CONTRIBUTION FROM ILLINOIS INSTITUTE OF TECHNOLOGY,
DEPARTMENT OF CHEMISTRY, CHICAGO, ILLINOIS 60619

The Spectral and Magnetic Properties of Copper(II) Cyanoacetate

BY JOHN R. WASSON, CHIN-I SHYR, AND CHARLES TRAPP

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The preparation of copper(II) cyanoacetate is described and the spectral and magnetic properties are compared with those of dimeric copper(II) acetate monohydrate. The available evidence supports a dimeric structure and suggests polymerization of dimer units *via* the nitrogen end of the cyano group. The esr spectrum of the powdered solid is consistent with spin $S = 1$. The exchange interaction parameter J is estimated to be 310 cm^{-1}, the zero field splitting parameters are $D = 0.39 \pm 0.01$ cm^{-1} and $E \cong 0.002$ cm^{-1}. The g values are $g_z = 2.40 \pm 0.02$ and $g_\perp = 2.08 \pm 0.02$. A general method for obtaining the magnetic parameters of dimeric copper compounds from esr powder spectra is presented. The visible, infrared, and far-infrared spectra of copper(II) acetate monohydrate and cyanoacetate are also discussed.

Numerous studies of compounds containing the copper(II) ion ($3d^9$) have shown that compounds with ionic or weak covalent bonds and those with strong covalent bonds exhibit magnetic moments of 1.9–2.2 and 1.72–1.82 BM, respectively. However, a large number of copper(II) compounds having subnormal magnetic moments, *i.e.*, less than 1.73 BM, have been reported. In most instances the compounds with subnormal magnetic moments have dimeric structures with bridging chloride or hydroxide ions, oxygen, or carboxylate groups.[1,2] Dimeric copper(II) acetate monohydrate and its homologs have been the most studied compounds showing this unusual magnetic behavior. In copper(II) acetate monohydrate the metal–metal distance of 2.61 Å[3] is only slightly longer than the 2.56-Å[4] separation in copper metal itself. This short copper–copper distance has been recognized as being responsible for the unusual magnetic behavior of copper acetate and its homologs; however the precise nature of the interaction, especially as regards the interpretation of the electronic spectra of these compounds, has been rather controversial.[1] Both σ-[5] and δ-bonding[6] explanations of the metal–metal interaction have been offered, but the weakly coupled chromophore model which allows for weak δ bonding[7] probably provides the best account of the various properties which have been measured. The present work was undertaken in order to investigate the effect of cyano substitution on the spectral and magnetic properties of copper acetate and to study the esr spectra of powdered inorganic solids containing a triplet state. The available data on the magnetic parameters D, E, g_x, g_y, and g_z in these compounds is very limited.[1] If the parameters can be determined from powder esr spectra, the understanding of these compounds can be greatly increased as very few of them are available in single crystals.

Experimental Section

Analyses for C, H, and N were performed by Alfred Bernhardt Mikroanalytisches Laboratorium im Max-Planck-Institut für Kohlenforschung, Mulheim (Ruhr), West Germany. A sample of cyanoacetic acid was generously supplied by the Kay-Fries Chemical Co., New York, N. Y. All other chemicals were of the best available reagent grade.

Infrared spectra in the region 4000–230 cm^{-1} were measured with a Beckman IR-12 instrument using Nujol and Fluorolube (Hooker Chemical Co.) mulls on CsI and CsBr cells. Electronic spectra of mulled solids were obtained using a technique described previously.[8] A Cary Model 14 recording spectrophotometer was used in measuring the mull spectra.

Electron spin resonance spectra were obtained with a modified Varian V-4502-12 X-band spectrometer using 100-kc modulation and a 9-in. electromagnet. The frequency was monitored with a Hewlett-Packard 5245L electronic counter with a 5253B frequency converter and a 540B transfer oscillator. A Magnion G-502 precision gaussmeter and probe were used to measure the magnetic field. In some of the measurements a small crystal of diphenyltrinitrophenylhydrazyl (DPPH) was also used. Cylindrical quartz sample tubes and a Varian V-4533 cylindrical cavity were employed. For temperatures other than room temperature a quartz dewar which fitted into the cavity was used.

Preparation of Copper(II) Cyanoacetate.—Ten grams of copper(II) nitrate trihydrate was dissolved in the minimum quantity of water and then mixed with an excess of a saturated aqueous solution of sodium carbonate. The pale blue-green copper carbonate so produced was then collected on a filter and washed with 500 ml of water and air dried for a short time. The copper carbonate was then dispersed in 250 ml of water and solid cyanoacetic acid was added with stirring until a pH of about 3 was obtained. The reaction mixture was stirred for another 10 min. The precipitated green copper(II) cyanoacetate was then isolated by filtration, washed with 200 ml of water, and air dried. The compound was purified by dispersing it in hot (not boiling) water and allowing the mixture to cool to room temperature. The green product was isolated and dried for 48 hr in a desiccator over anhydrous calcium chloride. Yield after purification: 20–30% of theory. *Anal.* Calcd for $CuC_6H_4O_4N_2$: Cu, 31.11; H, 1.74; N, 12.09. Found: C, 31.22; H, 1.78; N, 12.18.

Results and Discussion

Infrared Spectra.—The data given in Table I provide for a comparison of the infrared mull spectra of copper(II) acetate monohydrate and the cyanoacetate

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TABLE I

INFRARED DATA (CM^{-1})

	$\nu(\text{COO})^e$		
	ν_{as}	ν_s	Other bands[e]
$HC_2H_3O_2$[a]	1770	1284, 1184	
$NaC_2H_3O_2$[b]	1578	1414	
$Cu_2(C_2H_3O_2)_4 \cdot 2H_2O$[c]	1605	1425	(1413 m), 1350 m, 1052 s, 1033 s, (720 m), 692 vs
$HC_3H_2O_2N$[d]	1742	1460	ν(CN) 2285 br, w; 1350 m, 1311 m, 1220 m, 1185 vs, 965 s, 932 s, 878 m, 790 m, 670 m
$Cu(C_3H_2O_2N)_2$	1635	1424	ν(CN) 2285 vs, 2270 s; 1375 m, 1308 m, 1291 m, 1278 m, 1230 w, 1206 w, 987 w, 959 m, 931 s, 920 s, 732 vs

[a] W. Weltner, Jr., *J. Am. Chem. Soc.*, **77**, 3941 (1955). [b] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 197–201. [c] K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 4528 (1961). [d] Owing to the extreme hygroscopicity of cyanoacetic acid, these bands are somewhat uncertain. [e] vs, very strong; s, strong; m, medium; w, weak; br, broad; parentheses, shoulder.

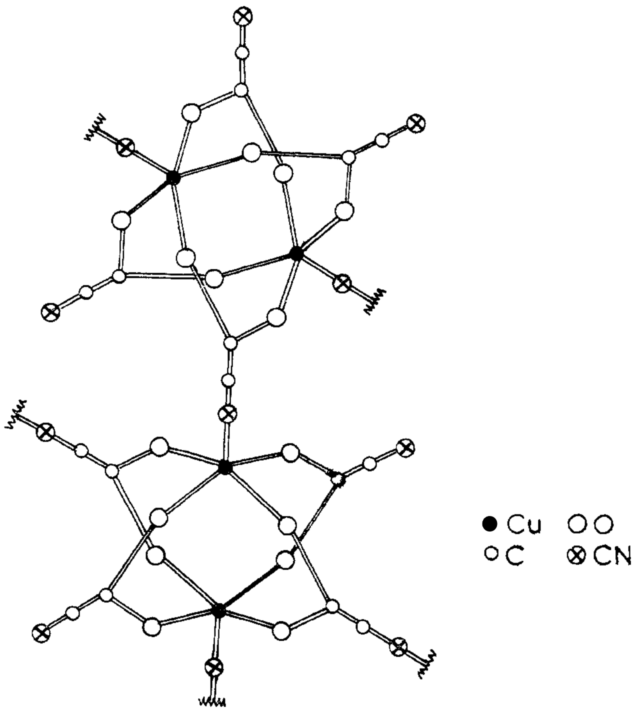

Figure 1.—Proposed structure for the copper(II) cyanoacetate molecule.

salt with the parent acids. The assignment of all of the bands has not been made, but the assignment of the antisymmetric and symmetric carboxy stretching frequencies is straightforward. As for the acetate,[9] it is noted that both of the COO stretching bands are shifted in the same direction upon coordination of cyanoacetate. The known Lewis basicity of the nitrogen end of cyano groups,[10,11] the basicity of the cyano group of cyanoacetic acid,[12] and the relative insolubility in various solvents of copper(II) cyanoacetate compared to copper(II) acetate monohydrate along with other evidence discussed below suggest that copper(II) cyanoacetate consists of carboxy-bridged dimer units which are polymerized together *via* the nitrogen end of the cyano group. An approximate representation of this structure is depicted in Figure 1. The two separate ν(CN) bands (Table I) of copper cyanoacetate are suggestive of two types of cyano groups, bridging and free, respectively. However, the evidence is not unambiguous since cyano bands are frequently split,[13] even when strong bridging[10,11] is not taking place. Coordination of the cyanoacetate ion to copper(II) should lead to a removal of electron density from the carboxy group and hence lower ν(CN), while the use of cyano groups for coordination polymerization is expected to cause ν(CN) to go to higher frequencies or to remain in the region where cyanoacetic acid itself absorbs. In summary, the relative insolubility of copper(II) cyanoacetate and the splitting of ν(CN) is suggestive of a polymeric structure. It is also noted that copper cyanoacetate is not particularly hygroscopic whereas cyanoacetic acid and barium cyanoacetate are extremely hygroscopic.

While many data have accumulated concerning the infrared spectra of acetate salts in the NaCl region,[9,14,15] very little[16] work in the region below 700 cm^{-1} has been reported. Table II compares the spectra of copper(II) acetate monohydrate and cyanoacetate and cyanoacetic acid in the region 700–240 cm^{-1}. The far-infrared spectra of dimeric hydroxy-bridged[17,18] but not alkanoate copper(II) complexes have been described. Since the bands of copper acetate monohydrate can reasonably be associated with the acetate ion,[16] it is safe to assume that the medium-to-strong bands of copper acetate and cyanoacetate below 400 cm^{-1} are for the most part associated with metal–oxygen stretching vibrations, especially those at about 375, 335, 268, and 250 cm^{-1}. Copper–oxygen stretching vibrations at 451 and 291 cm^{-1} have been found for copper(II) acetylacetonate,[19a] and in the region 440–370 cm^{-1} for copper(II) tertiary arsine oxide complexes.[19b]

Electronic Absorption Spectra.—The ultraviolet and visible spectra of many dimeric copper(II) alkanoates have been measured in the solid state and in solution.[1]

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(9) See footnote *c*, Table I.

(10) D. F. Shriver, S. A. Shriver, and S. E. Anderson, *Inorg. Chem.*, **5**, 725 (1965), and references therein.

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Table II

Far-Infrared Data (700–240 cm^{-1})[a]

$Cu_2(C_2H_3O_2)_4 \cdot 2H_2O$	$Cu(C_3H_2O_2N)_2$	$HC_3H_2O_2N$
692 vs		670 s
628 vs	(610 m)	
	(599 s)	
562 m	591 s	570 m, br
522 m	549 vs	
	498 m	500 m
	461 m	
	450 m	
376 s	373 w	395 m
	361 m	360 w
330 m	340 s	
(298 w)	(298 w)	
268 s		
	253 m	
(250 w)		
	240 w	

[a] vs, very strong; s, strong; m, medium; w, weak; br, broad; parentheses, shoulder.

It has been shown that these complexes have a new band at about 375 mμ both in solution and in the crystalline phase. The polarized absorption spectra have shown that three bands at about 700 (band I), 375 (band II), and 300 mμ (band III) are present when a copper-to-copper interaction exists. Band I has been identified with d–d transitions of the copper ions, but the origin of band II, originally suggested to be due to the copper–copper linkage, has been controversial. Band II has been attributed to a transition between Cu–Cu molecular orbitals[5] and various types of d–d transitions. More recently, band II has been considered to be characteristic of the bridging system rather than the Cu–Cu linkage.[7] Graddon[20] assigned band III to a carboxy–copper(II) charge-transfer absorption since no significant solvent effect on this band was observed.

The electronic spectra of copper(II) acetate monohydrate and copper(II) cyanoacetate are given in Figure 2. The mull spectrum of copper(II) acetate monohydrate is very similar to the solution[7] and single-crystal[21,22] spectra which have been reported. The mull spectrum of copper(II) cyanoacetate in Figure 2 agrees with the diffuse reflectance spectrum of the compound and is consistent with the structure which has been proposed for the compound (Figure 1).

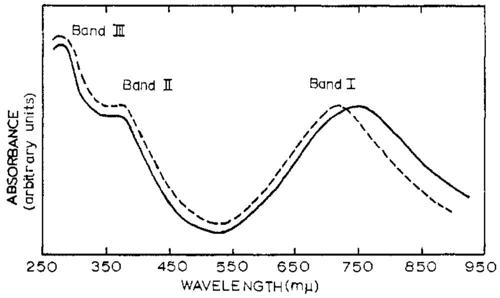

Figure 2.—Absorption spectra of copper(II) cyanoacetate monohydrate (- - - -) and copper(II) cyanoacetate(——); mulled solids.

Electron Spin Resonance Spectra.—The electron spin resonance absorption of copper(II) cyanoacetate was measured over the range 0–10,000 gauss with X-band radiation. There have been very few reports[23–27] of esr in dimeric copper compounds presumably because of difficulty in obtaining single crystals of these compounds. Most magnetic studies have been measurements of magnetic susceptibility.[1] Unfortunately, it has not been possible to obtain the zero-field splitting parameters from magnetic susceptibility measurements and only an average g value can be determined. We present here a general method for the determination of the magnetic parameters from the powder spectra of dimeric copper compounds. The method of analysis is based on the analysis of randomly oriented organic molecules in the triplet state by Wasserman, Snyder, and Yager.[28] The principal differences between the organic and inorganic triplets are that the g values of inorganic molecules are quite anisotropic, whereas in organic triplets they are isotropic, and the zero-field parameters of the inorganic molecules are usually much larger than those of the organic molecules.

The spin Hamiltonian for the triplet state of dimeric copper compounds is given by[23]

$$\mathcal{H} = \beta HgS + DS_z^2 + E(S_x^2 - S_y^2) - {}^2/_3D \quad (1)$$

D and E are the zero-field splitting parameters, β is the Bohr magneton, and x, y, and z are a principal axes coordinate system fixed with respect to the Cu–Cu bond. When the external magnetic field is in an arbitrary direction with respect to x, y, and z, we expect, in general, three esr transitions: two $\Delta M = \pm 1$ transitions and one $\Delta M = \pm 2$ transition. As the triplet wave functions are not in general pure states, this manner of labeling the transitions is somewhat deceptive; however, we follow the usual practice here. When the magnetic field is along, respectively, the x, y, and z directions, we obtain[28] from eq 1 the six $\Delta M = \pm 1$ resonance fields

$$\begin{aligned} H_{x_1}^2 &= (g_e/g_x)^2[(H_0 - D' + E')(H_0 + 2E')] \\ H_{x_2}^2 &= (g_e/g_x)^2[(H_0 + D' - E')(H_0 - 2E')] \\ H_{y_1}^2 &= (g_e/g_y)^2[(H_0 - D' - E')(H_0 - 2E')] \quad (2) \\ H_{y_2}^2 &= (g_e/g_y)^2[(H_0 + D' + E')(H_0 + 2E')] \\ H_{z_1}^2 &= (g_e/g_z)^2[(H_0 - D')^2 - E'^2] \\ H_{z_2}^2 &= (g_e/g_z)^2[(H_0 + D')^2 - E'^2] \end{aligned}$$

where $H_0 = h\nu/g_e\beta$, $D' = D/g_e\beta$, and $E' = E/g_e\beta$. H_{x_1} and H_{x_2} are, for example, the two $\Delta M = \pm 1$ resonance

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fields when the magnetic field is along the x direction. g_e is the free electron g value.

In a powder sample it is, of course, impossible to align the magnetic field along a given direction and the observed spectrum is a sum over all possible orientations. It has been shown,[28] however, that sharp discontinuities in the absorption curve occur at just the values of the magnetic field given by eq 2 so that even in a powder sample the axial resonance fields may be obtained and from them we may calculate g_x, g_y, g_z, D, and E. In addition to the six lines given by eq 2, there will occur, when $D < h\nu$, an additional line corresponding to the $\Delta M = \pm 2$ transition which is quite isotropic and thus will appear as only one additional line in the powder spectrum. When D is larger than $h\nu$, as is usually the case in compounds containing copper dimers, H_{x_1} and H_{y_1} and the $\Delta M = \pm 2$ line can no longer be observed so that the powder spectrum will consist of only four lines. If, in addition, $E = 0$, we may rewrite eq 2 as

$$\begin{aligned} H_{\perp_2}{}^2 &= (g_e/g_\perp)^2[H_0(H_0 + D')] \\ H_{z_1} &= -(g_e/g_z)(H_0 - D') \qquad (3) \\ H_{z_2} &= (g_e/g_z)(H_0 + D') \end{aligned}$$

and we note that only three lines now occur.

The esr powder spectra of copper(II) acetate monohydrate and copper(II) cyanoacetate taken at 296°K are shown in Figure 3. The axial resonance fields given by eq 3 are labeled. At 77.2°K we find that the line corresponding to $H_{\perp_2}$ for copper(II) acetate monohydrate is split into two (H_{x_2} and H_{y_2}) showing that E is nonzero (but small). For copper(II) cyanoacetate only a slight indication of a splitting is observable at 77.2°K, which shows that in this compound E is very nearly zero. We estimate that it is less than 0.003 cm^{-1}, perhaps about 0.002 cm^{-1}. The 77.2°K spectra are shown in Figure 4. From both the 296 and 77.2°K spectra we determine the magnetic parameters for copper(II) cyanoacetate as $D = 0.39 \pm 0.01$ cm^{-1}, $g_z = 2.40 \pm 0.02$, and $g_\perp = 2.08 \pm 0.02$.

In Figures 3 and 4 we note a line in both spectra at about 3200 gauss. This line corresponds to free, that is, nondimeric, copper ions, and we estimate from the intensity of the line that the concentration of this species is less than 2%. The proof that this line is not a part of the triplet spectrum is based on the fact that the intensity of the line increases with decreasing temperature whereas the lines arising from the triplet must decrease if J, the exchange parameter, is positive.

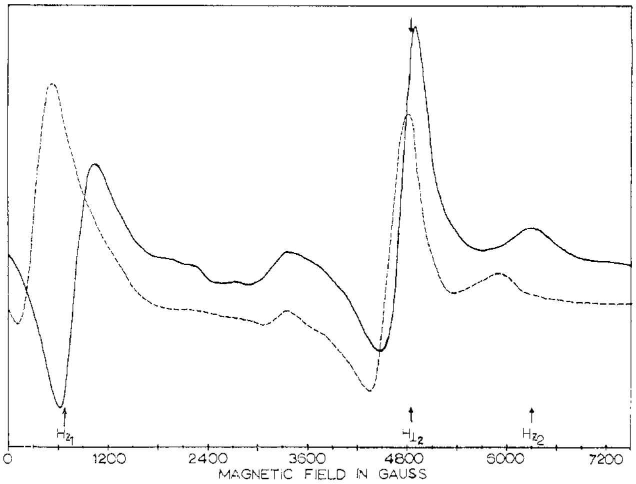

Figure 3.—Esr derivative spectrum for copper(II) cyanoacetate (——) and copper(II) acetate monohydrate (- - - -) at 296°K; powder spectra. The arrows show the positions of the axial resonance fields for copper(II) cyanoacetate. The frequency was 9.45 kMc.

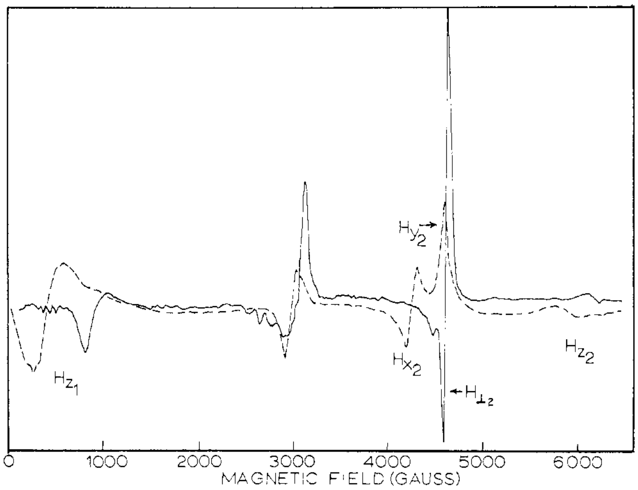

Figure 4.—Esr derivative spectrum for copper(II) cyanoacetate (——) and copper(II) acetate monohydrate (- - - -) at 77°K; powder spectra. The frequency was 8.94 kMc.

The exchange interaction parameter J may be determined from the temperature variation of the esr absorption lines. The relative intensity of the absorption is given by

$$R \propto \frac{1}{T} \frac{e^{-J/kT}}{1 + 3e^{-J/kT}}$$

We have compared the intensities of the lines H_{z_1} and $H_{\perp_2}$ at room temperature (296°K), the liquid ethane boiling point (184°K), and the liquid nitrogen boiling point (77.2°K). We found $J = +310$ cm^{-1} with a maximum uncertainty of 10%. J does not change within the stated uncertainty as a function of temperature. This is in contrast to the case of copper(II) acetate monohydrate. Intensities were measured relative to the signal from a small amount of DPPH mixed in with the sample. We have tested our method on copper(II) acetate monohydrate, for which J is known from previous work,[1,23] and found $J = +270$ cm^{-1}. This is within the range of values (260–310 cm^{-1}) given in the literature.[1]

In Figure 4 we note that on the low-field side of the H_{z_1} axial resonance line of copper(II) cyanoacetate some additional small lines appear. These are undoubtedly due to hyperfine interaction of the unpaired electrons with the copper nuclei in the dimer unit. The distance between the small lines is approximately 67 gauss and is just half the hyperfine splitting evident on the line corresponding to the free copper ion. This is just what is to be expected from a line, the origin of which is due to an exchange interaction.[29]

It would be interesting to compare the parameters determined in this experiment with the esr results on other dimeric copper compounds containing different ligands. Unfortunately, very little esr data are available. We note that our g values are approximately the same as all the others reported[23-27] within the experimental error. In addition, D and J in copper(II) cyanoacetate are only about 10–15% higher than in copper(II) acetate monohydrate. These relatively small changes in the magnetic parameters with respect to the considerably different nature of the ligand suggest that the interaction in both compounds is due to direct exchange. This is, of course, consistent with the presently accepted interpretation of the interaction in these compounds. A superexchange mechanism would probably be more ligand dependent. The observed differences in J, D, and E are explicable on the basis of small changes in the spatial arrangement of the complex. The fact that E is near zero in copper(II) cyanoacetate may be associated with the proposed polymeric structure which might tend to make the x and y directions equivalent.

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CONTRIBUTION FROM THE SAVANNAH RIVER LABORATORY,
E. I. DU PONT DE NEMOURS AND COMPANY, AIKEN, SOUTH CAROLINA 29801

The Hypersensitive Transitions of Hydrated Nd^{3+}, Ho^{3+}, and Er^{3+} Ions[1]

BY D. G. KARRAKER

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Hypersensitive and normal absorption bands in the spectra of aqueous Nd^{3+} change in shape as the concentration increases from 0 to 12 M for the electrolytes HCl, LiCl, and $HClO_4$, or as the temperature increases in concentrated LiCl solutions. Based on a comparison with the absorption spectra of 9-coordinate Nd^{3+} and 8-coordinate Nd^{3+}, the shape changes in aqueous Nd^{3+} spectra are considered evidence of a change in the coordination number of the aquo Nd^{3+} ion from 9 in dilute solutions toward 8 in concentrated solutions. The oscillator strengths of the hypersensitive bands of Nd^{3+}, Ho^{3+}, and Er^{3+} in HCl, LiCl, and $HClO_4$ solutions increase at higher electrolyte concentrations and at a higher temperature. This increase in the oscillator strengths of hypersensitive bands is attributed to the action of an enhanced electric field gradient from the proximity of anions and hydrated cations to the lanthanide ions, as predicted from theory. The change to 8-coordination of Nd^{3+} in concentrated chloride solutions is taken to indicate that other normally 9-coordinate lanthanide ions undergo a similar change. Thus, in concentrated chloride, it appears likely that all lanthanide ions are 8-coordinate, possibly $Ln(H_2O)_8^{3+}$ ions. In strong chloride solutions, trivalent actinide ions are chloro complexes. The explanation for the successful group separation of lanthanides and actinides by ion exchange or solvent extraction from strong chloride media may depend upon the existence of lanthanide and actinide ions as different aqueous species.

Introduction

The hypersensitive transitions in the absorption spectra of lanthanide ions are those characterized by variations in the intensity of absorption bands in different media. Since the first theoretical calculations of spectral intensities by Judd[2] and Ofelt,[3] hypersensitive transitions have been the subject of several theoretical and experimental investigations.[4-8] Original theoretical studies[4] attributed hypersensitivity to the enhancement of quadrupole transitions by the dielectric inhomogeneities in the media. Judd[7] has suggested that a change in the symmetry of the field on the lanthanide ion is also a probable cause.

This study investigated the effects of strong chloride and perchlorate solutions on the hypersensitive transitions of Nd^{3+}, Ho^{3+}, and Er^{3+}. These ions represent both the light and heavy lanthanides, and their relatively high extinction coefficients simplify spectral measurements. Concentrated chloride solutions are the most successful media for the group separation of lanthanide and trivalent actinide ions by ion exchange[9-12] or solvent extraction.[13] The investigation of lanthanide

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(1) The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

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