

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

J. R. FERRARO and M. BECKER†

Argonne National Laboratory, Argonne, Ill. 60439

(Received 28 October 1969)

**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  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$ . 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 ( $\text{CD}_3\text{COOD}$ ).

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 ( $\text{DCOOD}$ ).

\*Based on work performed under the auspices of the U.S. Atomic Energy Commission.

†Present address: Marquette University, Chemistry Department, Milwaukee, Wisconsin. Senior Undergraduate Thesis Program, 1968–69.

1. T. Moeller, V. Galasyn and J. Xavier, *J. inorg. nucl. Chem.* **15**, 259 (1960).
2. A. I. Grigor'ev and V. N. Maksinov, *Zh. neorg. Khim.* **9**, 19060 (1964).
3. K. C. Patil, G. V. Chandraskhan, M. V. George and C. N. R. Rao, *Can. J. Chem.* **46**, 257 (1968).
4. K. Nakamoto, *IR of Inorganic and Coordination Compounds*. Wiley, New York (1963).
5. D. D. Saralidze, L. P. Shklover, K. I. Petrov and V. E. Phyushates, *Zh. strukt. Khim.* **8**, 57 (1967).
6. J. R. Witt and E. I. Onstott, *J. inorg. nucl. Chem.* **24**, 637 (1962).
7. B. Sahoo, S. Panda and D. Patnaik, *J. Indian chem. Soc.* **37**, 594 (1960).

*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.  $\text{CD}_3\text{COOD}$  and  $\text{DCOOD}$  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  $70\text{ cm}^{-1}$ . The spectra from 4000 to  $650\text{ cm}^{-1}$  region were measured with a Beckman Ir-12 using KBr pellets. The spectra from 650 to  $70\text{ cm}^{-1}$  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  $6328\text{ \AA}$  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 %
$\text{Y(OAc)}_3$	3.40	27.08	33.41	3.40	26.96	33.66
$\text{Eu(OAc)}_3$	2.75	21.89	46.17	2.82	21.26	46.30
$\text{Tb(OAc)}_3$	2.69	21.44	47.29	2.68	21.49	47.10
$\text{Er(OAc)}_3$	2.63	20.92	48.56	2.58	21.09	48.55
$\text{La(HCOO)}_3$	0.97	11.63	56.19	1.49	11.72	55.89
$\text{Nd(HCOO)}_3$	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  $\sim 2950$ ,  $\sim 1540$ ,  $\sim 1430$ ,  $\sim 1018$  and  $\sim 670\text{ cm}^{-1}$  upon isotopic replacements of hydrogen with deuterium. These shifts to  $\sim 2250$ ,  $\sim 1088$ ,  $\sim 1030$ ,  $\sim 848$  and  $\sim 530\text{ cm}^{-1}$ . For the formates, the absorption bands shifting to lower frequencies were those at  $\sim 2856$  and  $\sim 1420\text{ cm}^{-1}$ , which moved to  $\sim 2200$  and  $1056\text{ cm}^{-1}$  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  $100\text{--}300\text{ cm}^{-1}$ . The strong absorptions occurring in the  $217\text{--}315\text{ cm}^{-1}$  in the acetates and at  $167\text{--}282\text{ cm}^{-1}$  in the formates are assigned to metal-oxygen stretching modes. For com-

8. J. R. Ferraro, S. S. Mitra and C. Postmus, *Inorg. & Nucl. Chem. Lett.* **2**, 269 (1966); L. J. Basile, C. Postmus and J. R. Ferraro, *Spec. Lett.* **1**, 189 (1968).