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The Infrared Spectra and Some Properties of Tris-(acetylacetonato) Lanthanide(III) Complexes

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The infrared spectra of tris-(acetylacetonato) complexes of praseodymium(III), neodymium(III), europium(III), gadolinium (III), dysprosium(III), and erbium(III) have been measured in the range between 4000 and 100 cm^{-1} in order to obtain information about the nature of lanthanide metal-oxygen bond; some properties of these complexes were studied, also. The calculated frequencies and assignments were used to elucidate the complex spectra and to show the relations between the calculated force constants and some physicochemical properties. Although the molecules of each complex were 1 : 3 complexes, the calculation of the vibrational frequencies was made by using a simplified model of the 1 : 1 complex (C_{2v}), because it may be supposed that this tris-(acetylacetonato) complex does not always have a regular octahedral symmetry in spite of the composition of Ln(acac)$_3$. The calculated frequencies were in good agreement with the observed ones; the lanthanide metal-oxygen stretching vibrations were found at 420—432 cm^{-1} (A_1-ν_5) and 304—322 cm^{-1} (B_1-ν_{14}). The lanthanide metal-oxygen stretching force constant increases with an increase in the atomic number, while the corresponding C=O stretching frequency (A_1-ν_1) decreases in the same order. For example, the values of K(Pr–O) and K(Er–O) are 2.10 and 2.29 md/Å respectively. As the result of the lanthanide contraction, the force constant of the lanthanide metal-oxygen bond increases with a decrease in the M–O bond length, thus increasing the stability constant, log β, and slightly increasing the electronegativity.

The preparations and infrared spectra of acetylacetonate complexes of various metal ions,[1–13] especially of the first transition metal ions, have been studied by many investigators. In this paper, some systematic studies of tris-(acetylacetonato) lanthanide(III) complexes, Ln(acac)$_3$, that is, their preparations, the measurements of the infrared spectra in the 4000—100 cm^{-1} region, the calculation of the stretching force constants of the metal-oxygen bonds of these complexes, and some physico-chemical properties, will be presented. Furthermore, the relations of the overall stability constants, the electronegativities of lanthanide metal ions, and the M–O bond distances to the band shifts and the force constants of metal-oxygen bonds will be discussed.

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TABLE 1. ANALYTICAL DATA AND DECOMPOSING POINTS

Complexes	Analytical data (%)						Decomposing point, °C
	C_{calcd}	C_{obsd}	H_{calcd}	H_{obsd}	M_{calcd}	M_{obsd}	
$Pr(acac)_3$	40.85	38.02	5.49	5.12	31.96	34.82	133
$Nd(acac)_3$	40.54	39.15	5.40	5.58	32.48	32.19	139
$Eu(acac)_3$	40.11	39.27	5.35	5.00	33.63	34.04	126
$Gd(acac)_3$	39.44	39.40	5.26	4.90	34.40	33.93	135
$Dy(acac)_3$	38.95	37.79	5.23	4.89	35.13	38.08	135
$Er(acac)_3$	38.55	37.89	5.18	4.34	35.80	36.19	178

Experiments

Preparation of Complexes. Tris-(acetylacetonato) lanthanide(III) complexes were prepared by the method reported in the literature.[12,13] About 0.5 g of each lanthanide oxide was converted into chloride with concentrated hydrochloric acid. After the excess hydrochloric acid had been removed completely, lanthanide chloride obtained was dissolved in 14 m*l* of the distilled water, to which a dioxane solution, containing 4 m*l* of acetylacetone (*i. e.*, 4 times the necessary volume), was then added gradually by stirring it vigorously. The solution, adjusted to pH 6.5 with a 6 N NH_4OH solution, was left standing for 20 to 24 hr in order to complete the reaction. The precipitated compound was then filtered with 4G-glass filter and washed with a small amount of ethyl alcohol.

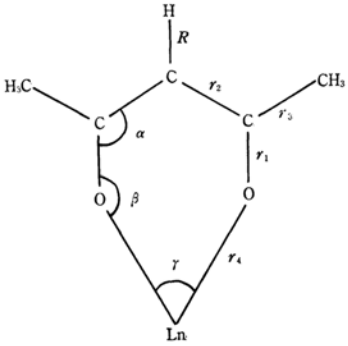
The compound thus obtained was recrystallized by using 50—100 m*l* of chloroform. The pure crystal of each tris-(acetylacetonato) lanthanide(III) complex had a needle-like form and was the same color as each lanthanide oxide.

The value of the molecular weight of the samarium complex, which was measured by the freezing point depression method, was found to be 445, coinciding with the calculated value of 448 for the 1 : 3 complex. The lanthanide metal ions obtained from the decomposed complexes were determined by using the chelating reagent, EDTA. The analytical data and the values of the decomposing points of the complexes prepared are shown in Table 1.

Infrared Spectra and X-Ray Measurements. The infrared spectra of tris-(acetylacetonato) lanthanide(III) complexes were measured with a Hitachi Infrared Grating Spectrophotometer, Model 125, by the KBr disk method and the Nujol mull method in the 4000—400 cm^{-1} region and with a Hitachi Far Infrared Spectrophotometer, Type FIS-1, by the polyethylene paraffin method in the 400—100 cm^{-1} region. There was no difference between the infrared spectra measured by the KBr disk and Nujol mull methods. A Rigaku Denki X-ray Diffraction Apparatus, Model D-3F, was used to obtain the spectra of some $Ln(acac)_3$ complexes; all the spectra were analogous, indicating only small shifts in the diffraction angles. Therefore, the crystal structure of each tris-(acetylacetonato) lanthanide(III) complex may be considered to be same as the others.

Method of Calculation

A normal coordinate treatment was carried out by simplifying the system by means of some reasonable assumptions. Although the molecule of the tris-(acetylacetonato) lanthanide(III) complex was the 1 : 3 complex, the 1 : 1 complex with a C_{2v} symmetry has been used in order to simplify the calculation of the force constant. Figure 1 illustrates the molecular model of the 1 : 1 complex schematically, where the values of r_1, r_2, r_3, R, and α were assumed to be equal to those of $Fe(acac)_3$, and where r_4 was assumed to be equal to the sum of the ionic radius of the lanthanide ion[14] and that of the oxygen ion. All the bonds lie on a plane.



$R=1.08\text{Å}$ $r_1=1.28$
$r_2=1.39$ $r_2=1.53$
$r_4=1.56-1.43$ $\alpha=120°$
$\beta=130-121°$ $\gamma=99-118°$

Fig. 1. Model of the 1:1 complex.

The molecular parameters satisfy strictly all the conditions for formation of a planar, six-membered ring.

The potential energy, V, in Urey-Bradly potential field,[15-18] where the repulsive force between nonbonded atoms was considered, was expressed as the following equation (1):

$$\begin{aligned} V = &\sum_i[K_i'r_{i0}(\varDelta r_i)+1/2\,K_i(\varDelta r_i)^2] \\ &+\sum_i[H_i'r_{i\alpha}{}^2(\varDelta\alpha_i)+1/2\,H_ir_{i\alpha}{}^2(\varDelta\alpha_i)^2] \\ &+\sum_i[F_i'q_{i0}(\varDelta q_i)+1/2\,F_i(\varDelta q_i)^2] \end{aligned} \tag{1}$$

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TABLE 2. FORCE CONSTANTS OF TRIS-(ACETYLACETONATO) LANTHANIDE(III) COMPLEXES IN 10^5 dyn/cm

Stretching	Bending	Repulsive
$K_1=K(\text{C-O})=7.20^a$	$H_1=H(\Delta\alpha_{12})=0.2^c$	$F_1=F(\text{C-O})=0.50^a$
$K_2=K(\text{C-C})=5.46^b$	$H_2=G(\Delta\alpha_{23})=0.25^c$	$F_2=F(\text{C-CH}_3)=0.40$
$K_3=K(\text{C-CH}_3)=3.30^a$	$H_3=H(\Delta\alpha_{31})=0.31^a$	$F_3=F(\text{O-CH}_3)=0.50^a$
$K_4=K(\text{M-O})=2.10_0$	$H_\beta=H(\Delta\beta)=0.05$	$F_4=F(\text{C-M})=0.05$
-2.29_1	$H_\gamma=H(\Delta\gamma)=0.05$	$F_5=F(\text{O-O})=0.05$
	$H_\delta=H(\Delta\delta)=0.33^b$	$F_6=F(\text{C-C})=0.37^b$
	$H_{\delta 1}=H(\Delta\delta_1)=0.20^b$	$F_7=F(\text{C-H})=0.54^b$

a: acetic acid; b: benzene; c: mean values of a and b

where the symbols (K_i', K_i), (H_i', H_i) and (F_i', F_i) represent stretching, bending, and repulsive force constants respectively. The symbols r_{i0}, $r_{i\alpha}$ and q_{i0} denote the bond lengths of directly-bonded and non-bonded atoms at equilibrium positions. Δr_i, $\Delta\alpha_i$ and Δq_i are the changes in bond lengths, bond angles, and the bond distances between non-bonded atoms respectively.

In Eq. (1), K_i' and H_i' can be replaced by the term containing F_i' under the equilibrium condition.[15-17] If repulsive energy between the non-bonded atoms is assumed to be proportional to $1/r^9$, the F' term is replaced by the $-1/10\,F$ term. Finally, the K_i', H_i' and F_i' quantities in Eq. (1) vanished. The force constants concerning the C-C and C-O bonds used in this calculation were taken from those of benzene and acetate ions,[2] since Mecke and Funck concluded that the stretching frequencies of C-C and C-O bonds in the enol-form of acetylacetone were similar to those in benzene and acetic acid anions.[19] Table 2 shows the force constants used in the calculation.

Since the vibrational modes of a molecule with C_{2v} symmetry were classified into in-plane ($8A_1$ and $7B_1$) and out-of-plane ($2A_2$ and $4B_2$) vibrations, if we take the CH_3 group as a single unit, only the former fifteen in-plane vibrations, which were infrared-active, were calculated by using an ALGOL-type electronic computer.

Results and Discussion

The calculated and observed frequencies for each complex are shown in Table 3 except for the CH stretching frequency (A_1); the former were in good agreement with the latter. The slight difference of frequencies would be due to the molecular coupling between three coordinated acetylacetone molecules, which were entirely neglected in this calculation, because of the fairly small interactions between ligands, except for the vibrations due to the displacements of the central metal ion.

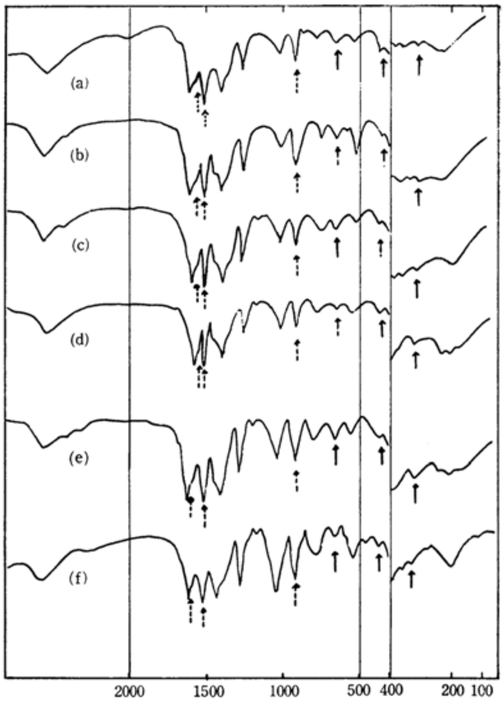

Fig. 2. Infrared spectra of Ln(acac)$_3$ complexes.
a. Pr(acac)$_3$, b. Nd(acac)$_3$, c. Eu(acac)$_3$
d. Gd(acac)$_3$, e. Dy(acac)$_3$, f. Er(acac)$_3$

Figure 2 shows the infrared spectra of tris-(acetylacetonato) lanthanide(III) complexes. The bands between 1600 and 1400 cm^{-1} and between 750 and 300 cm^{-1} are sensitive to the nature of lanthanide(III). The bands related to the C=O stretching mode were observed at 1558—1555 cm^{-1} (A_1-ν_1), 1511—1510 cm^{-1} (B_1-ν_9), and 914—917 cm^{-1} (A_1-ν_3). The ν_1 frequency decreased with an increase in the atomic number; that is, shifted to a lower frequency. The pure lanthanide metal-oxygen stretching bands were found at 420—432 cm^{-1} (A_1-ν_5) and 304—322 cm^{-1} (B_1-ν_{14}), while the coupled vibrations involving metal-oxygen stretching and vibrational modes other than C=O stretching were found at 650—651 cm^{-1} (A_1-ν_4) and 611—623 cm^{-1} (B_1-ν_{12}). The bands at 304—322 cm^{-1} were too

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TABLE 3. COMPARISON OF THE CALCULATED AND THE OBSERVED FREQUENCIES IN TRIS-(ACETYLACETONATO) LANTHANIDE(III) COMPLEXES (cm^{-1})

$Pr(acac)_3$		$Nd(acac)_3$		$Eu(acac)_3$		$Gd(acac)_3$		$Dy(acac)_3$		$Er(acac)_3$		Modes
calc'd	obs'd	calc'd	obs'd	calc'd	obs'd	calc'd	obs'd	calc'd	obs'd	calc'd	obs'd	
1596	1600 vs	1595	1567 vs	1596	1601 vs	1597	1602 vs	1598	1600 vs	1597	1599 vs	B_1-ν_8
1547	1558 sh	1558	1557 sh	1531	1557 sh	1514	1553 sh	1557	1557 sh	1559	1555 sh	A_1-ν_1
1500	1511 s	1492	1510 vs	1486	1510 vs	1492	1511 vs	1495	1510 vs	1497	1510 vs	B_1-ν_9
—	1386 s	—	1385 vs	—	1385 vs	—	1390 vs	—	1385 vs	—	1382 vs	a
—	1353 sh	—	1351 sh	—	1354 sh	—	1355 sh	—	1354 sh	—	1355 sh	b
1250	1255 m	1240	1254 s	1255	1255 s	1267	1256 s	1246	1258 s	1243	1256 s	A_1-ν_2
1223	1188 vw	1228	1184 vw	1236	1184 vw	1227	1197 vw	1229	1186 vw	1227	1182 vw	B_1-ν_{10}
—	1012 m	—	1011 m	—	1011 m	—	1011 m	—	1012 m	—	1011 s	c
903	914 m	912	915 s	917	914 m	912	917 m	912	916 m	905	917 s	A_1-ν_3
882	844 vw	889	840 vw	885	845 vw	881	848 vw	886	860 vw	874	860 vw	B_1-ν_{11}
—	764 w	—	763 w	—	761 w	—	760 w	—	761 m	—	760 m	d
638	650 sh	652	650 w	649	650 w	631	650 w	652	651 w	652	650 w	A_1-ν_4
614	617 w	611	623 vw	610	615 vw	620	629 vw	621	610 vw	620	611 vw	B_1-ν_{12}
—	527 w	—	526 w	—	527 w	—	529 w	—	531 w	—	531 m	e
412	420 sh	426	420 sh	422	424 sh	424	428 sh	426	428 sh	426	432 sh	A_1-ν_5
388	388 vw	393	390 vw	347	394 vw	368	397 w	402	400 w	386	400 w	B_1-ν_{13}
—	365 vw	—	365 vw	—	373 w	—	380 vw	—	384 vw	—	341 vw	f
315	304 br	276	305 br	291	317 br	291	320 br	267	320 w	282	333 br	B_1-ν_{14}
244	243 sh	260	235 sh	260	236 sh	260	236 vw	237	243 vw	260	242 sh	A_1-ν_6
206	214 br	210	328 w	203	203 br	210	200 br	210	208 br	200	206 w	A_1-ν_7

A_1-ν_1	CO str.	B_1-ν_8	CC str.
A_1-ν_2	CC str.+CCH_3 str.	B_1-ν_9	CO str.+CH bend.
A_1-ν_3	CCH_3 str.+CO str.	B_1-ν_{10}	CH bend.
A_1-ν_4	ring def.+MO str.	B_1-ν_{11}	CCH_3 str.
A_1-ν_5	MO str.	B_1-ν_{12}	CCH_3 bend.+MO str.
A_1-ν_6	CCH_3 bend.	B_1-ν_{13}	ring def.
A_1-ν_7	ring def.	B_1-ν_{14}	MO str.
a	CH_3 deg. def.	d	CH out-of-plane bend.
b	CH_3 sym. def.	e	$C\text{-}C\Big\langle{}^{C}_{O}$ out-of-plane bend.
c	CH_3 rock.	f	out-of-plane. displacement of central metal ion perpendicular to the plane.

TABLE 4. RELATIONS BETWEEN M-O BOND LENGTHS,[14] OVERALL STABILITY CONSTANTS[20-22] AND ELECTRONEGATIVITIES[23,24] OF LANTHANIDES(III)

Complexes	K(M-O) md/Å	(M-O) cm^{-1}		M-O bond length, Å	Stability constant log β	Electronegativity of Ln(III)
		$\nu_5(A_1)$	$\nu_{14}(B_1)$			
$Pr(acac)_3$	2.10_0	420	304	1.56	12.40	−1.1
$Nd(acac)_3$	2.12_6	420	305	1.54	12.60	−1.2
$Eu(acac)_3$	2.18_4	424	317	1.50	13.04	−1.1
$Gd(acac)_3$	2.20_2	428	320	1.49	13.79	−1.2
$Dy(acac)_3$	2.24_4	428	320	1.46	14.04	−1.2
$Er(acac)_3$	2.29_1	432	333	1.43	14.05	−1.2

Note: The values of K(M-O) for lanthanides(III) are supposed to be slightly larger than the true absolute values, because of the use of the 1:1 model (C_{2v}) for their calculations, But it is significant that these values are compared relatively with other values such as ν(M-O), r(M-O) and log β *etc.*

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broad to be analyzed precisely. It was observed that the lanthanide metal-oxygen stretching bands (A_1-ν_5) shifted to higher frequencies according to the lanthanide contraction, in the order from praseodymium(III) to erbium(III) complexes. The force constant of the metal-oxygen stretching bond increases with a decrease in the M–O bond length, thus increasing the stability constant, $\log\beta$, of complex[20-22] and slightly increasing the electronegativity. It may be seen in Table 4 that the lanthanide metal-oxygen stretching force constant increases with an increase in the atomic number. Although the lanthanide metal(III)-oxygen bond is considered to be ionic, it may be supposed that the increase in M–O stretching frequencies is due to the slightly increasing covalency in these acetylacetonate complexes by π bonding and to the increasing mass of the central metal ion.

As is shown in Table 4, the value of K(M–O) was proportional to the reciprocal value of the M–O bond length r(M–O) within the limits of the errors of frequencies. Gordy[25] introduced an empirical formula (2) of the force constant, K, expressed in terms of electronegativity, χ, and bond length, r;

$$K = \alpha N(\chi_A \chi_B / r^2)^{3/4} + b \tag{2}$$

where a and b were constans and N, the bond order. The value of the force constant, K (M–O), obtained coincided with the value calculated from Gordy's formula.

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