

I.R. INVESTIGATION OF SEVERAL RARE-EARTH ACETATES AND FORMATES*

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Abstract—The mid i.r. and the far i.r. spectra of several anhydrous rare-earth acetates and formates were measured. Deuteration studies aided in making the assignments for the COO stretching and the CH deformation vibrations in these compounds. Low frequency vibrations located in the region of 100–300 cm^{-1} lend support to a structure for these compounds possessing bidentate acetate and formate groups.

INTRODUCTION

SEVERAL i.r. investigations have been made on rare-earth acetates and formates [1–5]. A careful examination of these efforts illustrates that the following uncertainties concerning these compounds still exist: (1) confusion and disagreement concerning the assignment of the COO stretching and the CH deformation vibrations; deuteration studies to clarify this situation have not been undertaken; (2) doubt as to the structure possessed by these compounds; (3) lack of i.r. measurements lower than 600 cm^{-1} . To attempt to fill in these gaps, deuteration and low-frequency studies were undertaken. This paper reports on the results obtained from these investigations.

EXPERIMENTAL

Preparation of compounds

The anhydrous rare-earth acetates were prepared from the rare-earth oxides using the method of Witt and Onstott [6]. The procedure involves the dissolution of the oxides in 50 per cent acetic acid and subsequent evaporation to dryness. After recrystallization, the acetates were converted to the anhydrous salts by heating in vacuum at 150°C. The deuterated solids were prepared in a similar manner, using deuterated acetic acid (CD_3COOD).

The anhydrous formates were prepared by dissolving the rare-earth nitrate or chloride in formic acid, according to the procedure of Sahoo *et al.* [7]. The insoluble rare-earth formates precipitated and were filtered and dried at 120°C. The deuterated formates were prepared similarly, using deuterated formic acid (DCOOD).

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Materials used

The oxides were obtained from American Potash and Chem. Corp., West Chicago, Illinois. The rare-earth nitrates and chlorides were prepared at Argonne National Laboratory. CD_3COOD and DCOOD were obtained from Stohler Isotope Chemicals, Rutherford, New Jersey.

Spectroscopic studies

The i.r. spectra of the acetates and formates were recorded from 4000 to 70 cm^{-1} . The spectra from 4000 to 650 cm^{-1} region were measured with a Beckman Ir-12 using KBr pellets. The spectra from 650 to 70 cm^{-1} were made with a Beckman IR-11 using polyethylene pellets. Sampling and all grinding for the deuterated samples was done in a nitrogen atmosphere glove box. Low-frequency pressure studies were made using a diamond anvil cell with a Beckman IR-11 and a Perkin-Elmer Model 301 [8]. The Raman spectra were made on the polycrystalline solids using a Cary Model No. 81 Raman spectrophotometer and a helium-neon laser, which lased at 6328 Å at a power of 50 MW. However, results on the powders were not too satisfactory and are not reported in this paper.

Analytical results

Microanalytical methods were employed to determine the carbon and hydrogen analysis. Analyses for the rare-earth cations were made using EDTA titration. Table 1 records the analytical results for the compounds prepared in this study.

Table 1. Analytical results for several rare-earth acetates and formates

	Calc.			Experimental		
	H %	C %	Metal %	H %	C %	Metal %
Y(OAc)_3	3.40	27.08	33.41	3.40	26.96	33.66
Eu(OAc)_3	2.75	21.89	46.17	2.82	21.26	46.30
Tb(OAc)_3	2.69	21.44	47.29	2.68	21.49	47.10
Er(OAc)_3	2.63	20.92	48.56	2.58	21.09	48.55
La(HCOO)_3	0.97	11.63	56.19	1.49	11.72	55.89
Nd(HCOO)_3	1.08	12.90	51.64	1.10	12.83	50.40

RESULTS AND DISCUSSION

Some disagreement exists concerning the assignments made for the COO stretching and CH deformation vibrations in rare-earth acetates and formates. Table 2 tabulates the previous assignments. On the basis of deuteration studies new assignments have been made and these are listed in Table 3. For the acetates, major effects are observed for the vibrations at ~ 2950 , ~ 1540 , ~ 1430 , ~ 1018 and $\sim 670 \text{ cm}^{-1}$ upon isotopic replacements of hydrogen with deuterium. These shifts to ~ 2250 , ~ 1088 , ~ 1030 , ~ 848 and $\sim 530 \text{ cm}^{-1}$. For the formates, the absorption bands shifting to lower frequencies were those at ~ 2856 and $\sim 1420 \text{ cm}^{-1}$, which moved to ~ 2200 and 1056 cm^{-1} respectively. Figures 1 and 2 show the spectra of the deuterated and non-deuterated rare-earth acetate and formate salts in the mid-i.r. region.

The investigation of the low-frequency region for these compounds was the first of its kind. Table 4 lists the absorptions occurring in the 100–300 cm^{-1} . The strong absorptions occurring in the 217–315 cm^{-1} in the acetates and at 167–282 cm^{-1} in the formates are assigned to metal-oxygen stretching modes. For com-

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Table 2. Previous assignments of mid i.r. absorptions in rare-earth acetates and formates*

Acetate absorption band (range)	Assignments		
	Moeller[1]	Patel[3], Nakamoto[4]	Grigor'ev [2]
1545-1565	$\nu_{\text{asy}}\text{COO}$	$\nu_{\text{asy}}\text{COO}$	$\nu_{\text{asy}}\text{COO}$
1440-1462	$\nu_{\text{sym}}\text{COO}$	$\delta_{\text{asy}}\text{CH}_3$	$\nu_{\text{sym}}\text{COO}$
1425-1430		$\nu_{\text{sym}}\text{COO}$	$\nu_{\text{sym}}\text{COO}$
1375-1377}	$\nu_{\text{C}-\text{C}}$	$\delta_{\text{sym}}\text{CH}_3$	
1338-1345}	$\rho_{\text{r}}\text{COO}$		
1050-1057}	$\rho_{\text{r}}\text{CH}_3$	$\rho_{\text{r}}\text{CH}_3$	
1010-1020}			
935-948	ν_{CC}	ν_{CC}	ν_{CC}
660-670	δ_{COO}	δ_{COO} or π_{COO}	π_{COO}
606-620		π_{CH}	
Formate			
absorption band (range)	Assignments		
	Nakamoto[4]	Saralidze <i>et al.</i> [5]	
1585-1600	$\nu_{\text{asy}}\text{COO}$	$\nu_{\text{asy}}\text{COO}$	
1400-1440	$\rho_{\text{r}}\text{COO}$	π_{CH} in-plane	
	δ_{CH}		
1360	$\nu_{\text{sym}}\text{COO}$	$\nu_{\text{sym}}\text{COO}$	
1070	π_{COO} or π_{CH}	π_{CH}	
780	δ_{COO}	π_{COO}	

*Note - Nakamoto's results based on sodium salts.

parison the absorptions for the sodium salts are included. It may be observed that the heavier rare-earth acetates and formates manifest absorptions at higher frequencies than the absorptions of the sodium salts, which have been assigned as ionic lattice modes. This is similar to the observations made in the low-frequency region for the anhydrous rare-earth carbonates [9] and nitrates [10]. The trend in the position of the strong vibrations appears to shift with increasing mass of the rare-earths (e.g., $\text{Eu} < \text{Tb} < \text{Er}$ in the acetates and $\text{La} < \text{Nd}$ in the formates) as expected for a metal-oxygen bond of high covalent character. These absorptions were found to be unaffected upon application of high external pressures and thus, demonstrated non-lattice like behavior. As a consequence, these absorptions are assigned to the metal-oxygen stretching vibrations. At least two such absorptions occur for each salt as would be expected for ν metal-oxygen vibrations in a chelated-type structure. Contributing evidence comes from the separation of $\nu_{\text{asy}}\text{COO}$ and $\nu_{\text{sym}}\text{COO}$ vibrations. It would be expected that this

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Table 3. Assignments for $\text{Eu}(\text{OOCCH}_3)_3$, $\text{Eu}(\text{OOC}(\text{CD}_3)_3$ and $\text{La}(\text{OOCH})_3$, $\text{La}(\text{OOC}(\text{CD}_3)_3$ based on deuteration studies

$\text{Eu}(\text{OOCCH}_3)_3$	$\text{Eu}(\text{OOC}(\text{CD}_3)_3$	Assignment	$\text{La}(\text{OOCH})_3$	$\text{La}(\text{OOC}(\text{CD}_3)_3$	Assignment
2980(w)		$\nu(\text{CH})$	2856(w)		$\nu(\text{CH})$
2930(w)					
	2265(w)	$\nu(\text{CD})$		2208(w)	$\nu(\text{CD})$
	2230(w)				
1542(vs)	1542(vs)	$\delta(\text{COO})$ asym.	1605(vs)	1585(vs)}	$\nu(\text{COO})$ asym.
1430(vs)		$\delta(\text{CH}_3)$ asym.	1580(vs)	1550(vs)}	
1410(sh)	1410(vs)	$\delta(\text{COO})$ sym.	1428(vs)	}	$\delta(\text{CH})$
			1405(vs)		
1340(m)		$\delta(\text{CH}_3)$ sym.	1358(s)	1334(s)}	$\nu(\text{COO})$ sym.
1230(w)				1328(s)}	
1050(w)	1088(w)	$\delta(\text{CD}_3)$ asym.	779(s)	1056(m)	$\nu(\text{CD})$
				770(m)	$\delta(\text{OCO})$
	1030(w)	$\delta(\text{CD}_3)$ sym.			
1018(m)		$\rho_r\text{CH}_3$			
950(w)			262(s)	280(s, v. br)}	ν_{MO}
942(w)	930(s)	$\nu_{\text{C-C}}$	238(vs)		
	900(m)				
	848(s)	$\rho_r\text{CD}_3$	167(vs)		
			150(m)		
680(m)		π_{CH}	121(s)		
668(m)					
644(sh)	640(s)}	δ_{OCO}			
614(m)	620(s)}				
	530(m)	π_{CD}			
501(w)					
473(vw)	450(w), 430(w)				
266(s)	262(vs, v. br)}	$\nu_{\text{M-O}}$			
220(m, sh)					
205(vvw)	205(vvw)				
185(m)					
154(m)					

Table 4. Low-frequency absorptions for several rare-earth acetates and formates

$\text{Y}(\text{OAc})_3$	$\text{Eu}(\text{OAc})_3$	$\text{Tb}(\text{OAc})_3$	$\text{Er}(\text{OAc})_3$	$\text{Na}(\text{OAc})$	$\text{La}(\text{OOCH})_3$	$\text{Nd}(\text{OOCH})_3$	$\text{Na}(\text{OOCH})$
315(vs)			292(sh)		262(s)	282(vs)	
260(m)	266(s)	276(s)	280(s)		238(vs)	240(vs)	
		258(w, sh)	260(w, sh)			183(w, sh)	
217(m)	220(sh)	225(vw)	229(w)		167(s)		195(v. br)
	205(vvw)	205(vvw)		200(v. br)	150(m)	163(vs)	
165(sh)	185(m)	192(m)	194(m)				
156(m)	154(m)	160(m)	166(m)		121(m)	133(m)	
123(w)		133(w)	138(m)				
116(vw)		110(vw)					

Abbreviations: s = strong; m = medium; w = weak; v = very; br = broad; sh = shoulder.

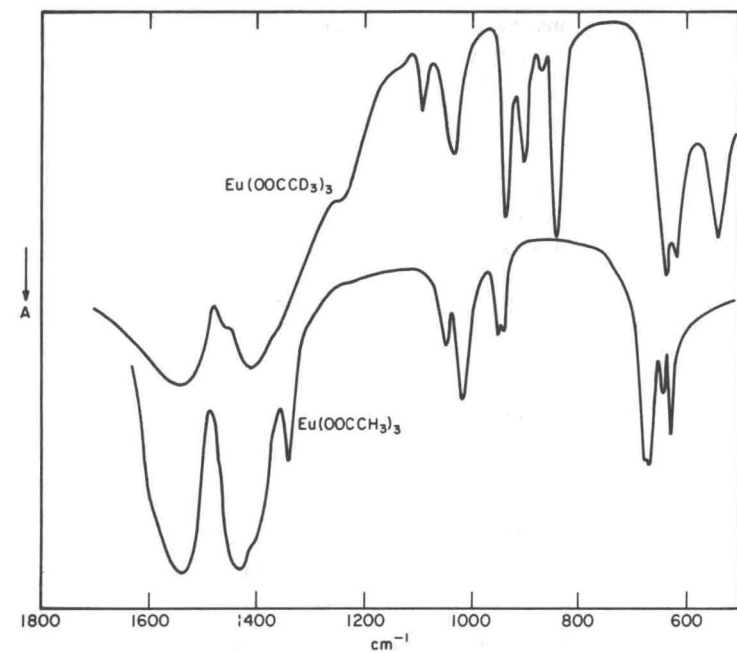


Fig. 1. Spectra of $\text{Eu}(\text{OOCCH}_3)_3$ and $\text{Eu}(\text{OOCCD}_3)_3$ from 1800 to 500 cm^{-1} .

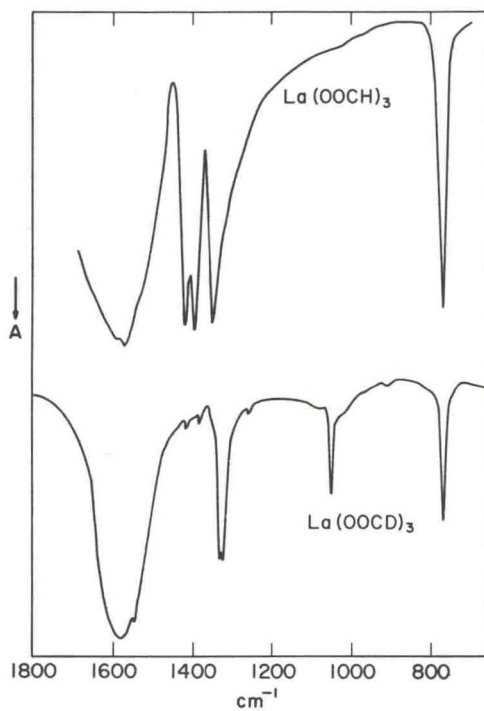
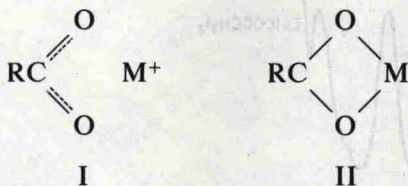


Fig. 2. Spectra of $\text{La}(\text{OOCH}_3)_3$ and $\text{La}(\text{OOCD}_3)_3$ from 1800 to 700 cm^{-1} .

Table 5. $\Delta\nu$ of symmetrical and asymmetrical carbonyl peaks

	Rare earth present (cm^{-1})	Sodium[4] (cm^{-1})
Acetate	132	153
Formate	234	201

difference should be similar for the ionic structure (I) and the covalent chelate structure (II):



where the two CO vibrations for each structure are not expected to be much different from each other. This is noted in the experimental results which are shown in Table 5.

