arise from octahedral ligand fields in both cases. Such fields are due to the formation of bridging oxygen to metal bonds.

The analytical results for chelates that produce pattern 1 type spectra are best explained by oligomeric molecules, also. The unusual number of water molecules per metal ion is caused by the fact that the waters occupy only a few coordination sites on the oligomer. The number of water molecules is determined by the number of octahedra involved and the type of bridging, *i.e.*, face sharing, edge sharing, or corner sharing between octahedra. The rigorous conditions needed to remove the water molecules leave no doubt that they are coordinated to the metal ion. It would be extremely interesting to determine the structures of the oligomers by X-ray analysis; however, as yet no suitable single crystals have been prepared. At this point, it seems likely that $Ni(HMC)_6(H_2O)_2$ exists as three octahedral units with two shared edges and that $Co_3(HMC)_6$ exists as three octahedral units with two shared faces.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF KENTUCKY, LEXINGTON, KENTUCKY 40506

Anhydrous and Hydrated Rare Earth Acetylacetonates and Their Infrared Spectra[1,2]

BY MARY FRANCES RICHARDSON, WILLIAM F. WAGNER, AND DONALD E. SANDS

Received June 6, 1968

Chemical analyses, X-ray powder diffraction patterns, and infrared spectra were used to characterize anhydrous, mono-, di-, and trihydrated rare earth acetylacetonates, and the densities of the hydrated chelates were determined. The anhydrous chelates were obtained by vacuum drying one of the hydrates. They are not appreciably volatile and slowly decompose *in vacuo* at elevated temperatures. Trihydrates precipitate from 60% aqueous ethanol, dihydrates from cold 95% ethanol, and monohydrates from hot 95% ethanol and a variety of other solvents. The infrared spectra are distinctive for each of the series of hydrates. For a given hydrate series, the spectra obtained are practically independent of the rare earth ion. The most notable exception is the 3100–3600-cm^{-1} region of the monohydrates where the high-energy O–H stretching frequency shifts to higher wave numbers and the low-energy O–H stretching frequency shifts to lower wave numbers as the ionic size of the rare earth decreases. Deuterium isotopic substitution studies on the mono- and trihydrates were used to locate the C–H and coordinated H_2O vibrations.

Rare earth acetylacetonates have been studied extensively because they are the simplest known β-diketone chelates. Because of conflicting data in the literature regarding the extent of hydration of rare earth acetylacetonates, Pope, Steinbach, and Wagner[3] carried out a study designed to resolve the problem of hydration number. Only mono- and trihydrated chelates were found, and there was no evidence that the anhydrous and dihydrated complexes existed. Pope believed that the "dihydrate" reported by several workers was actually a mixture of the mono- and trihydrates, and that the "anhydrous" chelate was a partly hydrolyzed sample of the monohydrate. There is little doubt that this has frequently been the case. However, the papers by Koehler and Bos[4] and others[5-7] contain substantial evidence that an anhydrous, unsolvated chelate has been made. The present study presents definitive evidence (chemical analyses, including Karl Fischer titrations, X-ray powder diffraction patterns, and infrared spectra) for the existence of anhydrous rare earth acetylacetonates. In addition, a dihydrated chelate has been characterized for the acetylacetonates of La, Pr, Nd, and Sm.

Many investigators have obtained infrared spectra for the rare earth acetylacetonates,[8-14] but a complete study of the effect of hydration number on the spectra has not been made. This study reports a systematic investigation of the spectra of the mono-, di-, and trihydrates, as well as of the anhydrous chelates and deuterated mono- and trihydrates.

---

[1] Abstracted in part from a thesis submitted by M. F. Richardson to the Graduate School of the University of Kentucky in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Louisville, Ky, Oct 27, 1966.

[3] G. W. Pope, J. F. Steinbach, and W. F. Wagner, *J. Inorg. Nucl. Chem.*, **20**, 304 (1961).

[4] J. M. Koehler and W. G. Bos, *Inorg. Nucl. Chem. Letters*, **3**, 545 (1967).

[5] C. Brecher, H. Samelson, and A. Lempicki, *J. Chem. Phys.*, **42**, 1081 (1965).

[6] R. C. Mehrotra, T. V. Misra, and S. N. Misra, *Indian J. Chem.*, **3**, 525 (1965).

[7] B. S. Sankhla and R. N. Kapoor, *Australian J. Chem.*, **20**, 685 (1967).

[8] C. Duval, R. Freymann, and J. Lecomte, *Bull. Soc. Chim. France*, 106 (1952).

[9] K. E. Lawson, *Spectrochim. Acta*, **17**, 248 (1961).

[10] J. P. Dismukes, L. H. Jones, and J. C. Bailar, *J. Phys. Chem.*, **65**, 792 (1961).

[11] D. Purushottam, V. Ramachandra Rao, and Bh. S. V. Raghava Rao, *Anal. Chim. Acta*, **33**, 182 (1965).

[12] C. Y. Liang, E. J. Schimitschek, D. H. Stephens, and J. A. Trias, *J. Chem. Phys.*, **46**, 1588 (1967).

[13] S. Misumi and N. Iwasaki, *Bull. Chem. Soc. Japan*, **40**, 550 (1967).

[14] A. I. Byrke, N. N. Magdesieva, L. I. Martynenko, and V. I. Spitsyn, *Zh. Neorgan. Khim.*, **12**, 666 (1967).

Experimental Section

Reagents.—Rare earth oxides were obtained in 99.9% purity or better from the Michigan Chemical Co. or the Lindsay Chemical Co. Acetylacetone (Hacac) was obtained from the Aceto Chemical Co. It was purified by extracting twice with 10% ammonia and three times with water, drying over sodium sulfate, and distilling through a 70-cm column packed with glass helices. The center fraction was collected and stored in a dark bottle, and discarded when a faint yellow color began to appear.

Chelate Preparations.—The crude rare earth acetylacetonates were prepared by the method of Stites, McCarty, and Quill.[15] Analytical data and infrared spectra show that this crude material is the rare earth acetylacetonate trihydrate for all rare earths from Ce through Yb and the dihydrated chelate for La.

Pure mono- and trihydrated chelates were prepared by the methods suggested by Pope, *et al.*[3] That is, the trihydrated chelate was obtained by recrystallizing the crude material from 60% ethanol, and the monohydrated chelate was obtained by recrystallizing from 95% ethanol, acetone, or acetylacetone. Recrystallization from the first two solvents gives adducts having the formulas $Ln(acac)_3 \cdot 3H_2O \cdot C_2H_5OH$ (Ln = Gd–Lu) and $Ln(acac)_3 \cdot H_2O \cdot 0.5CH_3COCH_3$ (Ln = Yb–Lu); therefore, acetylacetone was used to obtain the monohydrates of the heavier rare earth chelates. Representative analytical data are given in Table I.

Table I

Analytical Data for Rare Earth Acetylacetonates, $Ln(acac)_3 \cdot nH_2O$

Ln	n	% Ln_2O_3		% H_2O	
		Calcd	Found	Calcd	Found[a]
La	0	37.3	37.1–37.4	0.0	0.02–0.25
Nd	0	38.1	39.9	0.0	1.3
Ho	0	40.9	41.75	0.0	0.25
La	1	35.86	35.98	3.96	4.16
Nd	1	36.62	36.80	3.92	3.73
Gd	1	38.36	38.39	3.81	3.93
Ho	1	39.35	39.61	3.75	3.90
Yb	1	40.35	40.50	3.69	3.92
Y	1	27.93	28.03	4.45	4.85
La[c]	2	34.50	34.47	7.62	7.65
Pr[d]	2	35.83[b]	35.98	7.59	7.58
Nd[e]	2	35.24	35.10	7.54	7.77
Sm	2	36.11	36.08	7.46	6.88
Nd	3	33.95	33.89	10.90	10.70
Gd	3	35.64	35.62	10.62	10.69
Er	3	36.87	36.93	10.41	10.39
Yb	3	37.58	37.50	10.30	9.82

[a] Percentage water was determined by Karl Fischer titrations; the average error is ±0.2%. [b] As Pr_4O_7. [c] Calcd: C, 38.15; H, 5.34. Found: C, 38.14; H, 5.39. [d] Calcd: C, 37.99; H, 5.31. Found: C, 37.57; H, 5.41. [e] Calcd: C, 37.73; H, 5.28. Found: C, 37.80; H, 5.46.

The dihydrates of La, Pr, Nd, and Sm acetylacetonates were prepared by dissolving the trihydrates in 95% ethanol at 50°. The ethanol was immediately partially evaporated by aspiration. The primary purpose of aspiration was to cool the solution quickly. After a large part of the material had precipitated, aspiration was ceased and the solution was filtered. The precipitate was in the form of small plates. Analytical data for the dihydrates are given in Table I.

The anhydrous rare earth acetylacetonates were prepared by vacuum drying the hydrates at room temperature over magnesium perchlorate for several days. The resulting material was hygroscopic and was handled only under a dry atmosphere. Analytical data for these chelates are given in Table I.

Deuteration of the chelates was accomplished by carrying out the Stites, McCarty, and Quill preparation[15] in D_2O. The resulting product, $Ln(acac\text{-}d)_3 \cdot 3D_2O$, was 90% deuterated in the water of hydration and in the 3 position of the acetylacetonate anion. Deuterated chelates were handled in a glove bag, as the D_2O of solvation exchanged rapidly with the atmospheric moisture. $Ln(acac\text{-}d)_3 \cdot D_2O$ was prepared by drying the trisolvated chelate over $Mg(ClO_4)_2$.

Although the recrystallization methods described above usually give the desired hydrate, two other products occasionally precipitate instead of the hydrated tris chelate: A mixed complex containing acetate, $Ln(acac)_2OAc \cdot xH_2O$, and a hydrolyzed chelate, $Ln(acac)_2OH \cdot xH_2O$. The mixed complexes were usually obtained if recrystallization was carried out from acetylacetone which was kept hot for a long period of time. The Ce compound was characterized by elemental analysis. *Anal.* Calcd for $Ce(acac)_2OAc \cdot H_2O$: CeO_2, 41.5; H_2O, 4.3; C, 34.72; H, 4.58; N, 0. Found: CeO_2, 41.4; H_2O, 4.2; C, 35.86; H, 4.45; N, 0. The hydrolyzed chelates occasionally appeared as grainy crystals (square plates under the microscope) during the recrystallization of $Yb(acac)_3 \cdot 3H_2O$ or $Lu(acac)_3 \cdot 3H_2O$ from 60% ethanol. Whenever these crystals were observed, the solution was decanted and the grainy crystals were washed with 95% ethanol. *Anal.* Calcd for $Yb(acac)_2OH \cdot 0.5H_2O$: Yb_2O_3, 49.6; H_2O (as OH + $0.5H_2O$), 6.8; C, 30.2; H, 4.03. Found: Yb_2O_3, 49.5; H_2O, 6.5; C, 30.6; H, 4.61.

The infrared spectra (Table II) of the mixed chelates and the hydrolyzed chelates are fortunately distinctive enough so that their presence can be detected in a given sample. The mixed chelates have a peak at 945 cm^{-1}; peaks in these positions do not occur in the pure tris-chelate hydrates.

Table II

Infrared Spectra of Some Rare Earth Acetylacetonates and Related Compounds[a]

$Nd(acac)_3 \cdot H_2O$	$Nd(acac)_3 \cdot 2H_2O$	$Nd(acac)_3 \cdot 3H_2O$	$Ce(acac)_2\text{-}OAc \cdot H_2O$[b]	$Yb(acac)_2\text{-}OH \cdot 0.5H_2O$[c]
3377 m, br	3275 m, br	3535 sh	3420 m, br	3655 m, sp
3164 m, br	3075 vw	3300 m, br	3310 m, br	3475 w, br
3080 vw	1686 mw, br	3075 vw	3220 m, br	3080 vw
2985 w	1591 st	2990 w	1605 st	1650 sh
2915 w	1521 st	2920 vw	1599 st	1605 st
1643 mw	1438 sh	1675 mw, br	1519 st	1590 sh
1600 st	1394 st	1601 st	1455 m (OAc)	1516 st
1518 st	1359 sh	1523 st	1383 st	1264 m
1437 sh	1264 sh	1449 m	1260 m	1188 m
1397 st	1258 mst	1396 st	1254 m	1021 m
1354 m	1255 mst	1357 m	1186 w	940 sh
1259 mst	1194 w	1272 m	1047 sh (OAc)	925 m
1202 vw	1188 w	1260 mst	1015 m	774 mw
1194 w	1016 mst	1194 w	954 m (OAc)	760 m
1188 w	937 w	1017 mst	916 m	676 mw
1018 m	918 mst	939 sh	764 m	654 mw
935 sh	783 mw	920 mst	755 m	560 vw
918 mst	777 mw	782 mw	674 m (OAc)	534 m
787 w	758 mst	764 m	654 vw	430 w
765 m	656 m	754 m	644 vw (OAc)	405 m
757 m	650 mw, br	670 m, br	610 vw (OAc)	381 sh
655 m	561 vw	658 m		
630 mw, br	526 m	555 w		
558 vw	519 m	524 m		
523 m	407 m	407 m		
420 m	385 m	403 m		
400 m		390 sh		
393 sh				

[a] Abbreviations: w, weak; m, medium; st, strong; v, very; sh, shoulder; sp, sharp; br, broad. [b] Bands followed by (OAc) are found in the spectra of $Ln(OAc)_3$: T. Moeller, V. Galasyn, and J. Xavier, *J. Inorg. Nucl. Chem.*, **15,** 259 (1960). [c] Nujol mull only; bands in the 1300–1500-cm^{-1} region are not given.

Sublimation of the Anhydrous Chelates.—A small sample of the anhydrous chelate was loaded into a vacuum sublimator and the sublimator was heated in an oil bath. Sublimation began to occur for holmium and dysprosium acetylacetonates at 160–170°, but no evidence of sublimation was observed for $La(acac)_3$ at 185°. When sublimation seemed to have ceased (after a relatively small amount of material had sublimed), the oil bath was cooled, the vacuum was shut off, and the sublimator was

---

(15) J. G. Stites, C. N. McCarty, and L. L. Quill, *J. Am. Chem. Soc.*, **70,** 3142 (1948).

placed inside a glove bag. Mineral oil mulls were prepared of the sublimate and the residue, and samples of the residue were taken for gravimetric analysis. The amount of sublimate obtained was insufficient to permit analysis.

Analytical Procedures.—The rare earth content was determined by igniting the chelate to the oxide at 1000° for 1 hr.[16] The water content was determined by Karl Fischer titrations with anhydrous methanol as the solvent. The end point was determined visually. The reagent was standardized with sodium tartrate dihydrate (Baker and Adamson) before each use. Carbon, hydrogen, and nitrogen analyses were performed by Mr. Daryl Sharp and Miss Betty Snider, using an F & M Model 185 C-H-N analyzer at the University of Kentucky.

Glove bags from Instruments for Research and Industry were used to maintain a dry atmosphere over the moisture-sensitive anhydrous chelates. The purging gas was air which had been passed through columns of silica gel and magnesium perchlorate. All analytical operations, including preparation of mulls for infrared spectra and capillaries for X-ray powder patterns, were carried out inside these glove bags.

Infrared Spectra.—Infrared spectra in the 600-4000-cm^{-1} region were recorded on a Beckman IR-8 spectrophotometer under conditions of fairly high resolution (3–4 cm^{-1}). The spectrum was calibrated by using a polystyrene standard. The samples were mulled in Nujol mineral oil, Fluorlube (Fisher LG-160), or hexachlorobutadiene. Infrared spectra in the 350–600-cm^{-1} region were taken on a Perkin-Elmer Model 301 spectrophotometer by Mr. Steven E. Hannum and Mr. Glen G. Possley. The samples were mulled in Nujol and placed between KBr plates or in polyethylene cells.

X-Ray Powder Diffraction Patterns.—X-Ray powder patterns were obtained on a Norelco X-ray diffraction unit. The powdered samples were packed in 0.2-mm glass or 0.3-mm quartz tubes. Photographs were taken on Kodak film in a 114.6-mm Debye camera. The radiation was nickel-filtered Cu Kα. Line positions on the film were determined to the nearest 0.05 mm. Intensities were estimated visually.

Density Determinations.—Densities were determined for solid samples by immersing the coarsely powdered chelates in cyclohexane in calibrated pycnometers at 28.95 ± 0.10°. The chelates were weighed into the pycnometers and covered with cyclohexane. Adsorbed air on the chelates was removed by holding the pycnometers *in vacuo* for a few minutes. The samples were then thermostated at 28.95° and the excess cyclohexane was removed. The volume of the chelate was determined by subtracting the volume of the cyclohexane (determined from its weight and density) from the pycnometer volume. Corrections to vacuum were not made. The hydrated chelates were not significantly soluble in cyclohexane under the conditions employed.

Results and Discussion

Anhydrous Rare Earth Acetylacetonates.—The anhydrous chelates may be obtained by vacuum drying one of the hydrates over $Mg(ClO_4)_2$ for 1 or 2 days.[17] The purity of these compounds usually leaves something to be desired, however (Table I). The anhydrous chelates show somewhat peculiar behavior. The material which is vacuum dried just until most of the water is gone is quite hygroscopic, and analyses and X-ray diffraction patterns show that the anhydrous chelates pick up water from the air (gain weight) to give the dihydrate (for La and Nd) or the monohydrate (for Ho). This anhydrous material is soluble in nonpolar organic solvents such as hexane. However, if the compounds are stored under vacuum for a few days more, the resulting anhydrous material is not very soluble in nonpolar organic solvents and, further, *loses* weight when exposed to air. Such a weight loss has also been observed by Koehler and Bos.[4] The product resulting after weight loss has ceased has a metal analysis roughly corresponding to the compound $Ln(acac)_2OH$. The most probable explanation of the behavior as a function of vacuum-drying time is that the anhydrous chelate slowly polymerizes, probably through the acetylacetonate oxygen atoms in a manner similar to that which occurs in $Ni(acac)_2$.[18]

The infrared spectra of the anhydrous chelates are rather complex and depend on the treatment of the sample, although in over-all form they resemble the spectra of the hydrated chelates. We list some of the ways in which the spectra of the anhydrous and hydrated chelates differ. The hydrogen-bonded O–H stretching region (3100–3500 cm^{-1}) is usually flat or nearly so for all anhydrous chelates, but sharp, weak peaks appear at 3550 and 3600 cm^{-1} (see Figure 1). These peaks are probably due to a hydrolyzed chelate impurity, as similar sharp peaks are observed in a well-characterized, crystalline sample of $Yb(acac)_2OH \cdot 0.5H_2O$ (Table II). The peak at 1640–1680 cm^{-1} in the hydrated chelates is absent in the anhydrous chelates and thus is probably due to the H–O–H bending mode of water. This assignment is supported by isotopic substitution studies (see below). The band near 1260 cm^{-1} in the hydrated chelates occasionally splits into two peaks, one near 1260 and one near 1245 cm^{-1}, during vacuum drying of the heavier rare earth chelates. A weak, broad band at 1090 cm^{-1} was observed once for a sample of $Er(acac)_3 \cdot H_2O$ which had been vacuum dried for 2 days but which still showed fairly strong water bands in the O–H stretching region. The shoulder at 940 cm^{-1} which is present in all of the hydrated che-

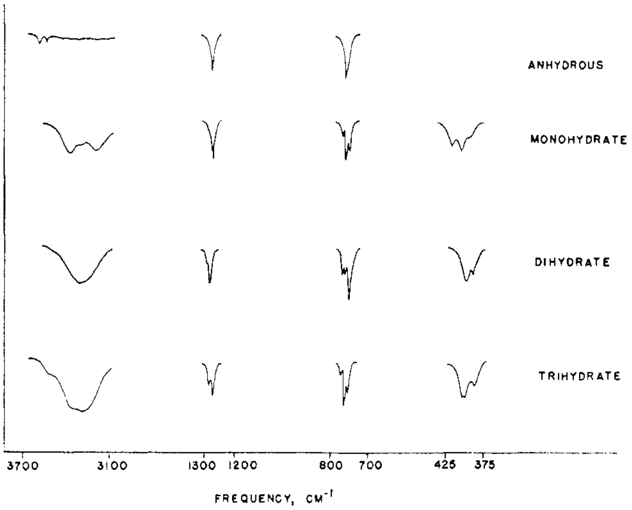

Figure 1.—Infrared spectra of the rare earth acetylacetonates. (The regions in which the spectra are similar are not shown. The spectrum of the anhydrous chelate was not obtained in the 375–425-cm^{-1} region.)

---

[16] M. F. Richardson, W. F. Wagner, and D. E. Sands, *Chemist-Analyst*, **56**, 65 (1967).

[17] This is in contradiction to the work of Pope, *et al.*,[3] which is now widely quoted; in retrospect, it seems likely that Pope failed to realize that the compounds would be very hygroscopic and pick up moisture from the air.

[18] G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, **4**, 456 (1965).

lates seems to be asbent in the anhydrous acetylacetonates. A weak, broad band at 865 cm^{-1} was observed occasionally for some of the vacuum-dried neodymium chelates. A single band appears in the 750–800-cm^{-1} region, instead of the three sharply defined peaks observed in each of the hydrates. La(acac)$_3$·2H$_2$O frequently developed a fairly strong band at 735 cm^{-1} and another at 631 cm^{-1} when vacuum drying took place. Incompletely dried erbium acetylacetonate had a band at 705 cm^{-1} which disappeared on further drying.

It is obvious that there is more to dehydration than the one-step removal of water from the hydrated chelate. The origin of the various bands which appear and then disappear after continued vacuum drying is not clear. It is probable that they are due to some intermediate compound(s) formed during the dehydration, although no evidence was found in the X-ray powder patterns for such a compound. The anhydrous chelates themselves are amorphous. The X-ray powder patterns have two broad halos at *d* spacings of 10 and 3.8 Å.

Pope[3] and others have already shown that the hydrated chelates are not volatile, a conclusion supported by the fact that direct ignition of the chelate to the oxide can be used as an analytical method for determining the oxide content.[16] Sievers and coworkers[19,20] have found that rare earth chelates which do not form stable hydrates are quite volatile. However, under the conditions employed in this work, the anhydrous rare earth acetylacetonates are not appreciably volatile and slowly decompose during attempted sublimation. For example, the residue from sublimation of Dy(acac)$_3$ contained 46.4% Dy$_2$O$_3$ in one instance, but the theoretical oxide content for Dy(acac)$_3$ is 40.5%. Similar results were obtained for other chelates.

The problem remained of establishing the composition of the sublimate, which, because of the small amounts available, had to be done on the basis of the infrared spectra alone. The spectra of the dysprosium and holmium acetylacetonate sublimates in all cases had peaks at 3550 and 3595 cm^{-1}, the same absorptions which were attributed to hydrolyzed impurities in the anhydrous chelates. Except for these peaks, the OH stretching region was flat, and the remainder of the spectrum in the 600–2000-cm^{-1} region resembled the spectrum of Yb(acac)$_2$OH·0.5H$_2$O (Table II). Thus, it seems that the hydrolyzed chelate impurity is somewhat volatile. It may be that some of the anhydrous chelate also sublimes before decomposition becomes extensive, but, if so, its presence was not detected by infrared methods.

Hydrated Acetylacetonates.—The dihydrated acetylacetonates, Ln(acac)$_3$·2H$_2$O, are of interest because their existence as a separate crystalline phase has not been definitely established before. Table III gives the X-ray powder diffraction pattern of Nd(acac)$_3$·2H$_2$O and, for comparison, the powder pattern of a mechanical mixture of Nd(acac)$_3$·3H$_2$O and Nd(acac)$_3$·H$_2$O. The X-ray data, in conjunction with the chemical analyses (Table I), show that a true dihydrated chelate is formed by the rare earth acetylacetonates. The dihydrated La, Pr, and Sm chelates are isomorphous to the Nd chelate.

TABLE III

X-RAY POWDER DIFFRACTION PATTERN OF Nd(acac)$_3$·2H$_2$O

Nd(acac)$_3$·2H$_2$O		Nd(acac)$_3$·H$_2$O + Nd(acac)$_3$·3H$_2$O	
11.12[a] vst	5.18 m	11.73 st	5.54 w
9.59 w	4.74 w	11.01 vst	5.34 w
8.15 st	4.44 w	9.24 m	4.90 m
7.43 m	4.09 w	8.54 mst	4.57 vw
6.95 w	3.88 w	7.75 mst	4.34 vw
6.61 w	3.72 m	7.20 mst	4.18 vw
6.32 vw	3.48 m	6.46 vw	3.60 m
5.85 w		6.14 m	3.49 w
		5.78 w	

[a] d_{hkl} in ångströms.

The dihydrates are stable over Mg(ClO$_4$)$_2$ at atmospheric pressure for at least several weeks, in contrast to the trihydrates, which rapidly lose water to form the monohydrates. The monohydrates are apparently stable over Mg(ClO$_4$)$_2$ at normal pressure and only lose water *in vacuo* over Mg(ClO$_4$)$_2$. The stability of the dihydrates is somewhat surprising, as the coordination spheres of the metal ions in the dihydrates[21] and trihydrates[22] are nearly identical.

Infrared spectra of the three hydrates are similar in many respects (Table II), but a closer examination reveals quite characteristic differences in the spectra as the hydration number changes and also as the crystal form changes in the case of Yb(acac)$_3$·H$_2$O. The most obvious differences are found in four regions: 3000–3700 cm^{-1} (O–H stretching), 1250–1270 cm^{-1} (C–C stretching[23]), 750–800 cm^{-1} (C–H out-of-plane bending[23]), and 380–430 cm^{-1} (complicated M–O stretching mode[12]). Figure 1 shows the spectra of the hydrates in each of these regions; the corresponding bands of the anhydrous compounds are given for comparison.

Other regions in the infrared spectrum are sensitive to changes in the state of solvation of the chelate, but differences are not as obvious as in the regions mentioned above. Bands at 1640–1680 cm^{-1} in the di- and trihydrates are assigned to the H–O–H bending mode of water. These bands are distinguished by a lot of fine structure, and the sharp shoulders which appear on the high-frequency side of the 1600-cm^{-1} peak of the monohydrates are probably due to this mode. The C–H in-plane bending frequency near 1200 cm^{-1}, just like the out-of-plane mode at 750–800 cm^{-1}, is sensitive to changes in solvation. Three weak bands appear in this region for the rare earth acetylacetonate monohydrates, two for the dihydrates, and one for the trihydrates. The relative intensities of the 918- and 1016-cm^{-1} bands also change as the extent of

---

[19] K. J. Eisentraut and R. E. Sievers, *J. Am. Chem. Soc.*, **87**, 5254 (1965).

[20] C. S. Springer, Jr., D. W. Meek, and R. E. Sievers, *Inorg. Chem.*, **6**, 1105 (1967).

[21] T. Phillips, II, D. E. Sands, and W. F. Wagner, *Inorg. Chem.*, **7**, 2295 (1968).

[22] J. A. Cunningham, D. E. Sands, and W. F. Wagner, *ibid.*, **6**, 499, (1967).

[23] K. Nakamoto, P. J. McCarthy, A. Ruby, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1066 (1961).

hydration changes. The 918-cm^{-1} peak is noticeably stronger than the 1016-cm^{-1} peak in the anhydrous compounds and monohydrates but is weaker than the 1016-cm^{-1} peak in the di- and trihydrates.

Changes in the extent of splitting of the aforementioned bands as the hydration number changes are probably consequences of the different molecular geometries of the hydrated chelates. The trisacetylacetonates of several transition metals were examined by Gillard, Silver, and Wood,[24] who showed that the 1:1 ring–metal model used by most authors[12,13,23] is not sufficient to account for the structure of the bands and that the over-all molecular symmetry is a factor in determining the splitting and the relative intensities of the components. A complete normal-coordinate analysis of the rare earth acetylacetonate hydrates has not been undertaken since the molecular structures are only now beginning to be elucidated.[21,22]

It should be noted that the infrared spectra in the 600–4000-cm^{-1} region of the various series of hydrates do not exhibit any changes as the rare earth ion changes, with four exceptions: the O–H stretching frequencies of the monohydrates depend markedly on the atomic number of the rare earth, while the 1200- and 1600-cm^{-1} bands of the monohydrate and the 1250–1270-cm^{-1} peaks of the trihydrate show slight variations as the rare earth ion is changed.

The spectra of the monohydrates (except for Yb(acac)$_3$·H$_2$O; see below) have two fairly strong bands and a shoulder in the hydrogen-bonded O–H stretching region. The positions of the strong bands (ν_1 and ν_2) depend on the rare earth ion in a regular manner. As the atomic number of the rare earth increases, the high-energy band shifts to higher frequencies, while the low-energy band shifts to lower frequencies (Table IV). The position of the shoulder does not seem to change, and the shoulder itself is covered by the high-energy absorption for the first few rare earths.

TABLE IV

O–H STRETCHING FREQUENCIES OF Ln(acac)$_3$·H$_2$O

Ln	ν_1, cm^{-1}	ν_2, cm^{-1}	$\nu_1 - \nu_2$, cm^{-1}	Ln	ν_1, cm^{-1}	ν_2, cm^{-1}	$\nu_1 - \nu_2$, cm^{-1}
La	3373	3179	194	Dy	3413	3126	287
Pr	3376	3169	207	Ho	3416	3124	292
Nd	3377	3164	213	Er	3424	3116	308
Sm	3391	3154	237	Y	3416	3118	298
Gd	3398	3138	260				

The water hydrogens are probably hydrogen bonded to the oxygen atoms in the chelate ring. A similar conclusion was reached by Davis and Fackler[25] in their studies of interactions of transition metal acetylacetonates with water, chloroform, and methanol (although these solvating agents were not coordinated to the metal ion). This assumption of hydrogen-bonding to the chelate oxygen atoms is supported by the crystal structure data for Y(acac)$_3$·3H$_2$O,[22] because the O-(coordinated water)–O(acetylacetonate anion) distances are 2.7–3.2 Å, close enough for hydrogen bonding to occur. Similar O(coordinated water)–O(acetylacetonate) distances are expected for the monohydrates.

The 1500–1650-cm^{-1} region has been of interest to many investigators of metal acetylacetonates.[26–28] We have found that the band near 1600 cm^{-1} for Ln(acac)$_3$·H$_2$O exhibits a slight shift to higher frequencies as the atomic number of the rare earth increases. La(acac)$_3$·H$_2$O absorbs at 1596 cm^{-1}, while Er(acac)$_3$·H$_2$O absorbs at 1605 cm^{-1}. A similar shift of this band was not observed for dihydrates or trihydrates.

Other bands which change slightly as the rare earth ion changes include the sets of bands in the 1250–1270-cm^{-1} region of the trihydrates and in the 1180–1210-cm^{-1} region of the monohydrates. In both cases, the splitting between the components in these bands decreases as the atomic number increases.

Isotopic substitution studies were carried out in order to locate the bands due to coordinated water. Table V summarizes the shifts of the water modes on deuteration. Because the preparation method also resulted in deuteration of the 3 position of the acetylacetonate anion, all modes involving the C–H vibrations were shifted to correspondingly lower wave numbers. The peaks at 3080, 1515, 1180–1210, and 750–800 cm^{-1} in the undeuterated chelates were replaced by bands at 1790, 1490, 1045, and 550–580 cm^{-1} in the deuterated chelates. The shift of the 1515-cm^{-1} peak on deuteration is of great interest. Ogoshi and Nakamoto[29] have carried out a normal-coordinate analysis on acetylacetone-d_2 (CH$_3$COCD$_2$COCH$_3$) and have found that the ν_4 mode is a combination of C═C stretching and C—D deformation vibration. Thus, in Nd(acac-d)$_3$·H$_2$O and Nd(acac-d)$_3$·3H$_2$O, the peak at 1500 cm^{-1} which shifted upon deuteration must be derived from the ν_4 mode of the free ligand. Hence, the band near 1600 cm^{-1} is primarily the C═O stretching frequency, and the band near 1500 cm^{-1} is primarily the C═C stretching frequency. This assignment was also deduced from oxygen-18 isotopic substitution studies,[30] although normal-coordinate analyses on various acetylacetonates[12,13,23] lead to the reverse assignment.

TABLE V

WATER VIBRATIONS IN RARE EARTH ACETYLACETONATES (CM^{-1})

Compound	O–H str	HOH bend	Coord H$_2$O modes
Nd(acac)$_3$·H$_2$O	3370, 3160	1643	630
Nd(acac-d)$_3$·D$_2$O	2505, 2380	. . .	495, 460
Nd(acac)$_3$·3H$_2$O	3650, 3350	1675	670
Nd(acac-d)$_3$·3H$_2$O	2580, 2465, 2400	1220	495

Finally, we note that Yb(acac)$_3$·H$_2$O has an infrared spectrum somewhat different from the spectra of the other monohydrated chelates and it is not isomorphous

---

(24) R. D. Gillard, H. G. Silver, and J. L. Wood, *Spectrochim. Acta*, **20**, 63 (1964).

(25) T. S. Davis and J. P. Fackler, *Inorg. Chem.*, **5**, 242 (1966).

(26) R. West and R. Riley, *J. Inorg. Nucl. Chem.*, **5**, 295 (1958).

(27) R. D. Hancock, A. W. Sacks, R. Thornton, and D. A. Thornton, *Inorg. Nucl. Chem. Letters*, **3**, 51 (1967).

(28) G. A. Domrachev and V. P. Ippolitova, *Zh. Neorgan. Khim.*, **12**, 459 (1967).

(29) H. Ogoshi and K. Nakamoto, *J. Chem. Phys.*, **45**, 3113 (1966).

(30) S. Pinchas, B. L. Silver, and I. Laulicht, *ibid.*, **46**, 1506 (1967).

to them.[3] Only one O–H stretching frequency is found, at 3250 cm^{-1}, instead of the three observed for the other monohydrates. Minor differences are found in the 1180–1210- and 380–430-cm^{-1} regions of the spectrum of $Yb(acac)_3 \cdot H_2O$.

The crystal structure of $Yb(acac)_3 \cdot H_2O$ shows that the ytterbium ion is coordinated to the seven oxygen atoms.[31]

Densities and Molar Volumes of $Ln(acac)_3 \cdot nH_2O$.—The densities of the rare earth acetylacetonates were originally determined by Marsh,[32] who melted the samples and added a little acetylacetone to them to prevent decomposition. Since this procedure is likely to give a mixture of hydrates and/or hydrolyzed compounds (Marsh stated that some of his compounds were basic), we decided to redetermine the densities and molar volumes of the three hydrated forms. The data are given in Table VI. Within experimental error, the molar volumes decrease linearly with increasing atomic number (decreasing ionic size) of the rare earth for all three hydrated series. The exception is $Yb(acac)_3 \cdot H_2O$, which is not isomorphous to the other hydrated chelates.[3] The yttrium chelates occupy a position between the dysprosium and erbium chelates in both the mono- and trihydrated series, in contrast to Marsh's data which placed yttrium much lower in the rare earth series. With the exception of the yttrium chelate, Marsh's densities have values between the values of the densities of the mono- and trihydrates given here.

Table VI

Densities and Molar Volumes of $Ln(acac)_3 \cdot nH_2O$

	$n = 1$		$n = 2$		$n = 3$	
Ln	*d*, g/cm^3	Vol, cm^3/mol	*d*, g/cm^3	Vol, cm^3/mol	*d*, g/cm^3	Vol, cm^3/mol
La	1.606	282.9	1.595	296.0		
Pr	1.636	278.9				
Nd	1.647	278.8	1.634	292.2	1.597	310.3
Sm	1.690	275.4	1.670	289.6	1.631	307.5
Gd	1.722	274.5			1.665	305.4
Dy	1.744	274.0			1.686	304.7
Er	1.769	272.7			1.714	302.5
Yb	1.720	283.9			1.732	302.6
Y	1.477	273.7			1.453	303.0

A Note on the Preparation and Analysis of Rare Earth Acetylacetonates.—In conclusion, attention should again be drawn to the fact that the Stites, McCarty, and Quill method[15] yields crude rare earth acetylacetonate trihydrates for the rare earths Ce–Yb. (The dihydrate is obtained for La, while an adduct, lutetium acetylacetonate–acetylacetonimine, is obtained for Lu.[33]) To summarize, pure trihydrates are obtained for Ce–Yb by recrystallization of the crude product from 50–60% ethanol; the dihydrates of La–Sm are obtained by recrystallization of the trihydrate from cold 95% ethanol; and the monohydrates of La–Lu are prepared by recrystallization of the di- or trihydrates from acetylacetone or by drying the trihydrate briefly over $Mg(ClO_4)_2$. (However, $Yb(acac)_3 \cdot H_2O$ and $Lu(acac)_3 \cdot H_2O$ cannot be prepared by drying over a desiccant, as the trihydrates hydrolyze.[3]) The equilibrium vapor pressure of water above the trihydrates is on the order of a few millimeters,[3] and so the trihydrates are stable in the normal laboratory atmosphere. With this in mind, it would seem that the magnetic susceptibility study made by Fritz, Field, and Grenthe[34] was carried out on the trihydrates and not the monohydrates. Further, the Eu chelate examined by Charles and Ohlmann[35] was probably the trihydrate rather than the dihydrate. Other examples similar to these show that more care needs to be taken in the characterization of rare earth acetylacetonate hydrates (and other compounds as well). Carbon, hydrogen, and metal analyses are relatively insensitive to the amount of water present in chelates. Presently, the best method for determining water is by Karl Fischer titration, which directly and unequivocally gives the amount of water present. Nearly as good, but much more time consuming, is the method used by Pope[3] of determining the vapor pressure of water as a function of the composition of the chelate.

With regard to characterization techniques, it may be mentioned that the method of molecular weights is often subject to error. It is said[36] that rare earth acetylacetonates are dimeric in benzene and other relatively nonpolar solvents but monomeric in acetone. Pope[3] has found, however, that the cryoscopic molecular weights in benzene depend very strongly on the treatment of the sample (*e.g.*, whether the solution is heated to effect dissolution and for how long). Such behavior was attributed to decomposition, and it was shown that the distillate from benzene solutions of $La(acac)_3 \cdot H_2O$ and $La(acac)_3 \cdot 3H_2O$ contained acetylacetone.[3]

Acknowledgments.—We are indebted to Dr. K. J. Eisentraut, Dr. R. E. Sievers, and Mr. H. Francis for helpful discussions and suggestions regarding the isotopic substitution studies. We also thank the U. S. Atomic Energy Commission for partial support of this work (Contract No. AT(40-1)-2124) and the National Science Foundation for a Cooperative Graduate Fellowship to M. F. R., 1962–1966.

---

[31] J. A. Cunningham, D. E. Sands, M. F. Richardson, and W. F. Wagner, *Inorg. Chem.*, in press.

[32] J. K. Marsh, *J. Chem. Soc.*, 1084 (1947).

[33] M. F. Richardson, W. F. Wagner, and D. E. Sands, *J. Inorg. Nucl. Chem.*, in press.

[34] J. J. Fritz, P. E. Field, and I. Grenthe, *J. Phys. Chem.*, **65**, 2070 (1961).

[35] R. G. Charles and R. C. Ohlmann, *J. Inorg. Nucl. Chem.*, **27**, 255 (1965).

[36] J. P. Fackler, *Progr. Inorg. Chem.*, **7**, 389 (1966), and references cited therein.