Table II. Values of Parameters Describing the α-cis-Co(EDDA)(OH$_2$)$_2$$^+$-H$_2C_2O_4$-HC$_2O_4$$^-$ System^a

Temp, °C	$10^4 k_0$, s^{-1}	K_2	K_3	K_4
62.00	1.77	0.24	4.9	20
69.00	4.33	0.34	2.9	16
75.00	8.55	0.37	2.8	18

^{a} Uncertainties in the parameters reported here are related to the standard deviations in the various slopes and intercepts (as determined by linear regression analysis) as well as to the experimental error involved in the determination of k_{obsd}. Using these guidelines we report the relative uncertainty for k_0 as ±5–10% and that for K_2, K_3, and K_4 as ±10–20%.

constants for the two pairs predict a varying intercept with H$^+$.) Such behavior has been previously reported,[1,2,8,9] and in one case[2] where the data could be separated, rate constants identical within experimental error were obtained for two distinct ion pairs.

Using $K_1 = 6.0 \times 10^{-2}$ in the temperature range studied and obtaining k_0 from the intercept of the various k_{obsd}^{-1} vs. C_{ox}^{-1} plots, a simultaneous solution of the slope equations yields values for K_2, K_3, and K_4. Table II depicts the results of such treatment.

K_2 is larger than K_1 as would be expected simply on the basis of charge factors alone. Similar behavior has been noted in other systems.[1,8,11] K_4 is identical, within experimental error, with the value obtained for the α-cis-Co(EDDA)(OH$_2$)$_2$$^+$,-HC$_2O_4$$^-$ ion pair at 50.5 °C in slightly acidic media.[1] K_3 is considerably smaller than K_4 as would be expected on an electrostatic basis. Within experimental error, K_3 and K_4 exhibit negligible temperature dependence in the range studied.

It does appear that the ability of the prospective ligand to hydrogen bond to the reactant complex is an important factor in ion-pair formation for these systems. In the two systems[8] studied to date, where two aquo ligands cis to one another are available on the reactant complex, ion-pair formation is observed between the complex and H$_2$C$_2$O$_4$. In the cases where only one aquo ligand is available on the reactant complex, no ion-pair formation is observed involving the neutral carboxylic acid.[2-5] It should also be noted that the magnitude of the formation constants for similar ion pairs is much larger when two cis aquo ligands are available on the complex rather than one. As an example, for cis-Co(en)$_2$(OH$_2$)$_2$$^{3+}$,HC$_2O_4$$^-$ K_f = 119 at 40 °C,[8] whereas K_f values for the Co(NH$_3$)$_5$-(OH$_2$)$^{3+}$,HC$_2$O$_4$$^-$, HCOO$^-$, CH$_3COO^-$, and CH$_3CH_2COO^-$ ion pairs are 1.8 (50 °C),[2] 0.85 (60 °C),[3] 5.1 (60 °C),[4] and 4.4 (60 °C),[5] respectively. Similar extrapolations can be made to systems where the reactant complex is of lesser charge than 3+.[1]

The temperature variation in k_0 was used to calculate its activation parameters. Linear regression analysis yields the values $\Delta H^{\ddagger} = 27.5 \pm 1.0$ kcal/mol and $\Delta S^{\ddagger} = +6.3 \pm 2.8$ eu. These are essentially identical, within experimental error, with those obtained in the less acidic media.[1] Further, these values conform to the established pattern of activation parameters for similar, representative anation and water-exchange reactions (see ref 2, Table IV).

Extrapolation of k_0 to 50.50 °C using the above parameters indicates that k_0 in the present case is approximately one-fourth the value of k_0 obtained in slightly acidic media[1] where β-cis-Co(EDDA)(C$_2$O$_4$)$^-$ is the product. This decrease in rate constant may be due to the nature of the prospective ligand, i.e., H$_2$C$_2$O$_4$ and HC$_2$O$_4$$^-$ in the present case as compared to mainly C$_2$O$_4$$^{2-}$ in the less acidic media. It should be noted that removing the contribution of HC$_2$O$_4$$^-$ from the proposed mechanism in ref 1 does not allow a satisfactory fit of the reported data in that system. This might be expected, however, simply on the basis that removal of HC$_2$O$_4$$^-$ allows the use

of three variable parameters instead of four for data fitting. Further, using the k_0 value obtained in the present study (extrapolated to the temperature under consideration in ref 1) does not allow a satisfactory fit of the data in ref 1. Hence we conclude that the k_0 values obtained at the two differing acidities are truly different.

The proposal in ref 1 that Co(EDDA)(OH)(OH$_2$)^0 plays an important role in generation of product in slightly acidic media seems borne out by the present study. The overall rate of reaction is much slower in the present study, as expected, and the attainment of a common intercept in the k_{obsd}^{-1} vs. C_{ox}^{-1} plots is as predicted.

The question related to the nature of product geometry as a function of pH still has not been satisfactorily answered. We are continuing our study of this general system, presently reacting the β-cis isomer of the parent diaquo complex with oxalate and malonate at various pH's.

Registry No. α-cis-Co(EDDA)(C$_2$O$_4$)$^-$, 26135-70-6; α-cis-Co-(EDDA)(OH$_2$)$_2$$^+$, 26135-74-0.

References and Notes

(1) Part 1: J. A. Weyh, A. K. Newlun, T. J. Baker, and T. K. Shioyama, *Inorg. Chem.*, **12**, 2374 (1973).
(2) R. van Eldik and G. M. Harris, *Inorg. Chem.*, **14**, 10 (1975).
(3) P. R. Joubert and R. van Eldik, *Inorg. Chim. Acta*, **14**, 259 (1975).
(4) P. R. Joubert and R. van Eldik, *Inorg. Chim. Acta*, **12**, 205 (1975).
(5) P. R. Joubert and R. van Eldik, *J. Inorg. Nucl. Chem.*, **37**, 1817 (1975).
(6) K. Kuroda and K. Watanabe, *Bull. Chem. Soc. Jpn.*, **44**, 1034 (1971).
(7) K. Kuroda and K. Watanabe, *Bull. Chem. Soc. Jpn.*, **44**, 2250 (1971).
(8) P. M. Brown and G. M. Harris, *Inorg. Chem.*, **7**, 1872 (1968).
(9) H. Kelm and G. M. Harris, *Inorg. Chem.*, **6**, 706 (1967).
(10) Because of the circular nature of the various equilibria $K_2 K_3 = K_1 K_4$.
(11) (a) S. E. Ting, H. Kelm, and G. M. Harris, *Inorg. Chem.*, **5**, 696 (1966); (b) C. Andrade and H. Taube, *ibid.*, **5**, 1087 (1966).

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Electron Paramagnetic Resonance and Ligand Field Spectra of Vanadium(II) in Crystals of Cesium Calcium Trichloride. Spectroscopic Properties of a Perfectly Octahedral VCl$_6$$^{4-}$ Complex

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The double salts of the formula M^{I}M^{II}X$_3$ (where M^I is a univalent cation, M^{II} a divalent metal ion, and X a halide) have been the subject of numerous structural, spectroscopic, and magnetic investigations. The fluoride salts of this formula usually adopt some type of perovskite structure, while the salts of the other halides generally crystallize in one of several hexagonal lattices. Exceptions to this general trend are the chloride salts CsCaCl$_3$ and CsSrCl$_3$ which have been shown to be cubic perovskites.[1] A cubic perovskite can be described as an infinite three-dimensional array of octahedra sharing corners. Each divalent ion is surrounded by a regular octahedron of anions.

It has been found that CsVCl$_3$ is soluble in CsCaCl$_3$ to the extent that crystals which contain concentrations of V(II) large enough for spectroscopic observation can be prepared. Thus, it is possible to study the electronic structure of a VCl$_6$$^{4-}$ complex that is perfectly octahedral. Previous spectroscopic investigations of divalent vanadium in chloride lattices have involved crystal systems in which the environment of the V(II) ion is significantly distorted from regular octahedral geometry.

Room Temperature
ν = 9.541 GHz

3238 gauss   3681 gauss
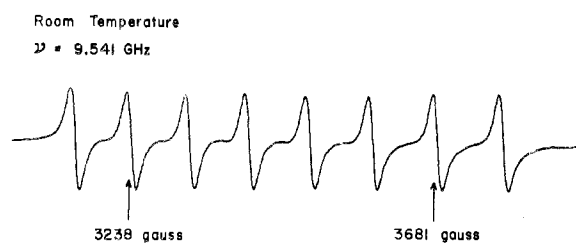
Figure 1. EPR spectrum of V(II) in CsCaCl₃ taken at room temperature.

This paper presents the results of a study of the EPR and ligand field spectra of V(II) doped into crystals of CsCaCl₃.

Experimental Section

Preparation of Materials. The host lattice, CsCaCl₃, was prepared by fusing equimolar amounts of CsCl and anhydrous CaCl₂ in evacuated Vycor ampules. The fusion requires a temperature of approximately 900 °C. The material is a hard white crystalline solid which rapidly absorbs atmospheric moisture. It must be handled and stored under a dry atmosphere. Anal. Calcd for CsCaCl₃: Cl, 38.07. Found: Cl, 38.02.

The preparation of CsVCl₃ has been described previously.[2]

Crystal Growth. Samples of CsCaCl₃ containing up to 1% CsVCl₃ were sealed in evacuated Vycor ampules. Single crystals suitable for spectroscopic study were then grown from the melt by the vertical Bridgman method. The apparatus has been described previously.[3] The doped crystals which are red tend to grow with a noticeable gradient in the V(II) concentration. The portion of the crystal which emerges from the furnace last has the highest concentration of V(II). The CsCaCl₃ crystals readily cleave normal to the cubic axes. This property greatly facilitates the preparation of samples for spectroscopic work.

Spectroscopic Measurements. The EPR spectra were obtained on a Varian E-3 spectrometer using 100-kHz field modulation. The g values were determined by comparison with DPPH (diphenyldipicrylhydrazyl; g = 2.0036) as a reference. The near-ir and visible spectra were recorded at room and liquid nitrogen temperature on a Cary 14 spectrophotometer. The crystals were mounted so that the light passed through the sample normal to one of the cubic faces. Since CsCaCl₃ is cubic, no polarization studies were made. The mounting procedure and dewar system have been described previously.[4] Molar extinction coefficients were determined by assuming Beer's law behavior. The vanadium contents of the samples were determined by chemical analysis and the crystal thicknesses were measured with calipers. The density of the material was calculated from the lattice constant. Oscillator strengths were determined by planimeter integration of the absorption bands. Because of the many errors involved (baseline, density, analysis, etc.) the oscillator strengths are only expected to be accurate within 25%; however, the relative accuracy should be considerably better.

Results and Discussion

In a cubic perovskite the atom positions are completely determined by symmetry. Thus, all of the interatomic distances can be calculated from the dimension of the unit cell. Ijdo has reported the lattice constant *a* of CsCaCl₃ to be 5.396 Å. Each calcium ion is surrounded by a regular octahedron of chloride ions with a Ca–Cl distance of 2.698 Å. The structural properties of CsCaCl₃ and CsSrCl₃ contrast with those of most of the other cesium metal trichlorides that have been characterized including CsMgCl₃ and CsVCl₃. Both CsVCl₃[5] and CsMgCl₃[6] adopt a hexagonal linear-chain structure which can be described as an infinite array of parallel linear chains of octahedra-sharing faces. The divalent metal ions occupy the centers of the octahedra with the chloride ions at the corners. In this type of lattice the divalent ions are surrounded by a trigonally distorted octahedron of chloride ions.[6]

The EPR spectrum of V(II) in CsCaCl₃ is shown in Figure 1. It consists of an eight-line pattern which is independent of crystal orientation. The eight-line structure results from

Table I. Spin Hamiltonian Parameters[a] of V(II) in CsCaCl₃

Parameter	296 K	77 K
g	1.958 (3)	1.959 (3)
A, cm⁻¹	±0.007 99 (8)[b]	±0.008 06 (8)[b]

[a] The numbers in parentheses are the estimated maximum error in the last decimal place of the reported parameter. [b] The relative accuracy between these two numbers is considerably better than the absolute errors imply.

the electronic–nuclear hyperfine interaction of the unpaired electrons with the ⁵¹V nucleus ($I = ^7/_2$). The isotropic behavior of the spectrum along with the lack of fine structure is clearly consistent with a V(II) ion in a regular octahedral environment. This spectrum can be described by the isotropic spin Hamiltonian

$$\mathcal{H} = g\beta(H_x\hat{S}_x + H_y\hat{S}_y + H_z\hat{S}_z) + A(\hat{S}_x\hat{I}_x + \hat{S}_y\hat{I}_y + \hat{S}_z\hat{I}_z)$$

The first term describes the electronic Zeeman interaction while the second term describes the nuclear hyperfine interaction. The spin Hamiltonian parameters for V(II) in CsCaCl₃ at room and liquid nitrogen temperature are given in Table I. (The g values have been corrected for second-order hyperfine shifts in the line positions.) No major changes in the spectrum take place when the crystal is cooled to 77 K; however, the hyperfine coupling constant (A) shows a small decrease.

The spin Hamiltonian parameters for V(II) in CsCaCl₃ differ noticeably from those of V(II) in CsMgCl₃. The g values are smaller and the ⁵¹V hyperfine constants are larger in CsCaCl₃ than in the CsMgCl₃ lattice. (At room temperature, V(II) in CsMgCl₃ has an average g value of 1.975 and hyperfine constant of 0.007 43 cm⁻¹.[6] Average values are used since the spin Hamiltonian for V(II) in CsMgCl₃ is not isotropic.) The differences in the properties of divalent vanadium in these two lattices can be rationalized by assuming that the vanadium–chlorine distances of the VCl₆⁴⁻ complex are significantly larger in CsCaCl₃ than in CsMgCl₃. For d³ ions, crystal field theory predicts that the magnitude of the g shift (g – 2.0023) is inversely proportional to the crystal field splitting energy (10Dq). Since V(II) in CsCaCl₃ has a larger g shift, it appears that the crystal field splitting energy is smaller in this lattice. The larger ⁵¹V coupling constant suggests that the unpaired electrons are less extensively delocalized in CsCaCl₃ than in CsMgCl₃. Both observations are consistent with the vanadium–chlorine distances being longer in CsCaCl₃. This conclusion is not unexpected since the calcium–chlorine distance in CsCaCl₃ is larger than the magnesium–chlorine distance in CsMgCl₃ by 0.2 Å (2.698 vs. 2.496 Å). Although a complete x-ray determination of the structure of CsVCl₃ has not been reported, it can be estimated from the lattice constants that the vanadium–chlorine bond length is on the order of 2.45 Å. Since CsVCl₃ and CsMgCl₃ have the same basic structure and have similar metal–chlorine distances, it appears that a V(II) ion doped into CsMgCl₃ has an environment which is quite similar to that of the pure vanadium salt. In contrast, the CsCaCl₃ lattice must force the V(II) ion into an environment which is significantly different.

As can be seen from Figure 2 the ligand field spectrum of V(II) in CsCaCl₃ consists of three main bands. This is consistent with crystal field theory which predicts that a d³ ion such as V(II) in an octahedral complex will have three spin-allowed transitions. These spin-allowed bands are the only significant features in the spectrum except for the weak, relatively sharp peak which appears on the high-energy side of the second spin-allowed band (see the inset in Figure 2). The assignment of the spin-allowed bands is quite straightforward in this case. Crystal field calculations were carried
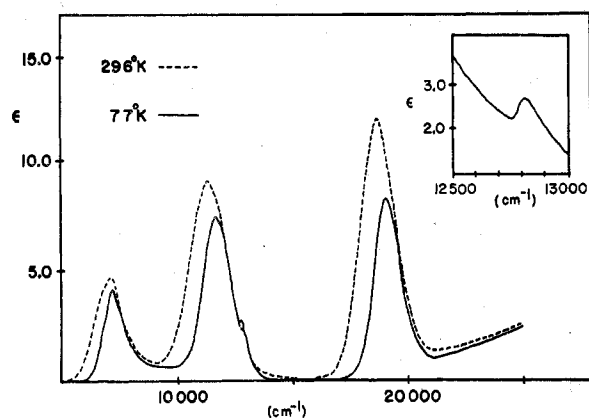
Figure 2. Ligand field spectrum of V(II) in CsCaCl$_3$ in the 5000–25 000-cm^{-1} region. The inset in the upper right corner shows an expanded view of the high-energy portion of the second band at 77 K.

Table II. Spectral Data for the Ligand Field Spectrum of V(II) in CsCaCl$_3$

Assignment	Temp, K	Oscillator strength (f)	Energy, cm^{-1} Obsd	Energy, cm^{-1} Calcd[a]
$^4A_{2g} \rightarrow {}^4T_{2g}$	296	3.2×10^{-5}	7 100	
	77	2.2×10^{-5}	7 200	7 200
$^4A_{2g} \rightarrow {}^4T_{1g}(F)$	296	8.4×10^{-5}	11 300	
	77	5.5×10^{-5}	11 700	11 620
$^4A_{2g} \rightarrow {}^2T_{1g}$	296			
	77		12 810	12 240
$^4A_{2g} \rightarrow {}^4T_{1g}(P)$	296	8.9×10^{-5}	18 700	
	77	4.9×10^{-5}	19 100	19 130

[a] Calculated values were obtained from the spectral parameters $Dq = 720$, $B = 610$, and $C = 2500$ cm^{-1}.

out in order to obtain a quantitative fit of the observed transition energies. The assignments and results of the calculations are presented in Table II. The calculated energies were obtained from the crystal field matrices for a d^3 system given by Tanabe and Sugano.[7] The value of the crystal field parameter, Dq, was taken from the energy of the first absorption band ($^4A_{2g} \rightarrow {}^4T_{2g}$; $E = 10Dq$). The interelectronic repulsion parameters, B and C, were varied until a good fit between the observed and calculated energies was obtained. The fit of the spin-allowed bands is quite good while the agreement between the observed and calculated energy of the spin-forbidden, $^4A_{2g} \rightarrow {}^2T_{2g}$, transition is noticeably poorer. The values of B and C are quite similar to those obtained by Smith in an analysis of the spectrum of VCl$_2$.[8] It should be pointed out that we have obtained the transition energies from the band maxima rather than from the position of the 0–0 transition. (This seems to be a reasonable procedure since the spectrum shows no resolved vibronic structure.) Thus, the actual value of Dq must be somewhat smaller than that used in our calculations.

The oscillator strengths of the three spin-allowed transitions are typical of those of d–d transitions in octahedral complexes. The intensities of all three bands decrease noticeably when the crystal is cooled from room to liquid nitrogen temperature (see Figure 2 and Table II). This decrease in intensity, especially in the low-energy portion of each of the bands, is characteristic of a vibronic intensity mechanism. The one spin-forbidden transition that is observed most likely becomes allowed by "borrowing" intensity from the nearby $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ transition.

The ligand field spectrum of V(II) in CsCaCl$_3$ differs from those of pure V(II) salts such as VCl$_2$[8,9] and KVCl$_3$[10] in two notable respects. The Dq value for V(II) in CaCaCl$_3$ is about 200 cm^{-1} smaller than those of the pure salts. This is consistent

with the argument presented earlier that the CsCaCl$_3$ lattice forces the V(II) ion into an environment which has greater than normal metal–chlorine separations. The other significant difference is that the spectra of VCl$_2$ and KVCl$_3$ contain a number of fairly intense spin-forbidden bands which do not appear in the spectrum of V(II) in CsCaCl$_3$. These bands are made allowed by the exchange interactions which take place between V(II) ions.[8,10] Since the V(II) ions in the doped CsCaCl$_3$ crystals are present in low concentrations, there are no significant exchange interactions. Thus, the spin-forbidden bands do not appear.

In summary, it appears that the spectroscopic properties of V(II) in CsCaCl$_3$ are consistent with those expected of a perfectly octahedral VCl$_6{}^{4-}$ complex which has somewhat longer than normal vanadium–chlorine distances.

Registry No. CsVCl$_3$, 59389-02-5; CsCaCl$_3$, 12323-36-3; VCl$_6{}^{4-}$, 28659-55-4.

References and Notes

(1) D. J. W. Ijdo, Ph.D. Dissertation, University of Leiden, 1960.
(2) G. L. McPherson and J. R. Chang, *Inorg. Chem.*, **12**, 1196 (1973).
(3) G. L. McPherson, L. J. Sindel, H. F. Quarls, C. B. Frederick, and C. J. Doumit, *Inorg. Chem.*, **14**, 1831 (1975).
(4) G. L. McPherson, T. J. Kistenmacher, J. B. Folkers, and G. D. Stucky, *J. Chem. Phys.*, **57**, 3771 (1972).
(5) H. J. Seifert and P. Ehrlich, *Z. Anorg. Allg. Chem.*, **302**, 284 (1959).
(6) G. L. McPherson, T. J. Kistenmacher, and G. D. Stucky, *J. Chem. Phys.*, **52**, 815 (1970).
(7) Y. Tanabe and S. Sugano, *J. Phys. Soc. Jpn.*, **9**, 753 (1954).
(8) W. E. Smith, *J. Chem. Soc., Dalton Trans.*, 1635 (1972).
(9) S. S. Kim, S. A. Reed, and J. W. Stout, *Inorg. Chem.*, **9**, 1584 (1970).
(10) W. E. Smith, *J. Chem. Soc. A*, 2677 (1969).

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Complex Formation of Copper(I) Perchlorate with Ethylene or Carbon Monoxide in Water and Isolation of Related Complexes[1]

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It is well-known that a solution containing a copper(I) salt absorbs alkenes[2] and carbon monoxide[2,3] and that ethylene at high pressure is absorbed by solid copper(I) chloride forming an unstable complex.[3–5]

Recently, Kochi and his collaborators synthesized very stable olefinic complexes of copper(I) trifluoromethanesulfonate[6–8] and they used the complexes as catalysts for some photochemical reactions of alkenes.[9,10]

Aquated copper(I) perchlorate is generated by a reduction of copper(II) perchlorate with metallic copper[11,12] or a metal ion such as hexaammineruthenium(II),[12] aquated chromium(II),[13,14] or aquated vanadium(II).[14] In the absence of a suitable ligand, the copper(I) ion disproportionates to copper(II) ion and metallic copper.[12] However, copper(II) ion in an aqueous solution is reduced to a stable complex, in the presence of some olefinic ligand, by contacting it with a reducing agent[15–19] or by electrolysis of the ion.[15,20,21]

In the present work we show that a copper(I)–ethylene or –carbon monoxide complex in an aqueous solution disproportionates into copper metal and copper(II) ion when the ligand is removed by pumping. The complex is re-formed by adding the same gas to the reaction mixture. The unstable and explosive complexes which are responsible for the reaction