Monatshefte für Chemie 120, 187—190 (1989)

Monatshefte für Chemie
Chemical Monthly

Far-Infrared Spectra of Lanthanide Complexes with 8-Hydroxyquinoline

Piotr M. Drożdżewski* and **Krystyna Kopacz**

Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wrocław, PL-50 370 Wrocław, Poland

Summary. Vibrational spectra of lanthanide oxines have been measured in the far-infrared region. In addition, the similar yttrium complex was investigated for further experimental evidence for the proposed band assignments. The most important metal-oxygen and metal-nitrogen bond vibrations have been attributed to absorptions between 390–350 cm^{-1} and 210–170 cm^{-1}, respectively.

Keywords. Lanthanide oxines; FIR; Metal-ligand vibrations.

Ferne IR-Spektren von Lanthanidenkomplexen mit 8-Hydroxychinolin

Zusammenfassung. Es wurden die Vibrationsspektren von Lanthanid-Oxinen im fernen IR-Bereich gemessen. Zusätzlich wurde der analoge Yttrium-Komplex untersucht, um die Bandenzuordnungen experimentell zu stützen. Die wichtigsten Metall-Sauerstoff- und Metall-Stickstoff-Bindungsschwingungen wurden den Absorptionen zwischen 390–350 cm^{-1} und 210–170 cm^{-1} zugeordnet.

Introduction

The metal chelating ability of 8-hydroxyquinoline (H*Q*) is still attracting much attention in vibrational spectroscopy. Among many transition metals which form oxine complexes, those of the f-electrons have also been investigated by IR spectroscopy [1]. However, these studies were limited to the middle IR region where the ligand vibrations are generally observed. In order to collect data about the positions of the metal-ligand vibrations, the far-IR region has to be examined. Such work seems to be important especially in the case of lanthanide complexes for which there are less data in the literature compared to the d-electron metals.

In the present paper, the lanthanide-oxines were examined by means of far-IR spectroscopy with the purpose of experimental determination of absorptions generated by the coordination sphere vibrations.

Experimental

Commercial 8-hydroxyquinoline was purified by twofold recrystallization from ethanol. Lanthanide oxides were dissolved in a small amount of nitric acid and evaporated to dryness to remove the excess of HNO_3. The precipitated salt was dissolved in water and used for complex syntheses according to the method presented by Charles et al. [2]. The middle-IR spectra has been measured to prove the proper complex formation. An additional yttrium-oxine complex was obtained as described by Cardwell et al. [3]. Routine IR spectra were recorded on a Specord 75 IR spectrophotometer. The KBr pellet or hexachlorobutadiene suspension techniques were applied for sample preparations. Far-IR absorptions were measured on a Perkin-Elmer 180 spectrophotometer using Nujol mulls between polyethylene plates.

Results and Discussion

In the low IR wavenumbers region several differences are observed between the spectra of 8-hydroxyquinoline and its lanthanide complexes (LnQ_3). Fig. 1 demonstrates these changes for free ligand absorptions and for the typical complex spectrum – a praseodymium one. After coordination of metal ion new bands appear at 379 and 361 cm^{-1} in the IR spectrum of the complex. A second important change is observed in the region between 250 and 150 cm^{-1}. The ligand spectrum exhibits there only one intense band at 196 cm^{-1} whereas the very broad and also intense absorption with its maximum at about 205 cm^{-1} and a shoulder at 180 cm^{-1} appears for the complex. These bands may be considered as resulting from metal-ligand vibrations. Aly et al. [1] have assigned the lanthanide-oxygen stretching vibrations to the bands around 490 cm^{-1}. Other authors [4, 5] have attributed the same band to the ligand vibrations in which the $\delta(C-O)$ deformation mode was a significant participation. This band has also been found to be sensitive to a $HQ-DQ$ substitution [4] which confirms its $\delta(C-O)$ origin and explains the small shift (from 493 to 485 cm^{-1}) after metal-oxygen bond formation.

As it has been stated before, the $\nu(Ln-O)$ stretching vibrations may absorb at about 370 cm^{-1}. It is a rule that IR bands sensitive to metal motion in the complex molecule exhibit a regular shift toward higher wavenumbers with an increase of the atomic number of the lanthanide. Similar examination of main bands in the far-IR region are presented in Fig. 2 for LnQ_3 complexes. The strongest and most linear dependence of band wavenumbers against lanthanide ionic radii

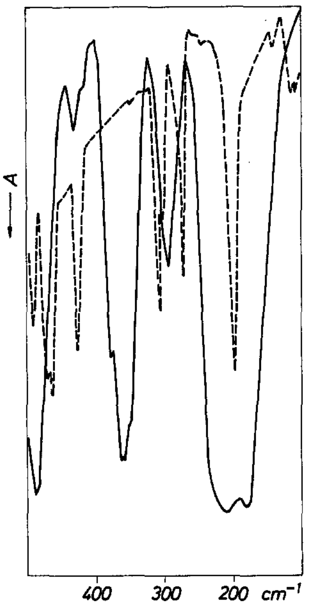

Fig. 1. Comparison of far-infrared spectra of 8-hydroxyquinoline (broken line) and its praseodymium complex (solid line)

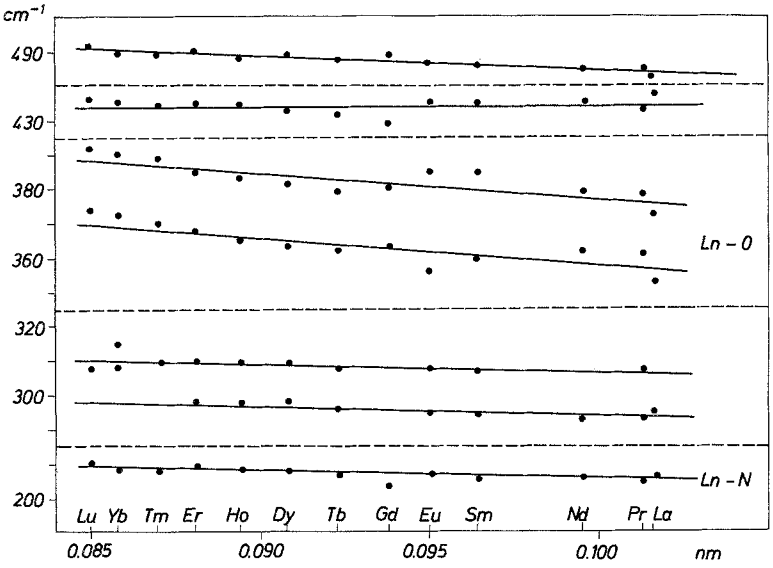

Fig. 2. Plot of far-infrared band positions against lanthanide ionic radii

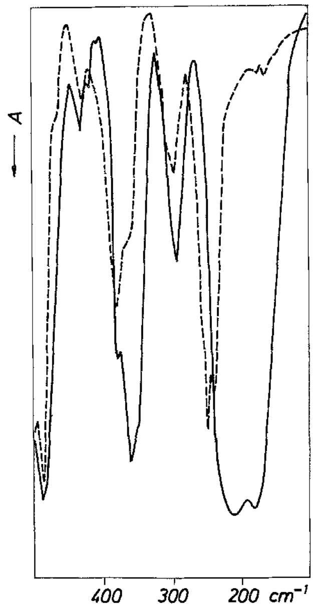

Fig. 3. Spectra of praseodymium (solid line) and yttrium (broken line) complexes with 8-hydroxyquinoline

is seen for previously mentioned bands around 370 and below 200 cm^{-1}. This result confirms that the bands at 379 and 361 cm^{-1} are due to the lanthanide-oxygen stretching vibrations. The same graph suggests that the metal-nitrogen vibrations can be attributed to the absorptions near 200 cm^{-1}.

Similar wavenumbers of bands generated by lanthanide-aromatic-nitrogen vibrations have been found for phenanthroline [6, 7] and dipyridil [8, 9] complexes. Since the last assignment is not quite clear because of the ligand vibration absorbing in the same region, an additional experiment had been carried out. For some of the d-electron metals the metal isotope technique is very useful for far-IR band

Table 1. Far-infrared band positions (cm^{-1}) of lanthanide and yttrium complexes with 8-hydroxyquinoline (sh = shoulder)

Metal	Band positions and assignments							
	Lig + δ_{CO}	Lig.	$\nu(Me-O)$		Lig.	Lig.	$\nu(Me-N)$	
La	483	438	372	353	–	295	206	172
Pr	485	433	378	360	307 sh	294	205	177
Nd	485	435	379	362	–	293	206	181
Sm	486	435	385 sh	370	307	295	206	–
Eu	487	435	374	356 sh	308 sh	295	207	–
Gd	489	429	380	363	–	267	203	–
Tb	488	432	379	362	308 sh	296	207	–
Dy	489	433	381	363	309 sh	298	208	–
Ho	489	435	383	365	309 sh	298	209	–
Er	490	435	385	367 sh	310 sh	298	209	–
Tm	490	434	389	370 sh	310	–	218 sh	208
Yb	490	435	390	372	315 sh	308	218 sh	209
Lu	491	436	392	374	–	308	–	210
Y	490	435	384	367	–	300	243	–

assignments. In the case of lanthanides, the mass effect is very small, even smaller than the one caused by the metal-ligand bond strength. Looking for a relatively bigger mass change the yttrium complex was compared with the lanthanide ones. Yttrium and lanthanides show a similarity in chemical behaviour but differ much in their masses. Thus the "isotope-like" effect may be observed as presented in Fig. 3. Bands already assigned to the $\nu(Ln-O)$ and $\nu(Ln-N)$ vibrations show the largest shift toward higher wavenumbers upon praseodymium-yttrium substitution. The remaining bands at about 430 and 300 cm^{-1} show smaller shift and can be assigned to the ligand vibrations. The wavenumbers of all far IR bands and their assignments are summarized in Table 1.

References

[1] Aly H. F., Abdel Kerim F. M., Kandil A. T. (1971) J. Inorg. Nucl. Chem. **33**: 4340

[2] Charles R. G., Freiser H., Friedel R., Hilliard L. G., Johnston W. D. (1965) Spectrochim. Acta **8**: 1

[3] Cardwell T. J., Magee R. J. (1968) Anal. Chim. Acta **43**: 321

[4] Tackett I. E., Sawer D. F. (1964) Inorg. Chem. **3**: 692

[5] Ohkaku N., Nakamoto K. (1971) Inorg. Chem. **19**: 798

[6] Hart F. A., Laming F. P. (1965) J. Inorg. Nucl. Chem. **27**: 1605

[7] Hart F. A., Laming F. P. (1964) J. Inorg. Nucl. Chem. **26**: 579

[8] Hart F. A., Laming F. P. (1965) J. Inorg. Nucl. Chem. **27**: 1825

[9] Sinha P. S. (1964) Spectrochim. Acta **20**: 879

Received January 11, 1988. Accepted February 29, 1988