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COORDINATION OF LANTHANIDE ACETATES

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Abstract — A study of the structures of hydrated and anhydrous lanthanide acetates by X-ray diffraction, infrared spectra, and absorption spectra demonstrates that there are three separate structures for hydrated lanthanide acetates and four structures for anhydrous acetates. The site symmetry of the lanthanide ion in each structure was shown to be different by comparing the absorption bands due to hypersensitive transitions for Nd^{3+}, Ho^{3+}, or Er^{3+} in their normal structure and "doped" into other structures.

The comparison of band shapes for the hypersensitive transitions allowed the following coordination numbers to be deduced: for the hydrated lanthanide acetates, 8-9 for Structure A (La-Ce$Ac_3 \cdot 3/2H_2O$), 8 for Structure B (Pr-Nd$Ac_3 \cdot 3/2H_2O$), and a coordination intermediate between 6 and 7 for Structure C ($SmAc_3 \cdot 4H_2O$ through $LuAc_3 \cdot 4H_2O$)

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(Ac = CH_3COO^-); for anhydrous lanthanide acetates, 9 or greater for Structure I (La, Ce, Pr), 8-9 for Structure II ($NdAc_3$), 7-8 for Structure III ($GdAc_3$-$HoAc_3$), and 6-7 for Structure IV ($YbAc_3$). The intermediate lanthanide acetates were dimorphic. Polymeric, bidentate, and monodentate acetate were inferred from lanthanide ion coordination and distinguished by infrared spectra.

INTRODUCTION

The hydrated and anhydrous lanthanide acetates have several coordination possibilities, because lanthanide ions may assume coordination numbers of 6 to 10[1] and the acetate ion may be either monodentate, bidentate, or polymerizing ligand.[2] Because the ionic radius decreases in the series of lanthanide ions[3] the coordination changes of both lanthanide ions and the acetate ligand can be studied as the size of the coordination sphere decreases. Previous studies have determined the composition of hydrated lanthanide acetates as $LaAc_3 \cdot 3/2H_2O$,[4,5] $CeAc_3 \cdot 3/2H_2O$,[5] $PrAc_3 \cdot 2H_2O$,[4] $NdAc_3 \cdot 4H_2O$[5] or $NdAc_3 \cdot H_2O$,[4] and $LnAc_3 \cdot 4H_2O$[6] for Ln = samarium through lutetium and (Ac = CH_3COO^-). These compositions in themselves suggest bidentate or polymeric acetate coordination for the acetate ion in lanthanum, cerium, and praseodymium acetates, and monodentate acetate ligands for the heavier (samarium through lutetium) lanthanide acetates.

(1) E. L. Muetterties and C. M. Wright, Quart. Rev. 21, 109 (1967).

(2) K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, 1963. John Wiley and Sons, N. Y. p 198.

(3) D. H. Templeton and C. H. Dauben, J. Amer. Chem. Soc. 76, 5237 (1954).

(4) R. J. Meyer and U. Müller, Z. anorg. allgem. Chem. 109, 1 (1920).

(5) A. I. Grigor'ev and V. N. Maksimov, Zh. Neorg. Khim. 9, 1060 (1964) (tr: Russian Journal of Inorg. Chem. 9, 580 (1964).)

(6) G. V. Nadezhdina, V. I. Ivanov, V. Shubina, and V. E. Plyushchev, Zh. Obshch. Khim. 36, 1560 (1966). Translation by E. L. Head, LA-TR-67-50.

Infrared spectra of the anhydrous[5,7] and hydrated[5] lanthanide acetates have been reported. The absorption spectrum of neodymium acetate in aqueous solution[8] has been investigated also. In this study, the infrared and absorption spectra of anhydrous and hydrated lanthanide acetates were remeasured to infer the coordination of the ligand and lanthanide ions in this series of compounds. Corroborative structural evidence was obtained from X-ray powder diffraction patterns.

EXPERIMENTAL LANTHANIDE ACETATES

Acetates of lanthanum, cerium, praseodymium, neodymium, and erbium were purchased from Research Organic/Inorganic Chemical Co., Sun Valley, Calif. as 99.9% metal purity, and recrystallized from dilute acetic acid. The acetates of samarium, gadolinium, dysprosium, and ytterbium were prepared by dissolution of the hydroxides in acetic acid, and crystallization of the acetate from this solution. Acetates of europium, terbium, and ytterbium were prepared by dissolution of the oxide in hot 25% acetic acid, followed by crystallization of the acetate from the solution, and then drying in vacuum.

Anhydrous lanthanide acetates were prepared by refluxing the corresponding hydrated acetates in acetic anhydride

(7) K. C. Patil, G. V. Chandrashekhar, M. V. George, and C. N. R. Rao, Can. J. Chem. 46, 257 (1968)

(8) G. R. Choppin, D. E. Henrie, and K. Buijs, Inorg. Chem. 5, 1743 (1966).

for 4 to 6 hours.[9] Anhydrous acetates prepared by vacuum dehydration at 115°C[10] to 170°C, except for lanthanum acetate, did not give reproducible X-ray diffraction patterns, and chemical analyses indicated that dehydration by this method was usually accompanied by some chemical decomposition.

"Doped" lanthanide acetates were prepared by dissolving a mixture of the acetates of the two lanthanides in water, then evaporating at room temperature to crystalling solids. Normally, doped samples contained 5 mole % of the lanthanide ion under investigation and 95 mole % of diluent lanthanide ion, i.e. one that would not absorb transmitted light at the same wavelength as the ion under investigation, such as 5% $NdAc_3 \cdot xH_2O$ - 95% $LaAc_3 \cdot 3/2H_2O$. Doped anhydrous lanthanide acetates were prepared by refluxing the doped hydrates with acetic anhydride.

ANALYSES

Lanthanide content of the solid acetates was estimated by titration with EDTA;[11] the water content of the acetates was determined by either Karl Fischer titration or with a CEC

(9) J. A. Seaton, F. G. Sherif, and L. F. Audrieth, J. Inorg. Nucl. Chem. 9, 222 (1959).

(10) J. R. Witt and E. I. Onstott, J. Inorg. Nucl. Chem. 24, 637 (1962).

(11) J. S. Fritz, R. T. Oliver, and D. J. Pietrzyk, Anal. Chem. 30, 1111 (1958).

moisture analyzer. Carbon and hydrogen analyses were made with an F & M Model 185 CHN Analyzer.

SPECTRAL MEASUREMENTS

Infrared absorption spectra were measured with a Perkin-Elmer 521 Infrared Spectrometer on samples pressed into KCl pellets. Visible absorption spectra were measured with a Cary 14 Spectrophotometer. Solid samples were prepared by mulling with paraffin oil; the mull was spread on a filter paper disk for measurement of the absorption spectrum. A paper disk dampened with paraffin oil was placed in the reference position.

X-RAY DIFFRACTION DATA

X-ray diffraction data were obtained using nickel-filtered copper X-rays and a Norelco recording diffractometer. Positions and intensities of the diffraction peaks were read from the recorder chart; 2θ values were converted to lattice spacings using standard tables.

ANALYTICAL, INFRARED, AND X-RAY RESULTS FOR HYDRATED ACETATES

The analytical data for the hydrated lanthanide acetates are shown in Table I. The hydration values found by earlier

investigations[4-6] were confirmed except for hydrated acetates of praseodymium and neodymium. Praseodymium acetate was a sesquihydrate, and neodymium acetates were either a monohydrate, a sesquihydrate, or a dihydrate depending on the conditions used for their preparation. The previous report[5] of a tetrahydrated neodymium acetate was not confirmed by analyses of any $NdAc_3 \cdot xH_2O$ preparations, but X-ray diffraction data include a pattern in $NdAc_3 \cdot xH_2O$ that corresponds to that of the tetrahydrated acetates. Under different experimental conditions, pure tetrahydrated neodymium acetate might be produced.

The infrared spectra of the hydrated lanthanide acetates exhibit three distinct patterns (Fig. 1) exemplified by the infrared spectra of $LaAc_3 \cdot 3/2H_2O$; $NdAc_3 \cdot 3/2H_2O$, and $SmAc_3 \cdot 4H_2O$. Their infrared absorption bands are cataloged in Table II. The absorption bands are nearly identical for lanthanum and cerium acetates, and for praseodymium and neodymium acetates. The samarium acetate spectrum is typical of the infrared spectra of the hydrated acetates of lanthanides samarium through lutetium.

Previous infrared studies[5,7] of lanthanide ion-acetate coordination differ in their frequency assignments of the symmetric $-CO_2^-$ stretching and CH_3 bending vibrations, both

[12] V. N. Maksimov, A. V. Novoselova, and K. N. Semenenko, Zh. Neorg. Khim. 2, 997 (1957); tr: Russian Journal of Inorg. Chem. 2 (5), 20 (1957).

of which occur between 1480-1390 cm^{-1}. Grigor'ev and Maksimov[5] assigned the symmetric $-CO_2^-$ stretch to the bands between 1460-1430 cm^{-1}, and by inference assigned the 1410 cm^{-1} band to CH_3 bending modes. Patil, et al.[7] make the opposite assignment for these bands. The assignment chosen here was that of the Russian workers.[5] The 1460-1430 cm^{-1} bands showed changes between lanthanide acetates as would be predicted for a $-CO_2^-$ stretching vibration in different acetate coordinations; the band at 1410 cm^{-1} is essentially the same for all lanthanide acetates, as would be predicted for a CH_3 bending vibration.

Major differences in infrared spectra among the three classes of hydrated acetates are observed in several regions:

(a) Coordinated water bands appear at 1680 cm^{-1} for $NdAc_3 \cdot 2H_2O$, at 1655 and 1695 cm^{-1} for $SmAc_3 \cdot 4H_2O$, but were too faint for observation in samples of $LaAc_3 \cdot 3/2H_2O$.

(b) Symmetric and asymmetric $-CO_2^-$ stretching vibrations occur at 1555 (asym) and 1445 (sym) cm^{-1} for $LaAc_3 \cdot 3/2H_2O$; at 1555 (asym), 1535 (asym), 1460 (sym), and 1440 (sym) cm^{-1} for $NdAc_3 \cdot 3/2H_2O$; and at 1545 (asym) and 1452 (sym) cm^{-1} for $SmAc_3 \cdot 4H_2O$.

(c) CH_3 rocking vibrations were observed at 1049 and 1015 cm^{-1} for $LaAc_3 \cdot 3/2H_2O$; at 1051, 1023, and 1006 cm^{-1} for $NdAc_3 \cdot 3/2H_2O$; and at 1048 and 1020 Cm^{-1} for $SmAc_3 \cdot 4H_2O$.

In agreement with infrared spectra, X-ray diffraction data for powder samples indicate three crystal structures for hydrated lanthanide acetates. Lanthanum and cerium acetates are isomorphous, and their powder pattern is assigned as Structure A. The powder pattern for $PrAc_3 \cdot 3/2H_2O$ is a mixture of Structures A and B, in roughly equivalent amounts. $NdAc_3 \cdot 3/2H_2O$ is a mixture of Structures A, B, and C, with Structure B dominant. $SmAc_3 \cdot 4H_2O$ shows Structure C with a trace of Structure B. $EuAc_3 \cdot 4H_2O$ and the remaining acetates have pure Structure C. The lattice spacings and line intensities are shown in Table III. The X-ray powder patterns of Structure C agree reasonably well with the patterns found for $LnAc_3 \cdot H_2O$ compounds by Russian workers,[6] whose single crystal studies identified the unit cell as triclinic, space group P_1, with 2 formula units per unit cell.

ANALYTICAL, INFRARED, AND X-RAY RESULTS FOR ANHYDROUS ACETATES

The analytical data for anhydrous lanthanide acetates are shown in Table IV. The infrared spectra of the anhydrous lanthanide acetates shows four types of patterns; the spectra of $LaAc_3$, $CeAc_3$, and $PrAc_3$ are nearly identical. $NdAc_3$ belongs to a second class, the anhydrous acetates of samarium and europium a third group, and the acetates of gadolinium through lutetium form a fourth class. The spectra

of $LaAc_3$, $NdAc_3$, $EuAc_3$, $ErAc_3$, and a portion of $YbAc_3$ are shown in Fig. 2, and their absorption bands are listed in Table V. The infrared spectra among the four classes mainly differ in the $-CO_2^-$ stretching frequencies. $-CO_2^-$ asymmetric and symmetric stretching frequencies are found at 1602 (asym), 1525 (asym), 1470 (asym), 1452 (sym), and 1432 (sym) cm^{-1} for $LaAc_3$, $CeAc_3$, and $PrAc_3$; at 1550 (asym), 1460 (asym), and 1430 (sym) cm^{-1} for $NdAc_3$; at 1540 (asym) and 1440 (sym) for $SmAc_3$ and $EuAc_3$; and at 1540 (asym) and 1440 (sym) cm^{-1} for anhydrous acetates of gadolinium through lutetium. A different ratio of intensities is observed for CH_3 rocking vibrations between $YbAc_3$ and the group Gd-$ErAc_3$ (Fig. 2).

The infrared spectra of Sm-$EuAc_3$ and $NdAc_3 \cdot 3/2H_2O$ strongly resemble each other in the $-CO_2^-$ stretching region (1550-1440 cm^{-1}), as do the spectra of $NdAc_3$ and $LaAc_3 \cdot 3/2H_2O$. Also, the infrared spectra of the anhydrous acetates of lanthanides gadolinium through lutetium resemble the spectra of $LnAc_3 \cdot 4H_2O$. Absorption between 1550-1440 cm^{-1} should be sensitive to acetate coordination, and the acetate-lanthanide bonding in these compounds is considered similar.

X-ray powder diffraction data indicate four different structures for the anhydrous lanthanide acetates. $LaAc_3$, $CeAc_3$, and $PrAc_3$ are isomorphous (Structure I), $NdAc_3$ has

Structure II, $TbAc_3$ and $HoAc_3$ have Structure III, and $YbAc_3$ has Structure IV. The diffraction pattern for $SmAc_3$ is interpreted as a mixture of Structures II and I, $EuAc_3$ is a mixture of Structures II and III, and $ErAc_3$ is a mixture of Structures III and IV (Table VI). The groupings obtained from the analysis of X-ray data, in general, correspond to those observed in infrared spectra. The groupings do differ some because the infrared spectra for anhydrous lanthanide acetates of Structures III and IV were not distinguishable, and the infrared spectra of acetates of mixed structures appear different from the spectrum of either pure structure.

The anhydrous lanthanide acetates were of poor crystallinity, and X-ray diffraction lines were normally weak. The best-defined structures were the isomorphous $LaAc_3$, $CeAc_3$, and $PrAc_3$; other structures gave weak diffraction patterns.

SPECTRAL RESULTS OF LANTHANIDE ION COORDINATION

A difference in the environment of lanthanide ions in acetates of different structures was confirmed by comparing the shape of absorption bands due to hypersensitive transitions of Nd^{3+}, Ho^{3+}, and Er^{3+} in acetates. The hypersensitive bands in the absorption spectra of lanthanide ions are sensitive to the environment of the ion, so a difference in band shape should be observed when these ions are introduced into acetates of different structures.

Hydrated Acetates

In the hydrated acetates, the different environments were shown by comparing the band due to the $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transitions of Nd^{3+} in Nd^{3+} doped-$LaAc_3 \cdot 3/2H_2O$, $NdAc_3 \cdot 2H_2O$, and Nd^{3+}-doped $SmAc_3 \cdot 4H_2O$ (Fig. 3). The intermediate position of the $NdAc_3 \cdot 3/2H_2O$ structure allows the substitution of the Nd^{3+} ion in the structures of $LaAc_3 \cdot 3/2H_2O$ and $SmAc_3 \cdot 4H_2O$. Neither La^{3+} nor Sm^{3+} ions absorb in the spectral region used for these observations.

Previous studies[13,14] have shown that the band shape for hypersensitive transitions of Nd^{3+}, Ho^{3+}, and Er^{3+} can be correlated with the coordination number and ligand geometry on the lanthanide ion. Figure 4 shows the absorption due to the Nd^{3+} $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition in $NdAc_3 \cdot 3/2H_2O$, $NdAc_3$, and for comparison, the 6-coordinate Nd^{3+} in $Nd[(CH_3)_3CCOCHCOC(CH_3)_3]_3$ and the 8-coordinate Nd^{3+} in the $Nd(CF_3COCHCOCF_3)_4^-$ ion. Although the comparison is not exact, Nd^{3+} in both the hydrated and anhydrous acetates corresponds best in band shape to the 8-coordinate Nd^{3+}. Nd^{3+} in $LaAc_3 \cdot 3/2H_2O$ and Nd^{3+} in $SmAc_3 \cdot 4H_2O$ does not agree in band shape with Nd^{3+} in known coordinations; in these compounds Nd^{3+} may have either an intermediate or mixed coordination.

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(13) D. G. Karraker, Inorg. Chem. 6, 1863 (1967).
(14) D. G. Karraker, Inorg. Chem. 7, 473 (1968).

The Ho^{3+} absorption band between 4400-4700 Å for solid $HoAc_3 \cdot 4H_2O$ due to the hypersensitive $^5I_8 \rightarrow {}^5G_6$ transition, does not correspond in shape to either the 6-coordinate Ho^{3+} in $Ho(DPPD)_3$ (DPPD = $C_6H_5COCHCOC_6H_5^-$) or 7-coordinate Ho^{3+} in $Ho(hfaa)_3 \cdot H_2O$ (hfaa = $CF_3COCHCOCF_3^-$)[15] (Fig. 5), but does suggest a shape intermediate between 6- and 7-coordinate Ho^{3+}.

The band shapes observed for the hypersensitive Er^{3+} $^4I_{15/2} \rightarrow {}^2H_{11/2}$ transition in $ErAc_3 \cdot 4H_2O$ are interpreted as showing the same effects as the Ho^{3+} compounds (Fig. 6). The shape of the absorption band due to the hypersensitive $^4I_{15/2} \rightarrow {}^2H_{11/2}$ transition does not agree with the Er^{3+} ion in either the 6-coordinate $Er(DPPD)_3$ or the 7-coordinate $Er(hfaa)_3 \cdot H_2O$, but appears to be intermediate between the spectra of Er^{3+} in both coordinations.

Anhydrous Acetates

The comparison of band shape between anhydrous acetates provided evidence that each of the structures proposed from the analysis of infrared spectra and X-ray diffraction patterns involved a change in the coordination sphere of the lanthanide ion. Figure 7 shows the absorption of the

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[15] Further spectral studies of Ho^{3+} chelates and comparison with the interpretation of spectral studies on Er^{3+} chelates has demonstrated that the spectrum in Figure 7b of Reference 11 is due to the 7-coordinate Ho^{3+} in $Ho(hfaa)_3 \cdot H_2O$ rather than $Ho(hfaa)_3$.

Nd^{3+} $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition in Nd^{3+}-doped $LaAc_3$, $NdAc_3$, and Nd^{3+}-doped $SmAc_3$; these spectra demonstrate different environments for the Nd^{3+} in each material. The band shape of Nd^{3+} in $NdAc_3$ is in fair agreement with that of 8-coordinate Nd^{3+}; the band shapes for Nd^{3+} doped in $LaAc_3$ or $SmAc_3$ do not fit previous correlations of coordination numbers with Nd^{3+} band shape.(11) The band shape of Nd^{3+} doped in $SmAc_3$ shows maxima that correspond to maxima in the spectra of Nd^{3+} doped in $LaAc_3$ and $NdAc_3$. Tentatively, this appears to confirm the mixed structures of $SmAc_3$ deduced from X-ray diffraction data.

The shape of the band due to the Er^{3+} $^4I_{15/2} \rightarrow {}^2H_{11/2}$ transition is different in $ErAc_3$ and Er^{3+}-doped $YbAc_3$ (Fig. 8). The shape of the band due to the Ho^{3+} $^5I_8 \rightarrow {}^5G_6$ transition in $HoAc_3$ and that in Ho^{3+}-doped $YbAc_3$ (Fig. 9) also demonstrates different lanthanide ion environments in $HoAc_3$ and $YbAc_3$.

Identical band shapes were found for the Er^{3+} ion in Er^{3+}-doped $EuAc_3$, Er^{3+}-doped YAc_3, and $ErAc_3$. There is an apparent contraction between the spectral evidence for identical Er^{3+} environments and infrared and X-ray data. As explanation, the spectral evidence has two limitations that should be considered. First, when a compound of mixed crystals is doped, the ion introduced may select one of the two structures - for the doped $EuAc_3$, the Er^{3+} ion could be

incorporated mainly into Structure III. A second limitation may result from a large difference in absorption probabilities for the ion in two different structures. As an example, X-ray data indicate roughly equal amounts of Structures III and IV in $ErAc_3$; but if the absorption of the Er^{3+} ion in one structure is a factor of 5-10 greater than the other, it will appear to be the only structure present. From these considerations, spectral evidence demonstrates that a common structure is present in $EuAc_3$, YAc_3, and $ErAc_3$, but other structures may also be present as shown by X-ray and infrared evidence.

The comparison of band shapes for Er^{3+} in anhydrous $ErAc_3$ and Er^{3+} in structures of known coordination indicates that the Er^{3+} ion is mainly 8-coordinate in $ErAc_3$. The band shape found for Er^{3+} in Structure III agrees best with that for an 8-coordinate Er^{3+} ion, and the Ho^{3+} band shape with a 7-coordinate Ho^{3+} ion. The correlation of Er^{3+} band shape with coordination is considered the more reliable; the lanthanide ion in Structure III acetates are all probably 8-coordinate. Neither the band shape of Ho^{3+} or Er^{3+} doped into $YbAc_3$ agrees with that of a known coordination for these ions, but it appears reasonable to presume that the lanthanide ion in Structure IV has a lower coordination than in Structure III.

DISCUSSION

A model for lanthanide-acetate coordination can be deduced that is consistent with the spectral evidence and the predicted effect[16] of the shrinkage of the ionic radii[3] for successive ions in the lanthanide series. The major features of this model are a coordination decrease for the lanthanide ion in hydrated and anhydrous acetates as the ionic radii decrease, and an accompanying change in acetate coordination from a polymeric acetate to a bidentate, then to a monodentate ligand. This model is certainly correct in its general outline, but uncertainties in its details remain that can only be resolved by single crystal X-ray studies.

The hydrated acetates divide naturally into three classes on the evidence of identical compositions for hydrated acetates of the same class, different infrared spectra, and different X-ray diffraction patterns[6] of acetates of different classes. Absorption spectra of Nd^{3+} in $LaAc_3 \cdot 3/2H_2O$, $NdAc_3 \cdot 3/2H_2O$, and $SmAc_3 \cdot 4H_2O$ also demonstrate that the lanthanide ion is in a different environment in each class of hydrated lanthanide acetate. Comparison of the shape of hypersensitive bands indicates that Nd^{3+} is 8-coordinate in hydrated $NdAc_3$. A definite

[16] J. L. Hoard, B. Lee, and M. D. Lind, J. Amer. Chem. Soc. 87, 1612 (1965).

coordination cannot be assigned to lanthanide ions in the tetrahydrated acetates, but the shape of the absorption band for Ho^{3+} and Er^{3+} in their hydrated acetates appears to correspond to a mixture of 6- and 7-coordinate ions.

The anhydrous acetates divide into four classes on the evidence of X-ray diffraction, infrared spectra, and absorption spectra. Generally, the transition between classes for anhydrous acetates is less abrupt than for the hydrated acetates; the occurrence of four structures suggests that the structures are nearly equal in energy. The assignment of a coordination number for the lanthanide ions in anhydrous acetates is uncertain; the absorption spectra for Structure III is either 7- or 8-coordinate, depending on whether the correlation with Ho^{3+} or Er^{3+} is accepted.

The infrared absorption spectra of $-CO_2^-$ stretching frequencies between 1560-1430 cm^{-1} show four distinct patterns for the lanthanide acetates. The acetate ligand can be monodentate, bidentate, or coordinate polymerically, where one or both of the carboxyl oxygens are shared between two adjacent metal ions (Fig. 10).[5] The infrared spectra observed for tetrahydrated lanthanide acetates are assigned to a monodentate acetate ligand; the infrared spectra observed for anhydrous acetates of lanthanum, cerium, and praseodymium are considered that of polymeric acetate ligands, and other infrared spectra represent mixtures of bidentate

and polymeric acetate. A strong similarity in the infrared spectra in the carbonyl region is noted between $LaAc_3 \cdot 3/2H_2O$ and $NdAc_3$, and between $NdAc_3 \cdot 3/2H_2O$ and $SmAc_3$.

Because the coordination of the lanthanide ion determined in some structures from spectral evidence, the coordination of lanthanide ions and acetate ligands can be estimated for all structures. The estimated coordination for the lanthanide acetates is shown in Table VII.

The assignment of intermediate coordination numbers to lanthanide ions in some lanthanide acetates is unusual, but coordination of two types-consistent with this assumption-is known to occur in lanthanide and actinide coordination polyhedra.[1] A possible intermediate coordination structure is that of U^{3+} in the $MF-UF_3$ system which is discussed by Muetterties and Wright.[1] In this structure, one ligand in the coordination sphere has a longer, and consequently weaker, bond to the metal ion than the remaining ligands, and its bond has a fractional value. This type of coordination apparently occurs also in hydrates of $Ln(C_6H_5COCHCOC_6H_5)_3$ chelates.[17]

[17] D. G. Karraker, unpublished data.

A second possible intermediate structure is the alternating pattern of 6- and 7-coordinate ions found in the monoclinic (B-type) lanthanide sesquioxides. The absorption spectra of lanthanide ions in a mixture 6- and 7-coordination would appear as a weighted average of a mixture of the two coordinations.

An intermediate coordination resulting from unequal lanthanide ion-ligand bonding appears most reasonable for lanthanide acetates, and infrared spectra help justify this choice. Polymerically coordinated acetates involve both metal-oxygen and metal-oxygen-metal coordination. The splitting of the $-CO_2^-$ stretching vibrations in $LaAc_3$ suggests complex metal-acetate bonding. The symmetric and asymmetric $-CO_2^-$ stretching vibrations are nondegenerate in the acetate ion; splitting of these bands, as in anhydrous $LaAc_3$, is therefore attributed[5] to complex metal-acetate bonding. The bands for bidentate acetates are also predicted[5] to split because bidentate acetate ligands bonded to the same metal ion interact, but polymeric and bidentate acetate ligands occur together in the lanthanide acetates. Unequal bonding is expected for the acetate ligand, and is considered the most likely cause of intermediate coordination.

A previous infrared study[18] of monodentate and bidentate acetate coordination in $NiAc_2 \cdot 4H_2O$ and $Cu_2Ac_4 \cdot 2H_2O$ distinguished the two types of acetate coordination by the frequency difference between the asymmetric and symmetric $-CO_2^-$ stretching vibrations. This difference was 112 cm^{-1} for monodentate acetate in the nickel complex, and 185 cm^{-1} for bidentate acetate in the copper complex. Frequency differences are respectively 85-95, 95-105, and 95-110 cm^{-1} for monodentate, bidentate, and polymeric acetate ligands coordinated to lanthanide ions. The increase in the difference of $-CO_2^-$ stretching vibrations is barely discernable, and does not make a useful criterion for coordination. The magnitude of the frequency difference for acetates of the lanthanides and transition metal ions may be attributed to the differences in metal-acetate bonding. Transition metal-acetate bonds involve an appreciable contribution from the orbitals of the metal ion, but bonding between acetate and lanthanides is essentially electrostatic, with slight, if any, contribution from the lanthanide orbitals. The participation of metal orbitals should produce larger effects between different acetate coordinations.

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[18] K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, J. Amer. Chem. Soc. 79, 4904 (1957).

TABLE I

Composition of Hydrated Lanthanide Acetates

$LnAc_3 \cdot xH_2O$		H_2O, %		Preparation
Ln	x	Calc.	Found	
La	3/2	7.87	7.50	Air dried
Ce	3/2	7.84	8.67	Air dried
Pr	3/2	7.82	7.40	Air dried
			6.91	Vac dried 100°C
Nd	2	10.08	10.49	Air dried
	3/2	7.76	7.69	Vac dried 30°C
	1	5.31	5.63	Vac dried
			5.34	Vac dried
			5.86	Vac dried 115°C, 4 hours
			5.02	Vac dried 115°C, 20 hours
Sm	4	18.05	18.83	Air dried
Dy	4	17.52	17.97	Air dried
Er	4	17.36	17.13	Air dried
			16.6	Vac Dry 30°C
Yb	4	17.05	17.36	Air dried

TABLE II

Infrared Absorption of Hydrated Lanthanide Acetates

Frequency, cm^{-1}

$LaAc_3 \cdot 3/2H_2O$	$NdAc_3 \cdot 2H_2O$	$SmAc_3 \cdot 4H_2O$	Band Assignments[a]
3360 s, bd	3350 s, bd	3280 vs, bd	OH stretch (H_2O) CH stretch
2470 sh		2450 sh	
2330 w			Combination bands
2240 w	2240 w	2240 w	
		1695 w	HOH bend
	1680 w	1655 w	
	1600 w		Asym stretch $-CO_2^-$
1555 s	1555 sh		
	1535 s	1545 s	
	1460 sh	1452 s	$-CO_2^-$ sym stretch[b]
1445 sh	1440 s		
1410 s, bd	1410 s	1410 s	CH_3 asym bend[b]
	1395 sh	1395 sh	
1346 w	1349 w	1350 sh	CH_3 sym bend
1332 w	1340 sh		
1049 m	1051 m	1048 w	
1015 m	1023 m	1020 m	CH_3 rocking
	1006 m		
938 m	955 m	965 w	C-C stretch
930 sh	942 sh	946 m	
663 s	672 s	677 m	OCO bend
645 sh	646 m	645 sh	
614 m	615 w	610 w	
	507 w		$-CO_2^-$ rocking
467 w		465 w	

s, strong; m, medium; w, weak; sh, shoulder; bd, broad, v, very.

[a] J. K. Wilmshurst, J. Chem. Phys. 23, 2463 (1955); Ref. 2, p 199, Ref. 5, Ref. 7.

[b] These assignments are discussed in the text.

TABLE III

Partial X-Ray Diffraction Data for $LnAc_3 \cdot xH_2O$

$LaAc_3 \cdot 3/2H_2O$ *Structure* A		$CeAc_3 \cdot 3/2H_2O$ *Structure* A		$PrAc_3 \cdot 3/2H_2O$ *Structure* A & B		$NdAc_3 \cdot 3/2H_2O$ *Structure* B, C, & A		$SmAc_3 \cdot 4H_2O$ *Structure* C & B		$EuAc_3 \cdot 4H_2O$ *Structure* C	
d, Å	I/Io	d, Å	I/Io	d, Å	I/Io	d, Å	I/Io	d, Å	I/Io	d, Å	I/Io
9.85	100	9.84	100	9.85	100						
						9.33	29	9.33	100	9.33	100
				8.46	60	8.42	100	8.44	10		
8.08	23										
						7.96	18	7.97	15	7.96	53
7.90	62	7.90	66	7.90	55						
7.74	15	7.70	15	7.70	18						
						7.60	50	7.60	30	7.57	74
				7.53	33	7.52	45				
6.89	19	6.86	15	6.86	7	6.86	2				
6.56	35	6.53	18	6.53	18						
5.81	15			5.82	24	5.81	15				
5.61	23	5.57	10	5.59	15						
5.42	77	5.41	51	5.40	72	5.42	30				
						5.37	23	5.37	15	5.35	28
						5.18	16	5.19	15	5.14	26
4.91	15			4.91	18						
						4.72	7	4.71	6	4.71	10
						4.70	9				
4.37	100	4.37	50	4.36	45						
4.00	80	4.01	40	4.00	33						

TABLE IV

Analyses of Anhydrous Lanthanide Acetates

Lanthanide	Carbon, %		Hydrogen, %		H_2O, %
	Calc.	Found	Calc.	Found	Found
La	22.78	23.19	2.85	2.70	
Ce	22.71	23.19	2.84	2.71	
Pr	22.64	22.92	2.83	2.66	
Nd	22.41	22.47	2.80	2.82	1.18
Sm	21.99	22.06	2.75	2.94	0.18
Eu	21.88	21.51	2.74	2.64	0.05
Gd	34.50	34.31	2.87	2.89	
Tb	21.43	21.13	2.68	2.57	0.42
Dy	34.35	34.24	2.86	2.84	
Ho	21.05	20.83	2.63	2.56	0.05
Er	20.90	20.55	2.61	2.52	0.24
Yb	20.57	20.55	2.57	2.60	0.006

TABLE V

Infrared Absorption of Anhydrous Lanthanide Acetates

Frequency, cm^{-1}

$LaAc_3$	$NdAc_3$	$EuAc_3$	$ThAc_3$	$YbAc_3$	Band Assignments[a]
3420 w, bd	3400 w, bd	3400 m, bd	3410 m, bd	3420 m, bd	
3020 w			3380 sh		
3005 w	3000 vw, bd	3000 vw, sh			CH stretch
2980 w					
2930 w	2930 w	2930 w			
	2340 w, bd	2340 w, bd		2340 w, bd	Combination bands
		2250 w	2240 w		
1602 m		1605 sh		1640 w	
1525 vs	1550 s, bd	1540 s	1540 s	1540 s	$-CO_2^-$ asym stretch
1470 m	1460 sh				
1452 m				1455 s	
1432 m	1430 sh	1440 s	1440 s		$-CO_2^-$ sym stretch
1405 s	1410 s	1412 sh	1405 sh	1415 sh	CH_3 asym bend
1348 w	1348 sh	1350 sh			
1338 m	1338 w	1343 w		1340 w	CH_3 sym bend
1332 w, sh			1332 m		
1052 m	1050 w	1053 m	1048 w	1048 w	
1032 m	1030 } m	1024 m	1024 sh	1025 m	CH_3 rock
1016 m	1015 }	1008 m	1014 m	1005 sh	
963 w	950 sh	960 w	950 w	960 m	
952 m	940 w	942 w	938 w		C-C stretch
670 sh	668 s	675 s	670 s	685 m	
662 m					
642 m	645 m	648 m	645 m	645 m	OCO bend, CO_2 rock
620 m		625 sh			
612 sh	610 w	615 m	612 m	618 m	

s, strong; m, medium; w, weak; sh, shoulder; bd, broad; v, very.

[a] See Table III for references.

TABLE VI

Partial X-Ray Diffraction Data for $LnAc_3$

$LaAc_3$ *Structure I*		$CeAc_3$ *Structure I*		$PrAc_3$ *Structure I*		$NdAc_3$ *Structure II*		$SmAc_3$ *Structure II & I*		$EuAc_3$ *Structure III & II*		$HoAc_3$ *Structure III*		$ErAc_3$ *Structure III & IV*		$YbAc_3$ *Structure IV*	
d, Å	I/Io	d, Å	I/Io	d, Å	I/Io	d, Å	I/Io	d, Å	I/Io	d, Å	I/Io	d, Å	I/Io	d, Å	I/Io	d, Å	I/Io
8.86	11	8.81	17	8.80	23	10.55	40										
6.91	100	6.87	100	6.85	100			8.80	17								
6.41	35	6.35	37	6.30	42	8.27	100	8.21	100								
4.80	11	4.79	13	4.79	21					8.10	50	8.01	50	7.97	1		
4.68	48	4.66	30	4.63	37	7.70	18										
4.39	14	4.39	7	4.38	28					7.37	100	7.35	100	7.30	90		
4.18	14	4.15	13	4.11	7									7.20	100	7.15	100
4.02	28	3.99	26	3.96	21											7.01	73
3.62	21	3.60	26	3.60	28			6.44	75								
3.57	46	3.55	50	3.52	37					6.35	50	6.32	37				
3.40	18	3.38	17	3.34	17			6.25	67								
3.29	39	3.27	53	3.25	50	5.42	53	5.44	25							5.41	7
3.16	48	3.16	46	3.15	50	5.28	50	5.23	22								
3.06	28	3.04	26	3.02	21	4.94	20										
3.03	18	3.01	23	3.01	17	4.89	15										
2.92	28	2.92	40	2.91	33	4.77	20										
		2.90	27	2.89	17			4.58	40								
2.39	21	2.38	27	2.36	17			4.40	20								
2.24	42	2.23	57	2.22	30					4.20	5	4.20	3	4.18	22	4.15	9
2.21	14	2.19	13	2.18	10			4.16	30	4.15	3						
2.08	18	2.07	26	2.06	17											4.07	20
						4.01	50	4.04	30								
								3.84	70	3.78	8	3.75	9				
						3.75	25	3.70	20			3.71	9				
										3.72	10	3.70	9	3.69	11	3.65	20
										3.64	40	3.66	20	3.64	11		
										3.60	40	3.60	40	3.58	24	3.57	50

TABLE VII

Estimated Coordination in Lanthanide Acetate Structures

Structure	Compounds	Ln^{3+} Coordination[a]	Acetate Coordination
A	$LaAc_3 \cdot 3/2H_2O$ $CeAc_3 \cdot 3/2H_2O$	8, 9	Mainly polymeric, bidentate
B	$PrAc_3 \cdot 3/2H_2O$ $NdAc_3 \cdot 3/2H_2O$	8	Mainly bidentate polymeric
C	$SmAc_3 \cdot 4H_2O$ - $LuAc_3 \cdot 4H_2O$	6, 7	Monodentate
I	$LaAc_3$, $CeAc_3$, $PrAc_3$	9 or greater	Polymeric
II	$NdAc_3$	8, 9	Polymeric, bidentate
III	$GdAc_3$ - $HoAc_3$	7, 8	Mainly bidentate, polymeric
IV	$YbAc_3$	6, 7	Mainly bidentate

[a]Two values are listed to indicate a mixture of two values or an intermediate coordination.

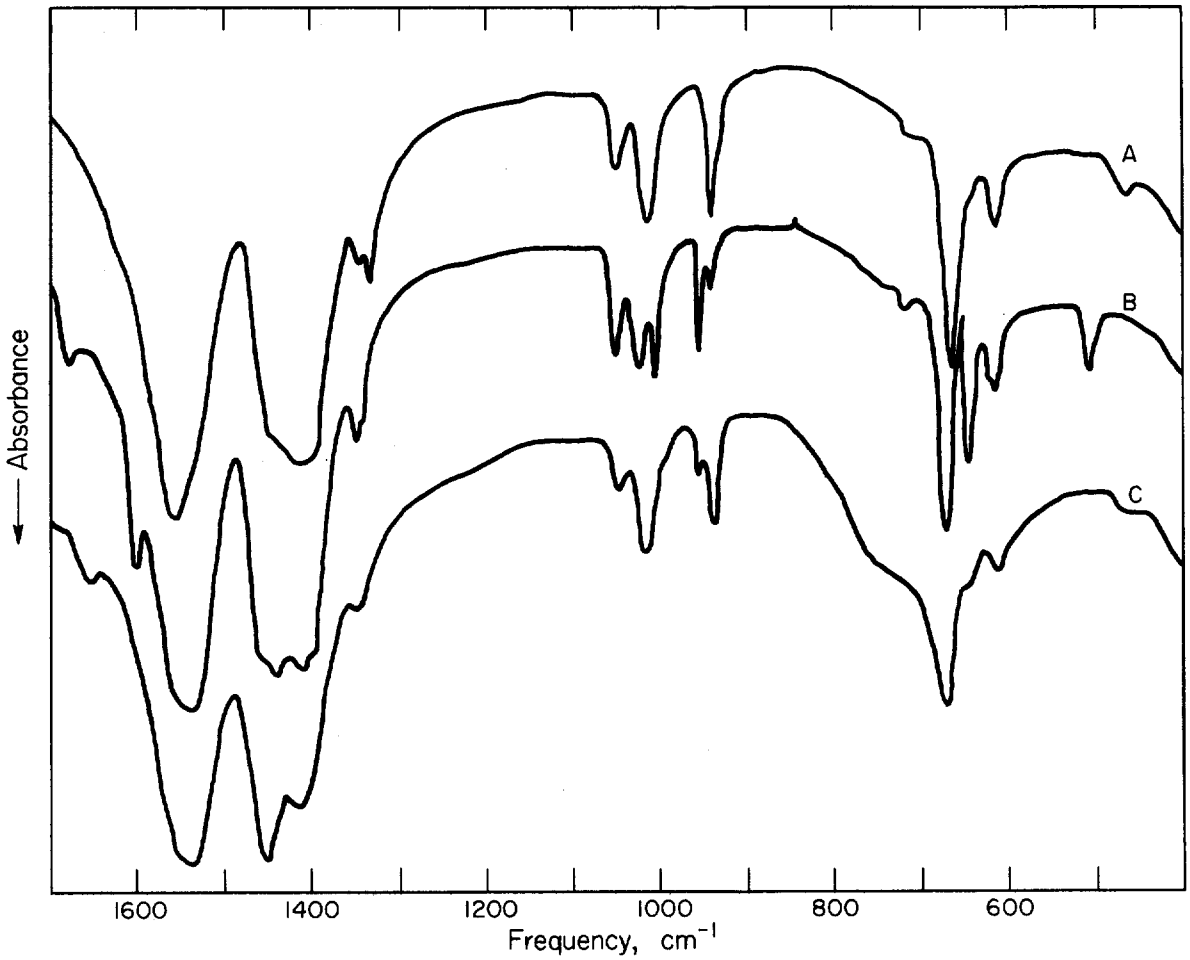


FIG. 1 INFRARED SPECTRA OF HYDRATED LANTHANIDE ACETATES

A $LaAc_3 \cdot 3/2H_2O$

B $NdAc_3 \cdot 3/2H_2O$

C $SmAc_3 \cdot 4H_2O$

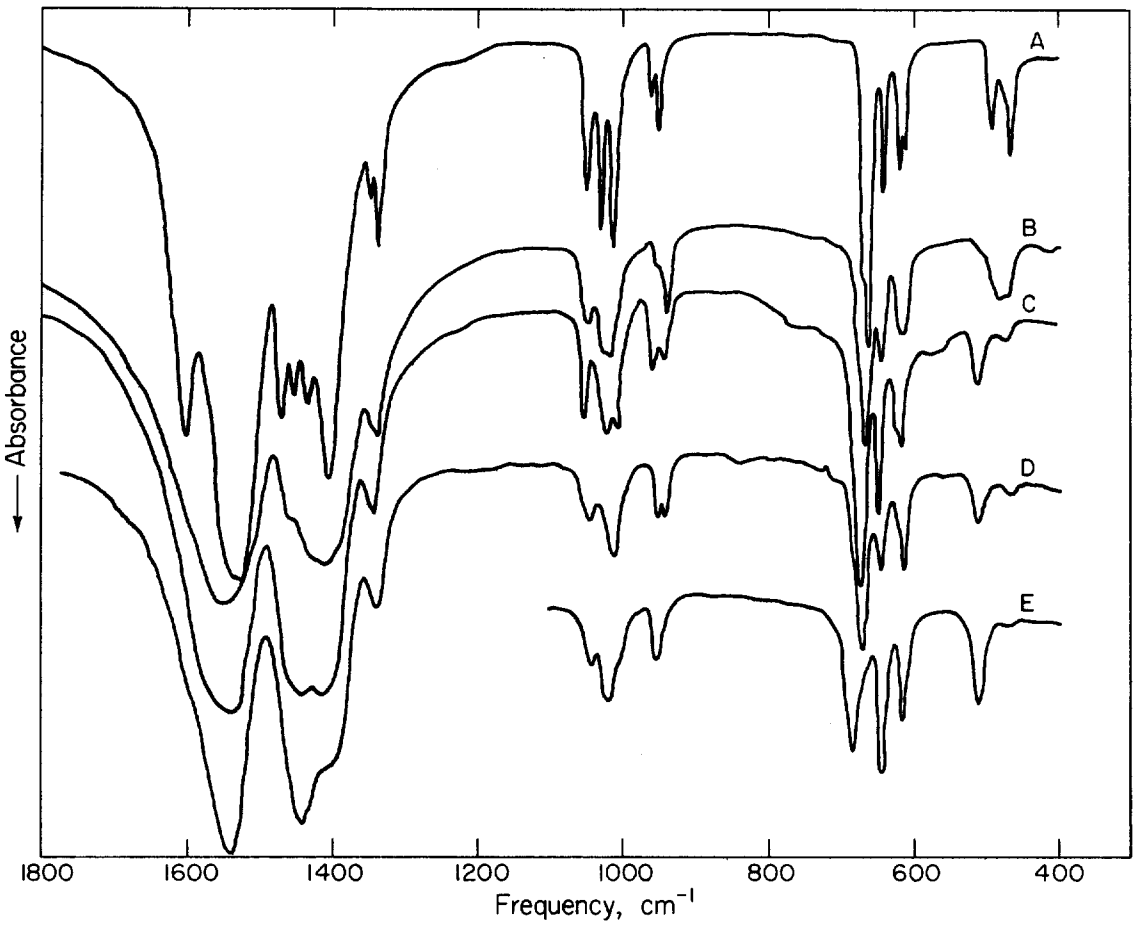


FIG. 2 INFRARED SPECTRA OF ANHYDROUS LANTHANIDE ACETATES

A $LaAc_3$ D $ErAc_3$

B $NdAc_3$ E $YbAc_3$

C $EuAc_3$

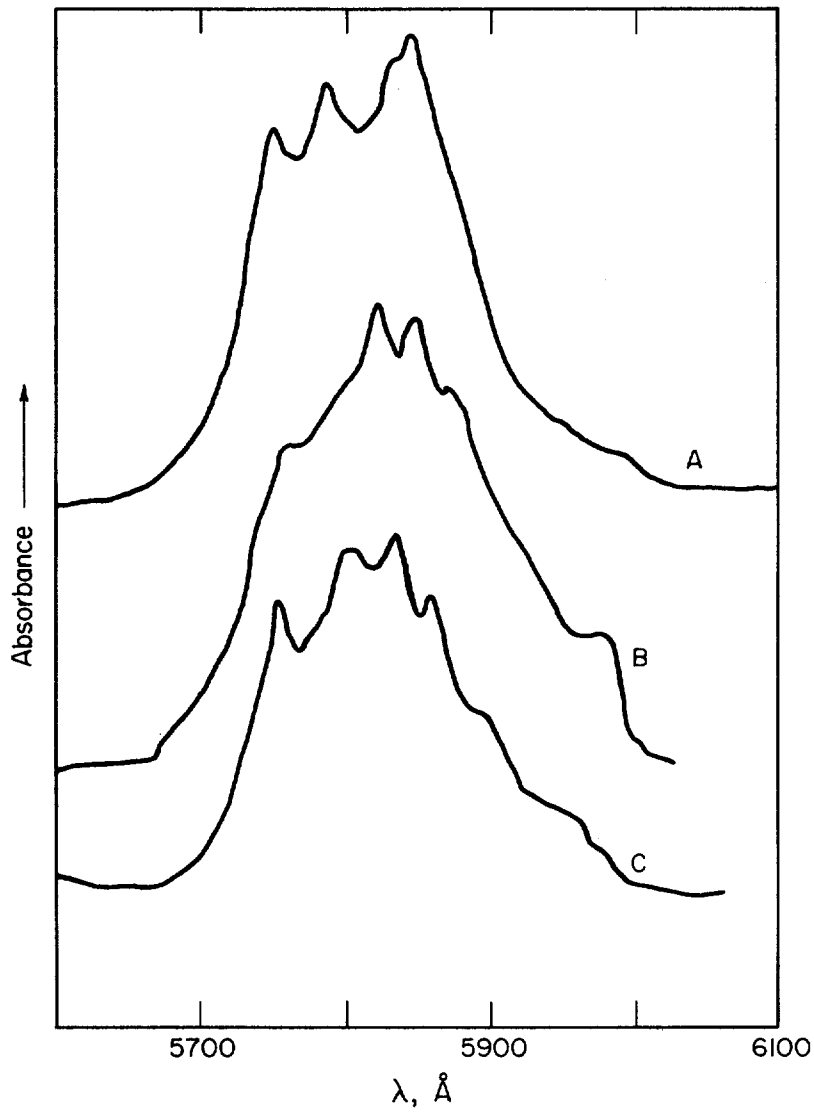


FIG. 3 Nd^{3+} $^4I_{9/2} \rightarrow {}^4G_{5/2}$ TRANSITION IN HYDRATED LANTHANIDE ACETATES
A Nd^{3+}-DOPED $LaAc_3 \cdot 3/2H_2O$ C Nd^{3+}-DOPED $SmAc_3 \cdot 4H_2O$
B $NdAc_3 \cdot 3/2H_2O$

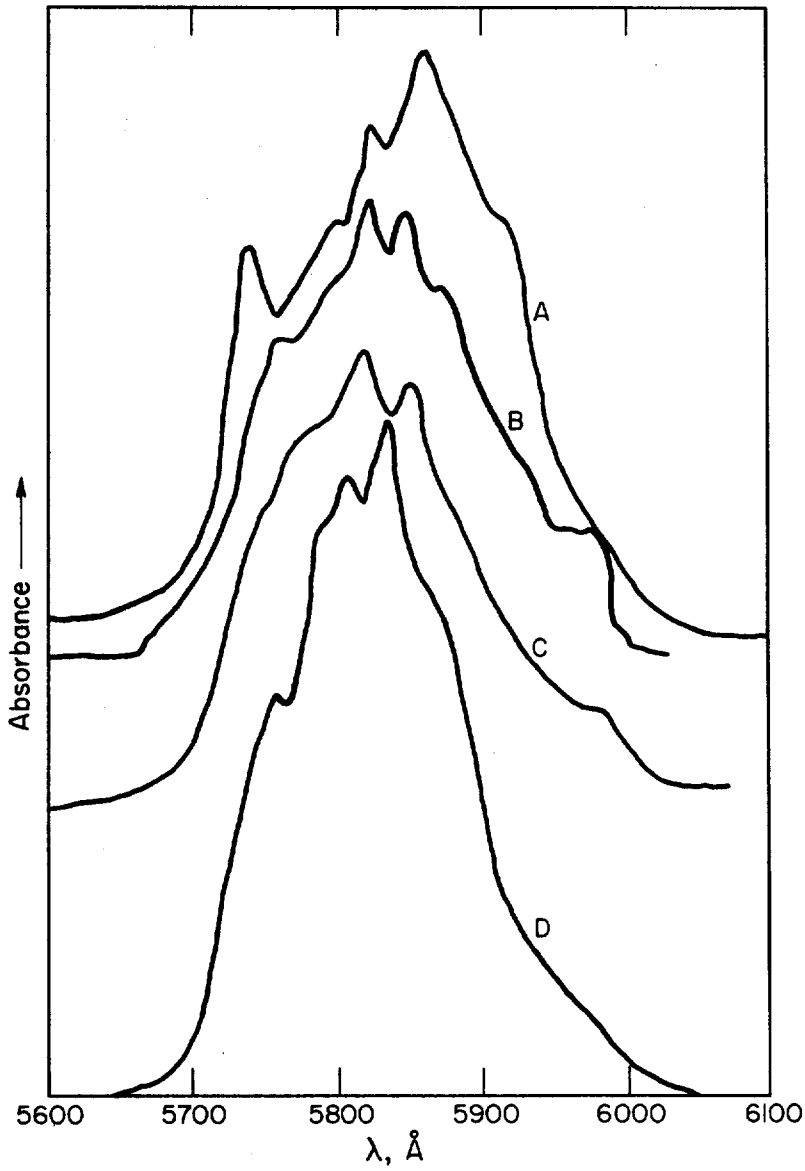


FIG. 4 Nd^{3+} $^4I_{9/2} \longrightarrow {}^4G_{5/2}$ TRANSITION FOR NEODYMIUM ACETATES

A 6 - COORDINATE Nd^{3+}

B $NdAc_3 \cdot 3/2H_2O$

C $NdAc_3$

D 8 - COORDINATE Nd^{3+}

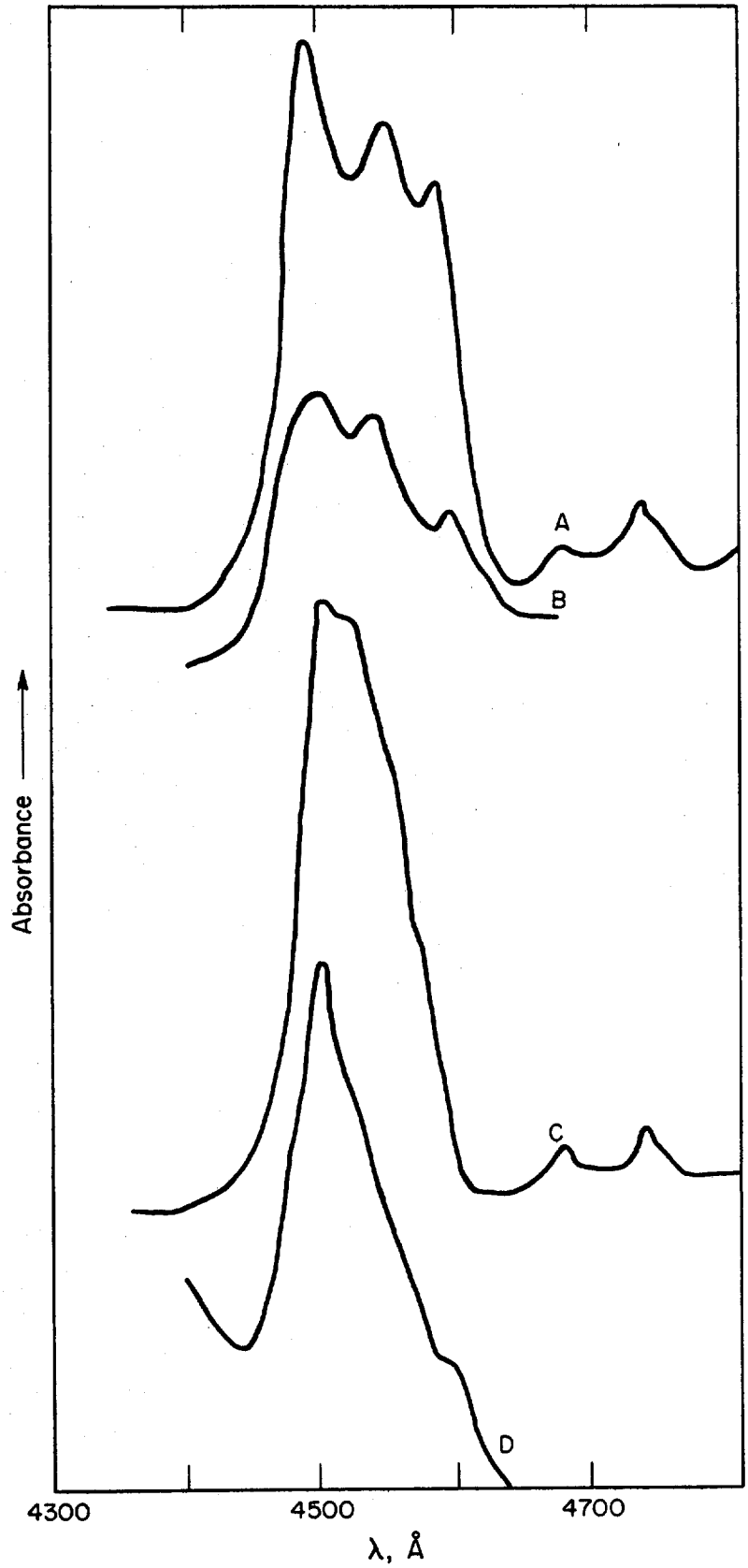


FIG. 5 Ho^{3+} $^5I_8 \rightarrow {}^5G_6, {}^5F_1$ TRANSITION

A $HoAc_3$

B 7 - COORDINATE Ho^{3+} IN $Ho(hfaa)_3 \cdot H_2O$

C $HoAc_3 \cdot 4H_2O$

D 6 - COORDINATE Ho^{3+} IN $Ho(DPPD)_3$

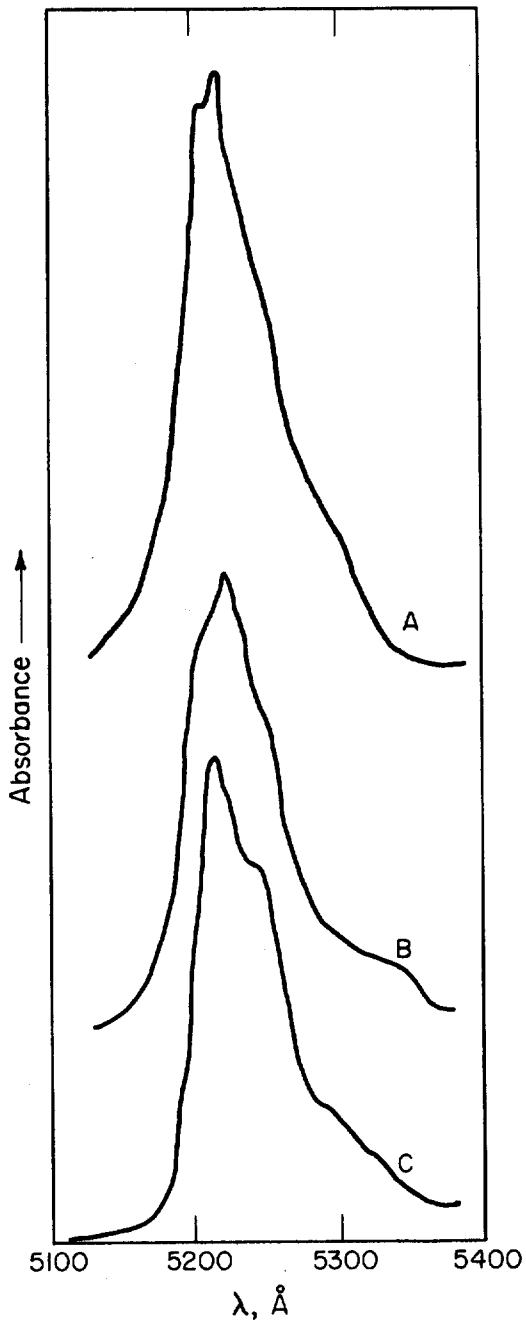


FIG. 6 Er^{3+} $^4I_{15/2} \longrightarrow {}^2H_{11/2}$ TRANSITION

A $ErAc_3 \cdot 4H_2O$

B 6 - COORDINATE Er^{3+} IN $Er(DPPD)_3$

C 7 - COORDINATE Er^{3+} IN $Er(hfaa)_3 \cdot H_2O$

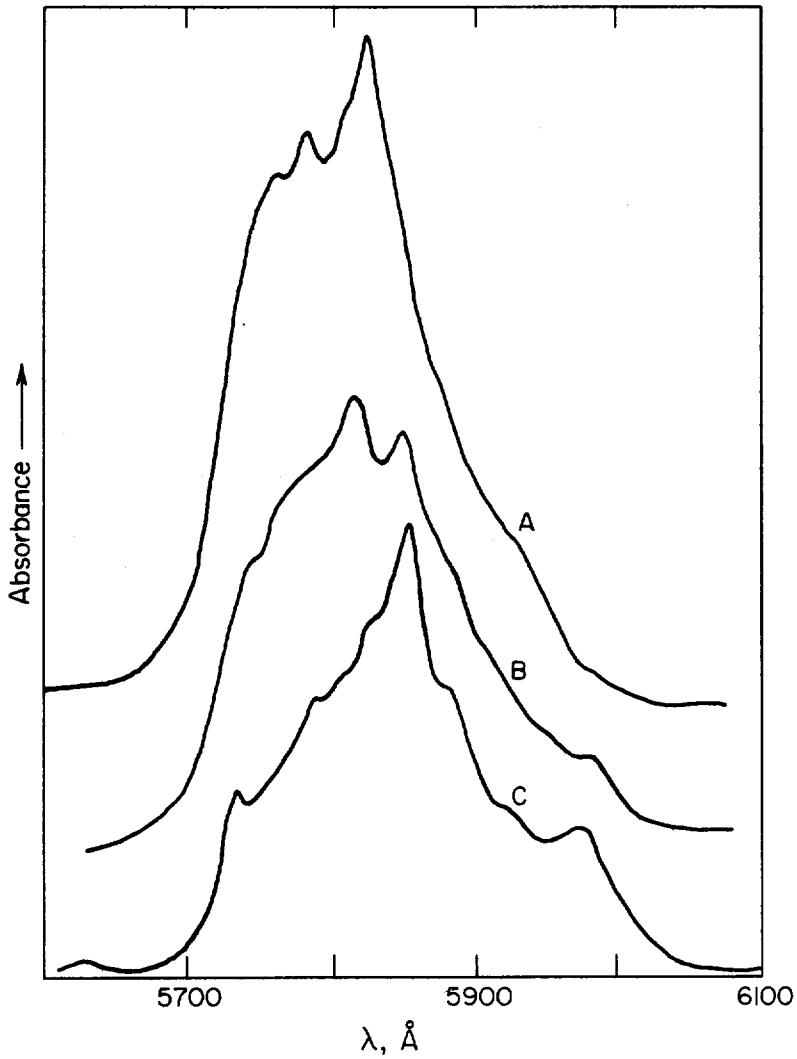


FIG. 7 Nd^{3+} $^4I_{9/2} \rightarrow {}^4G_{5/2}$ TRANSITION IN ANHYDROUS ACETATES

A Nd^{3+}-DOPED $LaAc_3$ C Nd^{3+}-DOPED - $SmAc_3$

B $NdAc_3$

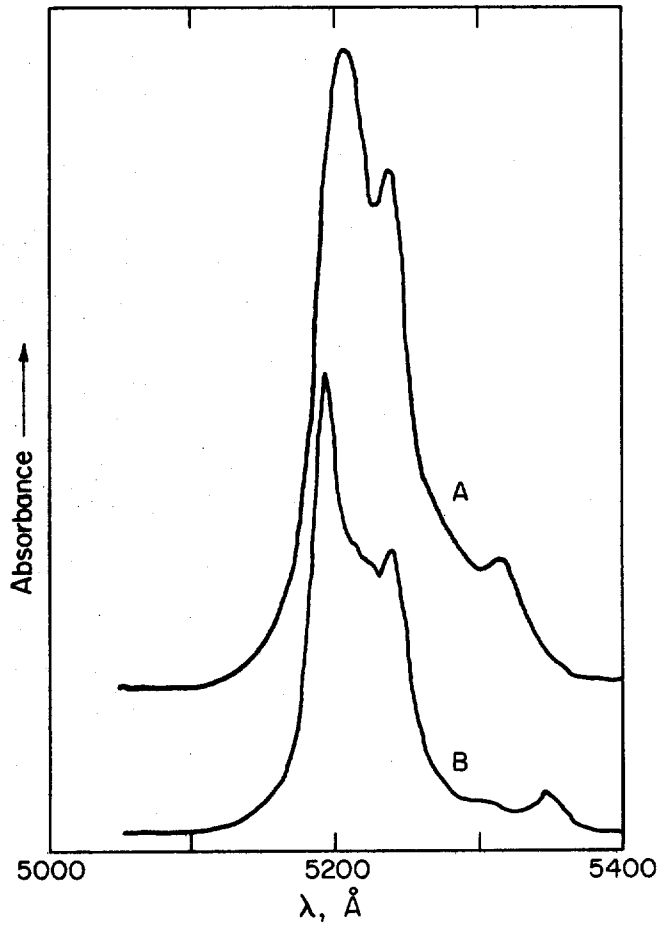


FIG. 8 Er^{3+} $^4I_{11/2} \rightarrow {}^2H_{15/2}$ TRANSITION
A $ErAc_3$
B Er^{3+}-DOPED $YbAc_3$

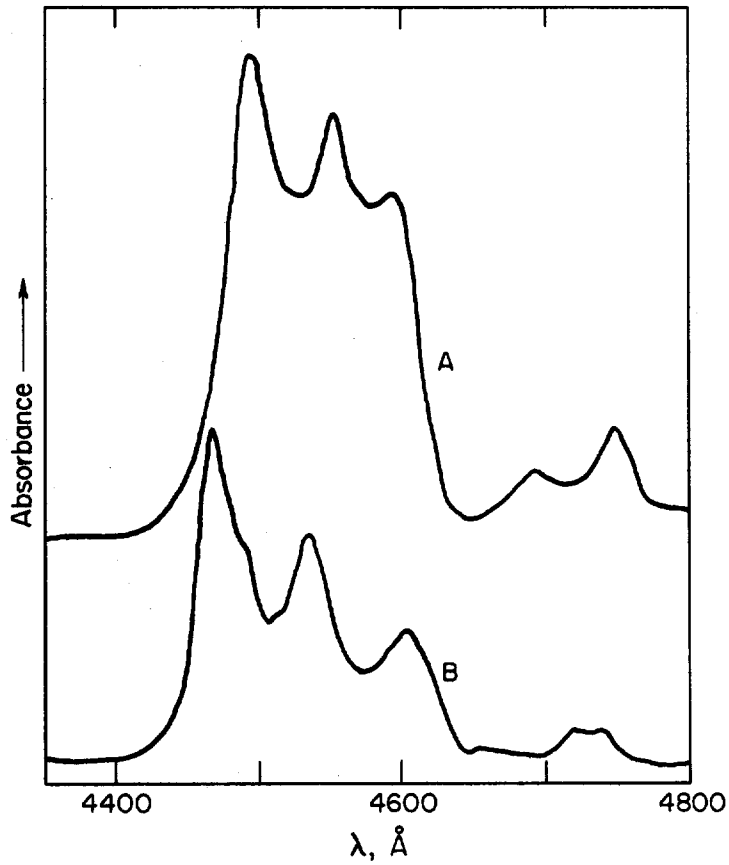
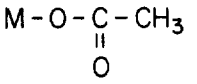
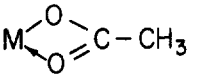


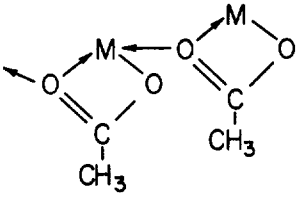
FIG. 9 Ho^{3+} $^5I_8 \rightarrow {}^5G_6$ TRANSITION
A $HoAc_3$
B Ho^{3+}-DOPED $YbAc_3$



Monodentate



Bidentate



Polymeric

FIG. 10 ACETATE COORDINATION