a lorentzian shape and a peak to peak width of 15 G. The relative intensities of the resonances from different spin states were varied until a good fit between the calculated and observed spectrum was obtained. Although the agreement is not perfect, the overall fit is quite good. A similar fit was obtained for the high-field portion of the spectrum. The outermost resonances of the $\Sigma = 2$ and $\Sigma = 3$ states are well resolved and are sufficiently separated from the other resonances that the angular dependences of these lines may be studied. The observed angular dependences are shown in Figure 6. The theoretical curves were obtained from the exact solutions to the $\Sigma = 2$ and $\Sigma = 3$ spin Hamiltonians. These solutions were calculated numerically by computer diagonalization of the Hamiltonian matrices. The fit of the angular dependences and the successful simulations strongly support the correctness of our analysis.

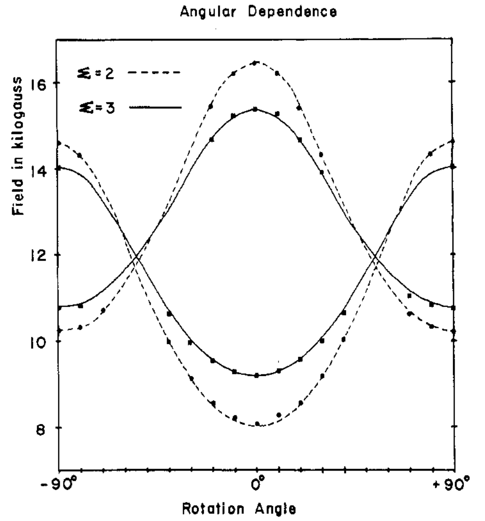

Figure 6. Observed and calculated angular dependence of the outermost pair of lines from the $\Sigma = 2$ and $\Sigma = 3$ states. The crystallographic *c* axis is out of the plane of rotation by approximately 10°. At rotation angles of +90 and −90° θ is equal to 90° while a rotation angle of 0° corresponds to a θ of 10.5°.

Table II. Energy Separations between the Spin States of the $Mn_2Cl_9^{5-}$ Dimer

Sepn	Energy, cm^{-1} Exptl	Energy, cm^{-1} Calcd[a]	Sepn	Energy, cm^{-1} Exptl	Energy, cm^{-1} Calcd[a]
Δ_{21}	~15	17	Δ_{43}	~30	34
Δ_{32}	~30	26	Δ_{54}	~50	43

[a] Calculated from the expression $\Delta_{ij} = J[i(i + 1) - j(j + 1)]$.

The energy separations between spin states can be evaluated from the temperature dependence of the intensities of the resonances from the different states. Assuming that the populations of the spin states obey Boltzmann statistics, the ratio of the intensities of resonances from two states can be described by

$$I_i/I_j \propto e^{-\Delta_{ij}/kT}$$

The Δ_{ij} represents the energy separation between the two spin states. The experimental energies reported in Table II were calculated by comparing the intensities of the different resonances at room and liquid nitrogen temperatures. These energy values are quite imprecise since they were determined from data taken at only two temperatures. An accurate determination would require several measurements at temperatures below 77 K. Although the analysis is crude, our computations show the exchange in the $Mn_2Cl_9^{5-}$ dimer to be antiferromagnetic and give an estimate of the magnitude of the interaction. The calculated energies in Table II were computed with an exchange constant of 4.3 cm^{-1} assuming the separations follow the Landé rule. The agreement between the experimental and calculated values is as good as can be expected considering the crudeness of the experimental energies. It is our feeling that the actual value of *J* may differ from the calculated value of 4.3 cm^{-1} by as much as 30%.

In a pair system, the anisotropic interactions between the two ions as well as the distortions in the crystal lattice contribute to the zero-field splittings. The following equation expresses the zero-field splitting for a particular spin state in

Table III. Analysis of the Zero-Field Terms

$D_\Sigma = 3\alpha D_e + \beta D_c$ (Owen Formalism[8,9])

	Σ				
	1	2	3	4	5
α	+37/10	+41/42	+47/90	+5/14	+5/18
β	−32/5	−20/21	−2/45	+2/7	+4/9

The $Mn_2Cl_9^{5-}$ Data ($D_e = -0.384$ cm^{-1} [a])

Σ	D_c, cm^{-1}	Σ	D_c, cm^{-1}
1	+0.0308	4	+0.0082
2	+0.0264	5	−0.0032
3	+0.0190		

[a] Calculated from the Σ = 3 state.

terms of these two contributions

$$D_\Sigma = 3\alpha D_e + \beta D_c$$

The D_e and D_c represent the contributions from the anisotropic interactions and the crystal lattice, respectively. The α and β values for the different spin states of various dimer systems have been given by Owen.[8,9] The values for a dimer containing d^5 ions are presented in Table III. Since β is quite small when $\Sigma = 3$, the contribution of the crystal lattice to the zero-field splitting of the $\Sigma = 3$ state is nearly insignificant compared with that from the anisotropic interactions. Thus, an approximate value of −0.038 cm^{-1} for D_e can be obtained directly from the experimental value of D_3. Using this value one can calculate D_c from the observed zero-field splittings of the other spin states. Once a reasonable value for D_c has been established, a more precise value of D_e can be calculated from D_3. The results of this analysis are also given in Table III. It is clear that if the D_e value is held constant D_c must vary considerably from one spin state to another in order to reproduce the observed zero-field splittings. The value of D_c actually changes sign between the $\Sigma = 4$ and $\Sigma = 5$ states. The failure to reproduce the observed zero-field splittings with single values for D_c and D_e may indicate that the separation between the Mn(II) ions in the dimer changes as a function of spin state. Similar effects have been observed by Harris in the zero-field splittings of Mn(II)–Mn(II) pairs in CaO and MgO.[12] Harris' careful study indicates that exchange striction causes the Mn(II)–Mn(II) separation to vary as a function of spin state. For states of low total spin, exchange striction produces an attraction between the paramagnetic ions of a dimer while a repulsion results in states of high total spin. These forces can be likened to weak bonding and antibonding interactions. The interionic separation for a dimeric system is smallest for the $\Sigma = 0$ state and increases with increasing spin. As was pointed out by Harris, the values of both D_e and D_c may depend quite critically on the separation between the two paramagnetic ions. The energy intervals between the spin states of the Mn(II)–Mn(II) pairs in MgO deviate noticeably from the Landé rule as a result of the exchange striction. Comparing the data for the pairs in MgO with our data it appears that the exchange striction is not as strong in the $Mn_2Cl_9^{5-}$ dimer. If this is true, the value of D_e would not be expected to vary by more than 10% from the $\Sigma = 1$ to the $\Sigma = 5$ states. This means that D_c still must change drastically. It is possible that D_c is more sensitive than D_e to the position of the Mn(II) ions. A very small change in the position of an ion may have a very large effect on the lattice contribution to the zero-field splitting. Although our analysis does not unequivocally prove that the variations in D_c and D_e parameters of the $Mn_2Cl_9^{5-}$ dimer are due to exchange striction, it provides a reasonable explanation. The fact that D_c varies in a regular way with respect to spin state is clearly consistent with an exchange striction model.

In pair systems containing d^5 ions, the anisotropic contribution, D_e, to the zero-field splitting is almost entirely due to magnetic dipole–dipole interactions.[12] If the two paramagnetic ions are treated as point dipoles, the interaction can be calculated from the simple expression

$$D_e = -g^2\beta^2/R^3$$

where R is the separation between dipoles. Assuming that the metal–chlorine distances in the $Mn_2Cl_9^{5-}$ dimer are intermediate between those of a pure manganese salt and a pure cadmium salt, the Mn(II)–Mn(II) separation is calculated to be 3.26 Å. (The structures of $CsCdCl_3$[2] and $CsMnCl_3$[13] were used for this computation.) Using this value of R, the anisotropic contribution is calculated to be 0.0528 cm^{-1} which is significantly larger than the experimentally determined quantity. The reduction of the actual interaction from that of the point-dipole computation is presumably the result of the partial delocalization of the unpaired electrons from the metal to the surrounding ligands.[9,12] A crude estimate of the extent of the delocalization can be made by taking the following simplistic approach. If f represents the fraction of the total magnetic amount of the Mn(II) ion that transferred to each chloride ligand, the fraction remaining on the metal ion is $(1 - 6f)$. Thus, the dipolar interaction can be expressed by modifying the point-dipole expression as

$$D_e = -(g^2\beta^2/R^3)(1 - 6f)^2$$

Using the observed value of D_e one obtains an f of approximately 0.025 which indicates that roughly 2.5% of the electron density is transferred to each chloride ion. This approach neglects the dipole–dipole interactions of the fractional magnetic moments centered on the chloride ions and does not allow for the fact that the chloride ions in the $Mn_2Cl_9^{5-}$ dimer are not all equivalent. In spite of these rather serious deficiencies, the calculated result seems chemically reasonable and is probably qualitatively accurate.

One interesting feature of the $Mn_2Cl_9^{5-}$ dimer is that the bridging between the two Mn(II) ions is very similar to the bridging system in the linear-chain salt $[(CH_3)_4N]MnCl_3$. The structure of the tetramethylammonium salt consists of infinite linear chains of $MnCl_6^{4-}$ octahedra sharing faces. The Cl–Mn–Cl angle is 78.8°[14] which is quite close to the Cl–Cd(2)–Cl angle of 78.3° in $CsCdCl_3$. The $[(CH_3)_4N]MnCl_3$ salt has been of considerable interest to chemists and physicists because the magnetic properties of this material approach those of a one-dimensional antiferromagnet.[15] The exchange parameter, J, for the interactions within the linear chains has been found to be 4.4 cm^{-1} in the 300–60 K region.[16,17] Thus, it appears that the magnetic interaction in the linear-chain system is quite similar to that of the $Mn_2Cl_9^{5-}$ dimer. If exchange striction is actually significant in the $Mn_2Cl_9^{5-}$ dimer, one might expect that exchange striction effects would have been observed for $[(CH_3)_4N]MnCl_3$. As would be expected the Mn(II)–Mn(II) separation does decrease as the temperature is lowered;[17,18] however, it is difficult to separate the effect of exchange striction from the normal thermal contraction of the lattice. It does seem reasonable that some of the contraction may be due to the magnetic interactions.

In conclusion, it has been shown that observable quantities of exchange-coupled Mn(II)–Mn(II) pairs are produced when $CsCdCl_3$ crystals are doped with Mn(II). These pairs result when two adjacent Cd(2) sites in the $CsCdCl_3$ lattice are occupied by Mn(II) ions. The coupling between the Mn(II) ions is antiferromagnetic with an exchange energy (J) of roughly 4 cm^{-1}. The zero-field terms in the spin Hamiltonians describing the pair resonances suggest that the Mn(II)–Mn(II) separation varies with spin state. This may be due to exchange striction. The measured dipole–dipole interaction is noticeably smaller than that predicted by a point-dipole calculation which suggests that the unpaired electrons are partially delocalized from the metal to the chloride ligands.

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Registry No. $CsCdCl_3$, 13845-08-4; Mn, 7439-96-5; $Mn_2Cl_9^{5-}$, 58396-13-7.

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Effect of High-Energy Radiation on a Range of Metal Pentacyanonitrosylferrate(II) and Pentacyanonitroferrate(II) Salts

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Exposure of a range of alkali and alkaline earth pentacyanonitrosylferrate(II) salts to ^{60}Co γ rays at 77 K gave electron-capture centers having the unpaired electron largely confined to the nitrosyl ligand, as judged by their ESR spectra. These ESR spectra were almost independent of the salt except that for the hydrated sodium salt which changed reversibly to that exhibited by the other salts on cooling to 4.2 K. In all cases, ESR spectra assignable to normal d^7 iron(I) salts are also obtained, and these were enhanced at the expense of the nitrosyl center on annealing above 77 K. At least two d^7 centers were obtained in most cases. One, having axial symmetry, is assigned the structure $Fe(CN)_4NO^{2-}$, formed by loss of the axial cyanide ligand, and the other, having nonaxial symmetry, is assigned the structure $Fe(CN)_5NO^{3-}$, with both the axial cyanide and the NO group present but bent slightly off the original axis. The nitroferrate(II) salts gave an electron-excess species having the unpaired electron largely confined to the NO_2 group, whose ESR spectra closely resembled that of the nitrosyl center. However, these were not converted into d^7 ferrate(I) salts under any circumstances. The Ag(I) salts also gave Ag(II) centers, whose ESR spectra exhibited hyperfine coupling to four equivalent ^{14}N nuclei in addition to that to ^{107}Ag and ^{109}Ag. These d^9 ions have their unpaired electrons in a $d_{x^2-y^2}$ orbital on silver with considerable delocalization onto four in-plane nitrogen atoms.

There has been considerable speculation about the nature of paramagnetic electron-excess species formed from sodium pentacyanonitrosylferrate(II). Three different types of ESR spectra have been reported. The first spectrum has $g_\perp \simeq 2.3$ and $g_\parallel \simeq 2.0$ with $A_\perp(N) \simeq 14.0$ G and $A_\parallel(N) \simeq 17.0$ G. We have assigned this spectrum to a d^7 iron complex (species I) having an unpaired electron in an a (d_{z^2}) orbital and a strongly coupled NO group which is bent about 10° from the z axis of the complex.[1] Van Voorst and Hemmerich[2] have assigned this spectrum to $Fe(CN)_5NOH^{2-}$ when studying the reduction products in DMF. A tetraethylammonium salt having similar ESR parameters has been isolated and shown by x-ray diffraction to be the pentacoordinated $Fe(CN)_4NO^{2-}$ d^7 species.[3] In addition, we have generated this spectrum by the thermal reduction of anhydrous pentacyanonitrosylferrates.[4] Most recently,[5] this same spectrum has been assigned to $[Fe(CN)_5NOH]^{2-}$ in DMF, $Cd[Fe(CN)_5NOH]\cdot 2DMF$ solid, and $Cd_3[Fe(CN)_5NO]_2\cdot$(formamide).

A second ESR spectrum has two g values near free spin with the third $g \simeq 1.93$ and A values of approximately 30 and 10 G, respectively. Less controversy seems to exist for this spectrum with general agreement that it represents a d^6 complex (species II), $Fe(CN)_5NO^{3-}$, with the unpaired electron largely in a π^* MO on the NO ligand.[2] However, a very similar ESR spectrum has been assigned to $Fe(CN)_5NO_2^{5-}$ (species IV)[6] and this has recently been substantiated.[5] Also, a similar ESR spectrum has been observed upon heating the potassium, rubidium, and cesium pentacyanonitrosylferrates(II) to temperatures of 240 °C.[7]

A third spectrum having a large hyperfine coupling to ^{14}N and two low g values (species III) was obtained by irradiating the hydrated sodium salt.[8] It was tentatively suggested that this species is chemically identical with the d^6 complex with the unpaired electron largely in the π^* MO on the NO ligand, differing only in the extent of NO group libration. Trapped radical pairs have also been observed upon prolonged exposure of $Na_2Fe(CN)_5NO\cdot 2H_2O$ to γ radiation at room temperature.[9]

The aim of the present study was threefold: to investigate the relationship between spectra II and III, to distinguish, if possible, between the spectra assigned to $Fe(CN)_5\dot{N}O^{3-}$ and $Fe(CN)_5\dot{N}O_2^{5-}$, and to examine the effects of environment upon the three different spectra. Incidental to this study, we

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