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(8) D_{6h} symmetry, C–C = 1.392 Å, C–C–C = 120°.
(9) C–H = 0.95 Å, C–C–H = 120°.
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Contribution from the Departments of Chemistry, Tulane University, New Orleans, Louisiana 70118,
and The University of Alabama, University, Alabama 35486

Electron Paramagnetic Resonance Spectra of Vanadium(II) and Nickel(II) Doped into Crystals of Cesium Cadmium Chloride and a Redetermination of the Structure of Cesium Cadmium Chloride[1]

JIN RONG CHANG,[2a] GARY L. McPHERSON,*[2a] and JERRY L. ATWOOD*[2b]

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The crystal structure of $CsCdCl_3$ has been redetermined using diffractometer-measured intensity data. The compound crystallizes in the hexagonal space group $P6_3/mmc$ with unit cell dimensions of a = 7.403 (2) Å and c = 18.406 (3) Å. Based on 354 observed reflections the structure was refined by full-matrix least-squares methods to R_1 and R_2 values of 0.044 and 0.050, respectively. There are two crystallographically distinct types of cadmium ions in $CsCdCl_3$. One of the cadmium ions, Cd(1), occupies a site having D_{3d} symmetry, while the other, Cd(2), exhibits C_{3v} site symmetry. The coordination sphere of Cd(1) contains six equivalent chloride ions which form a nearly perfect octahedron with a cadmium–chloride separation of 2.598 Å. In contrast, the coordination sphere of Cd(2) contains two distinct groups of chloride ions which form a noticeably distorted octahedron; the cadmium–chloride distances are 2.639 and 2.588 Å. The EPR spectrum of $CsCdCl_3$ doped with V(II) shows that both types of cadmium ion are replaced. The spectrum can be satisfactorily interpreted with an axial spin Hamiltonian. An analysis of the spin Hamiltonian parameters indicates that 90–95% of the V(II) ions enter sites normally occupied by Cd(1) while the remaining 5–10% enter the sites that would contain Cd(2). The spectrum of $CsCdCl_3$ containing Ni(II) shows resonances from only one kind of Ni(II) ion which suggests that only one of the two sites is occupied.

Introduction

When crystallized from the melt, $CsCdCl_3$ adopts a hexagonal lattice in which there are two crystallographically distinct types of cadmium ions.[3] Both cadmium ions (1 and 2) are surrounded by octahedra of chloride ions. Two octahedra containing type 2 cadmium ions share a face forming a $Cd_2Cl_9^{5-}$ unit which then shares corners with six different octahedra containing type 1 cadmium ions. Figure 1 shows a simplified view of the $CsCdCl_3$ structure. The point symmetry at cadmium 1 is D_{3d} while it is C_{3v} at cadmium 2. This structure can be considered as intermediate between the $CsNiCl_3$ structure which consists of infinite linear arrays of octahedra sharing faces and the perovskite structure which consists of a three-dimensional network of octahedra sharing corners.

An investigation of the EPR spectra of single crystals of

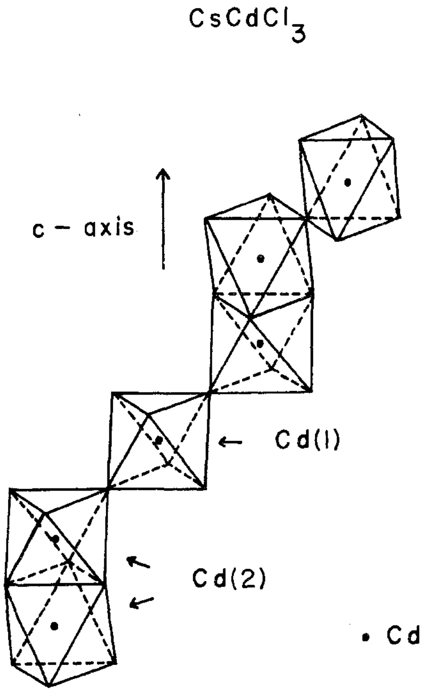

Figure 1. Perspective view of the $CsCdCl_3$ lattice. The cesium ions have been omitted.

$CsCdCl_3$ doped with V(II) and Ni(II) was undertaken as a part of a systematic study of the spectroscopic and magnetic properties of the $M^{I}M'^{II}X_3$ halides. The purpose of this particular investigation was to determine if V(II) and Ni(II) substitutes for both types of cadmium ions in this lattice and to compare the spin Hamiltonian parameters of the two sites if substitution into both sites did occur. It had been previously shown that Mn(II) substitutes into both cadmium sites in $CsCdCl_3$.[4]

Preliminary experiments indicated that V(II), like Mn(II), substitutes into both sites although V(II) shows a strong preference for one site over the other. The Ni(II) appeared to substitute into only one site. The spin Hamiltonian parameters for the two types of V(II) ions differed noticeably. This is in contrast to Mn(II)-doped $CsCdCl_3$ where the spin Hamiltonian parameters for the two sites are not significantly different.[4] The differences in the V(II) parameters suggest that the electronic structure of the V(II) ion varies significantly from one site to the other. This is somewhat surprising since the V(II) ion is surrounded by an octahedron of chloride ions in either case. It was assumed that these differences could be attributed to structural properties of the lattice. Since the structure determination reported by Siegel and Gebert[3] is not accurate enough ($R = 0.19$ with a standard deviation in the bond lengths of $\sim$0.02 Å) to describe precisely the coordination spheres of the cadmium ions, a redetermination of the $CsCdCl_3$ structure was carried out. This paper presents the results of the EPR and X-ray diffraction studies. The spin Hamiltonian parameters and the partitioning of the paramagnetic ions between the two sites are discussed in terms of the structural properties of the $CsCdCl_3$ lattice.

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 preparations of $CsVCl_3$ and $CsNiCl_3$ have been described previously.[5]

Table I. Crystal Data for $CsCdCl_3$

Fw 351.67	Hexagonal
$a = 7.403$ (2) Å	Space group $P6_3/mmc$
$c = 18.406$ (3) Å	$F(000) = 924$
$V = 873.7$ Å^3	$\mu = 112.0$ cm^{-1} (Mo Kα radiation)
$\rho_{calcd} = 4.03$ g cm^{-3} ($Z = 6$)	$\rho_{obsd} = 3.96$ g cm^{-3}

Crystal Growth. Single crystals of $CsCdCl_3$ suitable for spectroscopic and X-ray study were grown from the melt by the Bridgman method. Doped crystals were prepared by adding $\sim$0.1% $CsVCl_3$ or $CsNiCl_3$ to the $CsCdCl_3$. The apparatus and procedure have been described previously.[6]

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 ^{7}Li and ^{1}H NMR frequencies. The *g* values were determined by using polycrystalline diphenylpicrylhydrazyl ($g = 2.0036$) as a reference.

X-Ray Data Collection. A small single crystal of $CsCdCl_3$ was cleaved from a larger crystal which was grown from the melt. The small crystal was ground to a sphere of 0.30-mm diameter and mounted on a thin glass fiber. Preliminary X-ray examination and data collection were carried out on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite-crystal monochromator. The compound is hexagonal with systematic absences consistent with the space groups $P6_3/mmc$, $P6_3mc$, and $P\bar{6}c2$ (hhl, $l \neq 2n$). It was assumed that the compound, as previously reported,[3] belonged to the centric space group $P6_3/mmc$. Table I gives the lattice parameters which were determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 13 reflections with $\theta > 19°$.

The diffracted intensities were collected using the ω–2θ scan technique with a takeoff angle of 3.5°. The scan rate was variable and was determined by a fast 20° min^{-1} prescan. Calculated speeds for the slow scan ranged from 20 to 0.3° min^{-1}. Moving-crystal moving-counter backgrounds were collected for 25% of the total scan width at each end of the scan range. For each intensity the scan width was determined by the equation

$$\text{scan range} = A + B \tan\theta$$

where $A = 0.90°$ and $B = 0.45°$. Aperture settings were determined in a similar manner with $A = 4$ mm and $B = 4$ mm. Other diffractometer parameters and the method of estimation of standard deviations have been described previously.[7] As a check on the stability of the instrument and the crystal, three reflections, (203), (02$\bar{3}$), and (006), were measured after every 30 reflections; no significant variation was noted.

Three symmetry-related forms of data were measured out to $2\theta = 44°$; a slow scan was performed on a total of 1112 reflections. Since these data were scanned at a speed which would yield a net count of 4000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 10 was obtained in the prescan. The data were corrected for Lorentz, polarization, and absorption effects and finally averaged to yield a unique set of 354 observed reflections. (For most of these, $I > 3\,\sigma(I)$.)

Fourier calculations were made with the ALFF[8] program. The full-matrix, least-squares refinement was carried out using the Busing and Levy program ORFLS.[9] The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Scattering factors for Cd^{2+}, Cs^+, and Cl^- were taken from the compilations of Cromer and Waber,[10] and those for Cd^{2+} and Cs^+ were corrected for the real and imaginary components of anomalous scattering according to Cromer's table.[11] Final bond distances, angles, and errors were computed with the aid of the Busing, Martin, and Levy ORFFE program.[12] Crystal structure illustrations were obtained with the program ORTEP.[13]

Refinement of the Structure. Atomic coordinates obtained by Siegel and Gebert[3] (see Table II) were refined isotropically to $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.082$. Anisotropic refinement afforded final agreement indices of $R_1 = 0.044$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum(wF_o)^2]^{1/2} = 0.050$. Refinement in either of the two acentric space groups $P6_3mc$ or $P\bar{6}c2$ led to no significant improvement in the R values despite the additional parameters. Unit weights were used at all stages of refinement, and unobserved reflections were not included. The

Table II. Unit Cell Contents of $CsCdCl_3$[a]

Atom	Wyckoff designation	Point symmetry	Coordinates	No. of positions
Cs(1)	(b)	$\bar{6}m2$	0, 0, $^1/_4$	2
Cs(2)	(f)	$3m$	$^1/_3$, $^2/_3$, z	4
Cd(1)	(a)	$\bar{3}m$	0, 0, 0	2
Cd(2)	(f)	$3m$	$^1/_3$, $^2/_3$, z	4
Cl(1)	(h)	mm	x, $2x$, $^1/_4$	6
Cl(2)	(k)	m	x, $2x$, z	12

[a] Based on space group $P6_3/mmc$.

largest parameter shifts in the final cycle of refinement were less than 0.05 of their estimated standard deviations. (A final difference Fourier showed no unaccounted electron density.) The final values and standard deviations of the positional and thermal parameters are given in Table III.

Results and Discussion

The Structure of $CsCdCl_3$. Our X-ray determination shows that the structure of $CsCdCl_3$ is basically the same as that reported by Siegel and Gebert;[3] however, the greater accuracy of our diffraction data leads to considerably more precise structural parameters. The interatomic distances and angles calculated from our analysis are reported in Table IV. In terms of the interpretation of the EPR spectra, the most important structural features are the environments of the two crystallographically distinct cadmium ions. Figure 2 shows an ORTEP drawing of the coordination spheres of one Cd(1) ion and two Cd(2) ions. The six chloride ions (Cl(2)) which surround Cd(1) are equivalent and form an octahedron which is regular within experimental error (within one standard deviation Cl(2a)–Cl(2b) is equal to Cl(2b)–Cl(2c) and the Cl(2a)–Cd(1)–Cl(2b) and Cl(2b)–Cd(1)–Cl(2c) angles are equal to 90°). The octahedron containing Cd(1) joins corners with six octahedra containing Cd(2) ions forming Cd(1)–Cl(2)–Cd(2) bridges that are nearly linear. Each of the octahedra containing a Cd(2) ion also shares a face with a second Cd(2)-containing octahedron forming three bent Cd(2)–Cl(1)–Cd(2) bridges. Thus, the coordination sphere of each Cd(2) ion contains two distinct groups of chloride ions (1 and 2) which have significantly different Cd–Cl distances. Presumably, the electrostatic repulsion between the two Cd(2) ions causes the Cd(2)–Cl(1) distances to lengthen relative to the Cd(2)–Cl(2) distances (2.639 Å compared with 2.588 Å). In contrast to the environment of Cd(1), the coordination sphere of Cd(2) is noticeably distorted from that of a regular octahedron.

A variety of structures have been observed for $M^IM'^{II}X_3$ halides depending on the nature of M^I, M'^{II}, and X. Of these structures, the linear-chain $CsNiCl_3$ structure and the perovskite lattice can be thought of as structural extremes. The $CsNiCl_3$ structure contains only face-shared octahedra while the perovskite structure consists entirely of corner-shared octahedra. Thus, $CdCdCl_3$ represents an intermediate between the two extremes since it contains octahedra sharing faces and corners. Longo and coworkers have shown that many of the $M^IM'^{II}X_3$ salts undergo pressure-induced structural transformations.[14-18] In some cases, salts which adopt the $CsNiCl_3$ structure undergo several phase changes with increasing pressure. The face-shared $CsNiCl_3$ lattice is successively converted to lattices containing greater fractions of corner-shared octahedra until the perovskite structure is ultimately obtained. The $CsCdCl_3$ structure usually appears as one of the intermediate phases. Each phase change is accompanied by a decrease in the volume occupied by a formula weight of the $M^IM'^{II}X_3$ salt. Their work convincingly demonstrates that corner-shared structures require less volume than face-shared structures. From these studies it seems reasonable to conclude that the volume occupied by Cd(1) is somewhat smaller than that occupied by Cd(2) in $CsCdCl_3$. This conclusion is supported by the observed Cd–Cl distances in the redetermined structure. The average Cd(1)–Cl distance is 2.598 Å compared with the average Cd(2)–Cl distance of 2.614 Å.

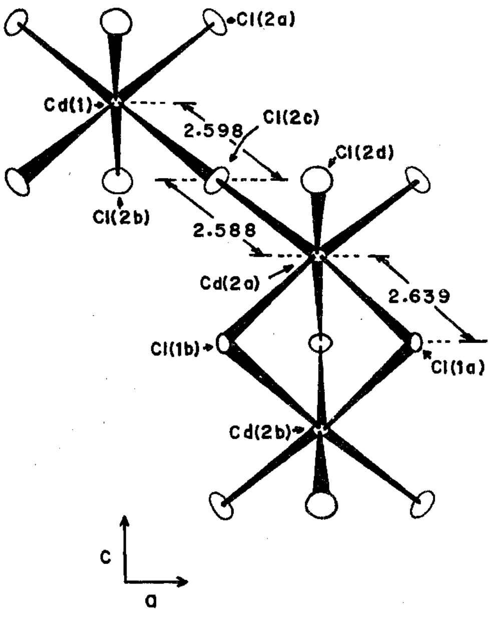

Figure 2. ORTEP drawing of the coordination spheres of two adjacent Cd(2) ions and a Cd(1) ion.

The EPR Spectra. The structural studies show that the two unique cadmium ions, Cd(1) and Cd(2), have point symmetries of D_{3d} and C_{3v}, respectively. Thus, the EPR spectra of paramagnetic ions occupying sites normally occupied by Cd(1) or Cd(2) ions would be expected to exhibit axial symmetry. As expected the spectra of all of the doped $CsCdCl_3$ crystals showed axial symmetry about the crystallographic c axis. All of the spectra could be satisfactorily interpreted with axial spin Hamiltonians. The spectrum of each ion will be discussed in some detail.

Divalent vanadium is a d^3 ion which has an $S = {}^3/_2$ spin system in the ground state. The spectrum of a V(II) ion in a crystal site having axial symmetry would be expected to contain a three-line fine structure. The fine structure results from the zero-field splitting of the $S = {}^3/_2$ manifold by the axial component of the ligand field. The ^{51}V nucleus, which

Table III. Positional and Thermal Parameters[a]

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cs(1)	0	0	$^1/_4$	0.0102 (6)	0.0102	0.0013 (1)	0.0051	0.0000	0.0000
Cs(2)	$^1/_3$	$^2/_3$	0.0890 (1)	0.0092 (4)	0.0092	0.0014 (1)	0.0046	0.0000	0.0000
Cd(1)	0	0	0	0.0032 (5)	0.0032	0.0003 (1)	0.0016	0.0000	0.0000
Cd(2)	$^1/_3$	$^2/_3$	0.8405 (1)	0.0045 (3)	0.0045	0.0003 (1)	0.0022	0.0000	0.0000
Cl(1)	0.5069 (8)	1.0138	$^1/_4$	0.0085 (10)	0.0036 (10)	0.0006 (1)	0.0018	0.0000	0.0000
Cl(2)	0.8349 (9)	1.6698	0.0816 (2)	0.0125 (8)	0.0065 (8)	0.0014 (1)	0.0032	0.0010	0.0020 (3)

[a] Anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The following constraints are placed on the thermal parameters: for Cs(1), Cs(2), Cd(1), and Cd(2), $\beta_{11} = \beta_{22} = 2\beta_{12}, \beta_{13} = \beta_{23} = 0$; for Cl(1), $\beta_{22} = 2\beta_{12}, \beta_{13} = \beta_{23} = 0$; for Cl(2), $\beta_{22} = 2\beta_{12}, \beta_{13} = \beta_{23}$.

Table IV. Selected Interatomic Distances and Angles[a]

Distances, Å

Cd(2a)–Cd(2b)	3.331 (3)	Cs(2)–Cl(2)	3.705 (3)
Cd(1)–Cl(2)	2.598 (5)	Cl(1a)–Cl(1b)	3.546 (9)
Cd(2)–Cl(1)	2.639 (4)	Cl(1b)–Cl(2c)	3.745 (4)
Cd(2)–Cl(2)	2.588 (5)	Cl(2a)–Cl(2b)	3.678 (6)
Cs(1)–Cl(1)	3.703 (3)	Cl(2b)–Cl(2c)	3.672 (10)
Cs(1)–Cl(2)	3.754 (5)	Cl(2c)–Cl(2d)	3.731 (10)
Cs(2)–Cl(1)	3.706 (3)		

Angles, Deg

Cl(2a)–Cd(1)–Cl(2b)	90.1 (1)	Cl(2c)–Cd(2a)–Cl(2d)	92.4 (2)
Cl(2b)–Cd(1)–Cl(2c)	89.9 (1)	Cd(2a)–Cl(1a)–Cd(2b)	78.3 (2)
Cl(1a)–Cd(2a)–Cl(1b)	84.4 (2)	Cd(1)–Cl(2c)–Cd(2a)	178.3 (2)
Cl(1a)–Cd(2a)–Cl(2d)	91.5 (1)		

[a] Atom designations refer to Table II and Figure 2. The numbers in parentheses are the standard deviations in the last decimal place of the reported parameters.

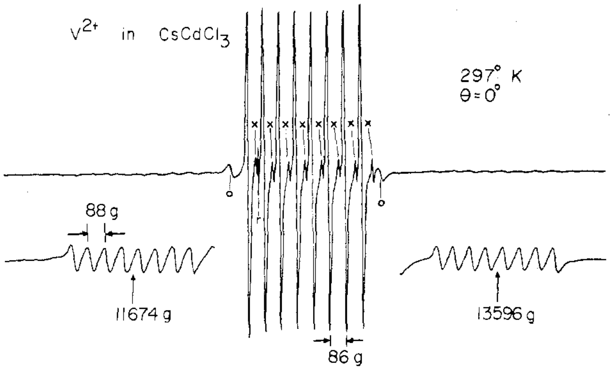

Figure 3. Q-Band EPR spectrum of $CsCdCl_3$ doped with V(II) at room temperature with the field parallel to the *c* axis. The resonance marked with an r is from DPPH.

Table V. Spin Hamiltonian Parameters for V(II), Mn(II), and Ni(II) in $CsCdCl_3$

V(II)

Parameter[a]	296 K		77 K	
	Site 1	Site 2	Site 1	Site 2
D, cm^{-1}	∓0.0043 (1)	±0.0444 (2)	±0.0148 (4)	±0.0234 (4)
A, cm^{-1}	±0.0078 (1)	±0.0080 (1)	±0.0079 (1)	±0.0081 (1)
B, cm^{-1}	±0.0078 (1)	±0.0080 (1)	±0.0078 (1)	±0.0081 (1)
$g_\parallel$	1.9635 (5)	1.9559 (5)	1.963 (1)	1.957 (1)
$g_\perp$	1.9638 (5)	1.9559 (5)	1.962 (1)	1.957 (1)

Mn(II)

Parameter	296 K		77 K	
	Site α	Site β	Site α	Site β
D, cm^{-1}	±0.00065 (5)	∓0.00174 (5)	±0.0010 (1)	∓0.0015 (1)
A, cm^{-1}	±0.0081 (1)	±0.0081 (1)	±0.0081 (1)	±0.0081 (1)
B, cm^{-1}	±0.0081 (1)	±0.0082 (1)	±0.0081 (1)	±0.0081 (1)
$\|a - F\|$ cm^{-1}	0.00010 (5)	0.00010 (5)	0.00010 (5)	0.00010 (5)
$g_\parallel = g_\perp$	2.002 (2)	2.002 (2)	2.002 (2)	2.002 (2)

Ni(II)

Parameter	77 K
D, cm^{-1}	0.905 (5)
$g_\parallel$	2.28 (1)
$g_\perp$	2.29 (1)

[a] The number in parentheses is the estimated experimental error in the last decimal place of the parameter. The ± signs denote the relative signs of the zero-field and hyperfine parameters. It should be noted that the relative accuracies of the *A* and *B* values for the two V(II) sites are considerably greater than the quoted absolute errors indicate.

is approximately 100% abundant in naturally occurring vanadium, has a nuclear spin of $^7/_2$. An eight-line hyperfine structure for each of the three fine-structure components would result in a 24-line spectrum, assuming that the spectrum has a first-order appearance. The EPR spectrum of $CsCdCl_3$ doped with V(II) clearly indicates the presence of paramagnetic ions in two different axial sites. The differences in intensities of the lines from the two sites suggest that V(II) has a strong preference for one site. The spectrum of V(II) in $CsCdCl_3$ at room temperature is shown in Figure 3. The eight lines with the greatest intensity arise from the center fine-structure component (the $|-^1/_2\rangle \rightarrow |+^1/_2\rangle$ transition) of the V(II) ions occupying Cd(1) sites. (This assignment will be discussed later.) Only the first line of the low-field component and the last line of the high-field component of the fine structure are observed because the zero-field splitting is quite small. These lines are designated by small circles in Figure 3. The lines resulting from V(II) ions substituted for Cd(2) are much less intense; however, all 24 lines can be observed since the zero-field splitting is considerably larger. The eight lines of the center fine-structure component are marked by ×. The low-field and high-field components are centered at 11674 and 13596 G, respectively. The intensities of the lines associated with the stronger V(II) resonance are between 10 and 20 times as large as those of the corresponding lines of the weaker resonance. It appears that 90–95% of the V(II) ions substitute for Cd(1) while only 5–10% substitute for Cd(2).

The spectra of both V(II) ions can be satisfactorily described by the axial spin Hamiltonian

$$\mathcal{H} = g_\parallel \beta H_z \hat{S}_z + g_\perp \beta (H_x \hat{S}_x + H_y \hat{S}_y) + A \hat{I}_z \hat{S}_z + B(\hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y) + D[\hat{S}_z^2 - {}^1/_3(S(S+1))]$$

Since the zero-field parameter, *D*, is in all cases small compared with $h\nu$, the line positions can be accurately calculated with the perturbation solution to the spin Hamiltonian given by Bleaney.[19] The values for the spin Hamiltonian parameters were obtained by varying the parameters until a good agreement between the calculated and observed line positions was obtained. The parallel parameters were obtained from the $\theta = 0°$ spectrum while the perpendicular parameters were found from the $\theta = 90°$ spectrum. (θ is the angle between the applied field and the crystallographic *c* axis.) The values of the spin Hamiltonian parameters are reported in Table V for both sites at room and liquid nitrogen temperatures. The relative signs of the zero-field (*D*) and hyperfine (*A* and *B*) parameters were obtained from an analysis of the second-order effects in the hyperfine structure.[20]

The spectrum of V(II)-doped $CsCdCl_3$ was carefully studied to see if any resonances arising from exchange coupled pairs of vanadium ions could be observed. Pair resonances had been observed in the spectrum of $CsCdCl_3$ doped with Mn(II).[4] The Mn(II)–Mn(II) pairs were shown to result from the substitution of manganese for cadmium in two adjacent Cd(2) sites. No evidence for the presence of similar V(II)–V(II) pairs was found in the spectrum of V(II)-doped $CsCdCl_3$, even in crystals containing as much as 1% V(II). Clearly the formation of the coupled Mn(II)–Mn(II) pair is a much more likely process than the formation of the analogous V(II)–V(II) pair.

One unusual feature of the spectrum of the V(II)-doped $CsCdCl_3$ is the large temperature dependence of the zero-field splittings. The zero-field parameter, *D*, for site 1 actually changes sign between room and liquid nitrogen temperature. These large variations indicate that significant changes in the coordination spheres of the two cadmium sites take place between 296 and 77 K. A variable-temperature experiment was carried out to determine if the changes were due to a structural phase change or to the simple contraction of the lattice with decreasing temperature. A gradual change in the *D* values with temperature would be expected if the environments of the two types of V(II) ions were perturbed only by the temperature-induced expansion or contraction of the material. In contrast, a phase change involving an alteration in the basic structure would be expected to produce an abrupt change in D at the temperature at which the transformation occurs. For both sites, the value of D was found to vary gradually with temperature with no indication of an abrupt change. The D value for site 1 passes through zero at approximately 263 K. These observations indicate that there are no phase changes; however, the thermal expansion of the lattice must be extremely anisotropic in order to produce such large changes in the zero-field splittings.

Perhaps the most interesting conclusion which can be drawn from the spectral analysis is that the electronic structures of V(II) in the two crystal sites are appreciably different. The g values and hyperfine constants as well as the zero-field splittings for the two sites differ noticeably. At both temperatures, the more intense V(II) resonance is characterized by g values that are closer to the free-electron value and hyperfine constants that are somewhat smaller than those of the weaker V(II) resonance. (The differences in the hyperfine constants are more accurate than the absolute errors reported in Table V indicate. The A and B values assigned to site 1 are smaller than those assigned to site 2 by 0.00020 (4) cm^{-1}.) The assignment of the weak and strong resonances to the particular cadmium sites in the $CsCdCl_3$ crystal was made by relating the differences in the EPR parameters of the two V(II) ions to the structural properties of the host lattice. The basis for this assignment will be discussed in detail.

The g values of d^3 ions usually deviate from the free-electron value due to a small orbital contribution to the angular momentum. Assuming that the primary source of the orbital contribution is the spin-orbit interaction on the central metal ion, the g shift ($g - 2.0023$) can be approximately calculated from the simple crystal field expression

$$g - 2.0023 = -8\lambda/\Delta$$

(where λ is the spin-orbit coupling constant for the metal ion and Δ is the crystal field splitting energy). This expression shows the magnitude of the g shift to be inversely proportional to the crystal field splitting. Of the two V(II) resonances in $CsCdCl_3$, the more intense one has the smaller absolute g shift. It appears that the crystal field splitting energy of V(II) is larger in the crystal site associated with this stronger resonance. Since the V(II) ion is surrounded by an octahedron of chloride ions in either site, the larger crystal field energy suggests that the average vanadium-chloride distance is shorter in the site producing the more intense resonance.

It has been generally established that the hyperfine constants for the central metal ion of a complex will decrease as the metal-ligand bonding becomes more covalent.[21] The differences in ^{51}V coupling constants for the two sites suggest that the metal-ligand delocalization is greater in the site associated with the more intense V(II) resonance. The extent of delocalization would certainly be expected to increase as the metal-ligand distance becomes shorter. Thus, the hyperfine constants as well as the g values indicate that the average vanadium-chloride distance in the site associated with the more intense resonance is shorter than that of the site producing the weaker V(II) signal.

Additional insight into the differences between the two sites in $CsCdCl_3$ can be obtained from the zero-field splittings. The zero-field splitting of the $S = {}^3/_2$ manifold arises from the presence of an axial component of the crystal field. In a lattice such as $CsCdCl_3$, the magnitude of the axial component is dependent on the extent to which the environment of the metal ion deviates from perfect octahedral geometry. A very small zero-field splitting implies that the coordination sphere of the metal ion is approaching that of a regular octahedron. At room temperature the magnitude of the zero-field splitting parameter, D, for the stronger resonance is only about one-tenth that of the weaker resonance. (The room-temperature values are presumed to be more pertinent to this discussion since the X-ray studies were carried out at room temperature.) The zero-field parameters clearly indicate that the coordination sphere of the V(II) ion producing the more intense resonance is less distorted than that of the other V(II) ion.

It is clear that the properties of the more intense V(II) resonance are much more compatible with the structural characteristics of Cd(1) than Cd(2). The X-ray data and pressure studies indicate that the average cadmium-chloride distance of the site containing Cd(1) is shorter than that of the Cd(2)-containing site. The coordination sphere of Cd(1) is very nearly octahedral (within experimental error) while that of Cd(2) is noticeably distorted. On this basis, the intense resonance was assigned to V(II) in Cd(1) sites and the weak resonance to V(II) in Cd(2) sites. The fact that no pair resonances were observed supports this assignment. The formation of a V(II)-V(II) pair by the substitution of vanadium into two adjacent Cd(2) sites would be very unlikely if 90-95% of the V(II) enters Cd(1) sites. (The separation between Cd(1) sites is too great to produce a strongly coupled V(II)-V(II) pair.)

Taken as a whole, the evidence supporting our assignment seems quite strong. Perhaps the weakest part of the argument is the implicit assumption that the structural characteristics of the two paramagnetic centers can be directly inferred from the crystal structure of the host lattice. Replacement of a cadmium ion with a vanadium ion will undoubtedly cause some localized distortion of the lattice, since V(II) is smaller than Cd(II). Unfortunately, there is no reliable method for obtaining an accurate detailed description of this type of distortion. For a relatively rigid ionic lattice like $CdCdCl_3$, it seems unlikely that the distortion would change the structural character of the two sites to the extent that our assignment would be incorrect.

At room temperature, the spectrum of $CsCdCl_3$ doped with Ni(II) consists of a very broad, poorly resolved resonance. Cooling the crystals to 77 K results in considerable sharpening and the features expected of an $S = 1$ system can be observed. The spectrum contains resonances from only one type of Ni(II) ion. At certain orientations the normally forbidden $\Delta m_s = \pm 2$ absorption as well as the two expected $\Delta m_s = \pm 1$ transitions can be seen in the spectrum at Q-band frequency. At X band, $h\nu$ is smaller than the zero-field splitting and only one resonance is observed regardless of orientation. The spectrum can be described by the spin Hamiltonian that was presented earlier except that the hyperfine terms can be dropped. An exact rather than perturbation solution to the Hamiltonian is necessary because of the large zero-field splitting. The exact resonance fields were obtained by computer diagonalization of the Hamiltonian matrix. The parameters reported in Table V gave the best overall agreement with the experimental data. The observed and calculated angular dependences of the Q- and X-band spectra are shown in Figures 4 and 5. (The disagreement between the observed and calculated fields in the region near $\theta = 0°$ in Figure 5 is thought to result from a small misalignment of the crystal.) It appears that Ni(II) substitutes almost exclusively into one of the two cadmium sites. Although it is possible that a small fraction of the Ni(II) ions actually enter the other site, no indication of a second Ni(II) resonance was observed. It should be noted that a weak Ni(II) resonance might be quite difficult to detect because of large line widths or a large zero-field splitting.

The spin Hamiltonian parameters of Mn(II) in $CsCdCl_3$ have been included in Table V for the purpose of comparison. The spectrum shows that Mn(II), like V(II), substitutes for

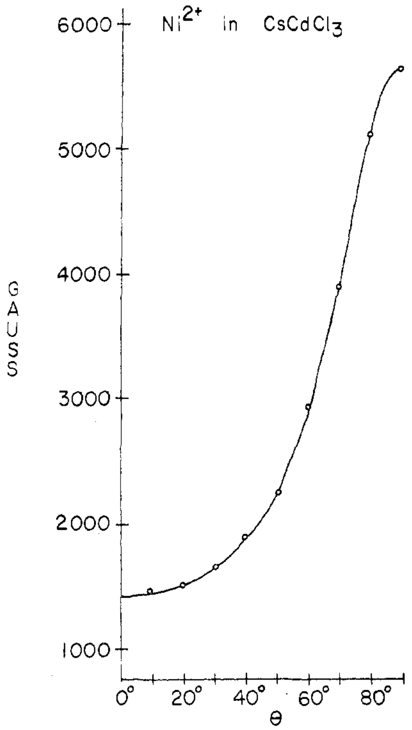

Figure 4. Angular dependence of the X-band spectrum of Ni(II) in $CsCdCl_3$.

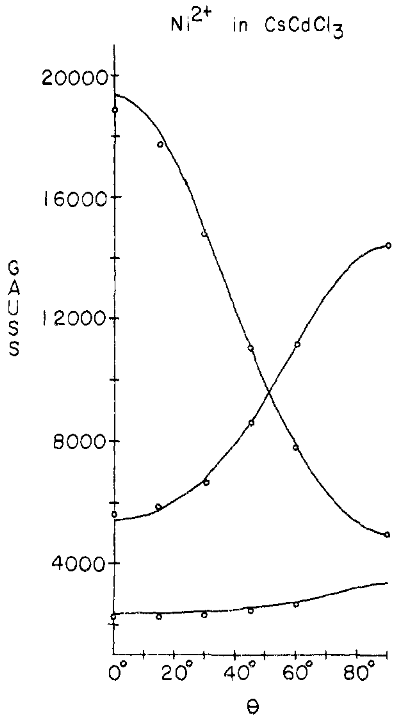

Figure 5. Angular dependence of the Q-band spectrum of Ni(II) in $CsCdCl_3$.

both cadmium sites. The ratio of the line intensities from the two sites indicates that approximately 70% of the Mn(II) ions are in one cadmium site (α) while 30% of the Mn(II) ions occupy the other (β). Apparently Mn(II) does not have as great a preference for one site as V(II). The spin Hamiltonian parameters in Table V are those of ref 4. (One minor error has been corrected. The $|a - F|$ parameter was erroneously reported as "a" in reference 4.) Since there are no really significant differences between the parameters of the two sites, it is not possible to determine which crystal site is associated with a particular set of parameters. For this reason the parameters were designated with α and β rather than 1 and 2. It seems that the d^5 configuration of Mn(II) is much less sensitive to subtle structural features of the environment than the d^3 configuration of V(II).

The spin Hamiltonian parameters of V(II), Mn(II), and Ni(II) in $CsCdCl_3$ are similar to those that have been reported for these ions in related lattices such as $CdCl_2$[22-27] and $CsMgCl_3$.[28] The unique feature of the $CsCdCl_3$ system is the partitioning of the paramagnetic ions between the two nonequivalent cadmium sites. Assuming that our spectral analysis is correct, V(II) substitutes into the sites containing Cd(1) 20–40 times more readily than into the sites occupied by Cd(2). (This takes into account that there are twice as many Cd(2) sites as Cd(1) sites in a unit cell.) The structural studies show that the coordination sphere of Cd(1) is more symmetrical and has a shorter average cadmium–chloride separation than that of Cd(2). The site containing Cd(1) can be thought of as being smaller than that occupied by Cd(2). It is reasonable to assume that an impurity ion would preferentially replace the cadmium ions in either the larger or the smaller site depending on how the size of the impurity ion compares with that of divalent cadmium. The fact that V(II), which is smaller than Cd(II), substitutes more readily for the cadmium in the smaller site (Cd(1)) tends to support this hypothesis. Divalent nickel appears to replace the cadmium ions in only one of the two sites. Since Ni(II) is even smaller than V(II), it is tempting to conclude that the Ni(II) exclusively enters the smaller Cd(1) sites. Unfortunately, it is not possible to determine directly from the EPR parameters which of the two sites has been occupied. Of the three paramagnetic ions, Mn(II) shows the least site discrimination. This seems reasonable since manganese(II) closely resembles divalent cadmium in terms of size and electron distribution.

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Registry No. $CsCdCl_3$, 13845-08-4; $CsVCl_3$, 15455-69-3; $CsNiCl_3$, 20959-74-4.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC504483-12-75.

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Contribution from the Departments of Chemistry, University of Alabama, University, Alabama 35486, and University of New Orleans, New Orleans, Louisiana 70122

Crystal Structure and Mössbauer Spectrum of [2]Ferrocenophanethiazine 1,1-Dioxide

R. A. ABRAMOVITCH,*[1a] J. L. ATWOOD,*[1a] M. L. GOOD,*[1b] and B. A. LAMPERT[1a]

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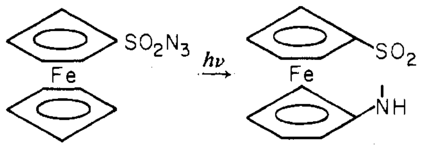
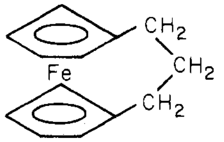
The cyclopentadienyl rings of the title compound are tilted by 23°. A comparison of its Mössbauer spectrum with those of ferrocene derivatives in which the rings are less tilted or parallel and antiprismatic supports the hypothesis that a large degree of ring tilt can occur without its affecting the bond energy. $(C_5H_4)Fe(C_5H_4)SO_2NH$ crystallizes in the monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] with unit cell dimensions a = 10.566 (7) Å, b = 11.802 (7) Å, c = 7.671 (6) Å, β = 93.35 (5)°, and Z = 4. Full-matrix least-squares refinement has led to a final R value of 0.051 based on 978 independent observed reflections collected by counter techniques. The Fe–C bond lengths range from 1.962 (8) to 2.096 (8) Å, and the bond lengths and angles involving the bridging groups are normal; there is no evidence of delocalization of ring electron density into the bridge.

Introduction

Photolysis of ferrocenesulfonyl azide (I) in hydrocarbon solvents using 3500-Å radiation yielded [2]ferrocenophanethiazine 1,1-dioxide (II) in good yield.[2] The structure of II was established on the basis of its microanalysis and spectral properties. In particular, the NMR spectrum exhibited two sets of A_2B_2 patterns associated with the two monosubstituted cyclopentadienyl rings, as did the N-methylated product.



I II



III

Molecular models clearly indicated that in II the two rings could not be parallel and that the molecule would have to have a prismatic conformation (as opposed to ferrocene itself which is antiprismatic and has parallel cyclopentadienyl rings). Ballhausen and Dahl[3] suggested that in protonated ferrocene the cyclopentadienyl rings are no longer parallel and calculated that the bonding of the rings to the metal atom is relatively insensitive to the value of the angle between the radius vectors from the metal atom to the centers of the rings. Considerable splaying of the rings could thus occur without any significant loss in bond energy.

It seemed to us that ferrocenophane (II) would provide a good model for testing such a hypothesis since the angle between the two rings appeared (in Drieding models) to be larger than in [3]ferrocenophane (III) and 6-keto[3]ferrocenophane (8.8°).[4] We now report the crystal structure and Mössbauer spectrum of II.

Table I. Crystal Data

Compd	$(C_5H_4)Fe(C_5H_4)SO_2NH$
Mol wt	263.1
Linear abs coeff	17.99
Obsd density	1.82 (2)
Calcd density	1.83
Max crystal dimensions	0.08 × 0.08 × 0.70 mm
Space group	$P2_1/c$
Molecules/unit cell	4
Cell constants,[a] a	10.566 (7) Å
b	11.802 (7)
c	7.671 (6)
β	93.35 (5)°
Cell vol	955.0 Å^3

[a] Mo Kα radiation, λ 0.71069 Å. Ambient temperature of 22°.

Experimental Section

X-Ray Data Collection and Structure Determination. Single crystals of the red-orange air-stable substance were sealed in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 12 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table I. The space group was uniquely determined to be $P2_1/c$ [C_{2h}^5; No. 14] from the systematic absences in $0k0$ for $k = 2n + 1$, and in $h0l$ for $l = 2n + 1$. The density was measured by flotation methods, and it indicated that there are four formula units per unit cell.

Data were taken on an Enraf-Nonius CAD-4 diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were collected by the ω–2θ scan technique with a takeoff angle of 3.0°. The scan rate was variable and was determined by a fast (20° min^{-1}) prescan. Calculated speeds based on the net intensity gathered in the prescan ranged from 7 to 0.6° min^{-1}. Moving-crystal, moving-counter backgrounds were collected for 25% of the total scan width at each end of the scan range. For each intensity