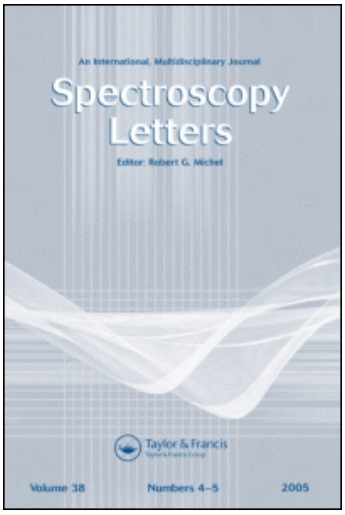

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Some Characteristics of Infrared and Raman Spectra and Bonding of a Series of Lanthanide Complexes with L-Proline

Zhang Nengwu[a]; Pan Long[a]; Liu Maiming[a]; William R. Robinson[b]
[a] Department of Applied Chemistry, University of Science and Technology of China, P. R. China [b] Department of chemistry, Pudue University, West Lafayette, In, USA

To cite this Article Nengwu, Zhang , Long, Pan , Maiming, Liu and Robinson, William R.(1997) 'Some Characteristics of Infrared and Raman Spectra and Bonding of a Series of Lanthanide Complexes with L-Proline', Spectroscopy Letters, 30: 1, 61 — 70
To link to this Article: DOI: 10.1080/00387019708002589
URL: http://dx.doi.org/10.1080/00387019708002589

SPECTROSCOPY LETTERS, 30(1), 61-70 (1997)

SOME CHARACTERISTICS OF INFRARED AND RAMAN SPECTRA AND BONDING OF A SERIES OF LANTHANIDE COMPLEXES WITH L-PROLINE

Key words: lanthanide complexes,proline,IR and Raman sprctra

Zhang Nengwu[1] , Pan Long[1] , Liu Haiming[1] and William R. Robinson[2]
[1]Department of Applied Chemistry,University of Science and Technology of China, Hefei Anhui 230026, P.R.China
[2]Department of chemistry, Pudue University, West Lafayette, In 47907,USA

Abstract

The crystalline lanthanide complexes (except Ce and Pm) with proline were synthesized. The general formula of $[Ln(Pro)_2(H_2O)_4]_3(ClO_4)_3$ of the complexes were obtained from chemical analysis, elemental analysis, TG-DTA analysis and electrical conductivity. Infrared spectra reveal a considerable shift of the symmetric co_2^- stretching mode from lower to higher energies in the lanthanide complexes and a decrease of $\Delta\nu(\Delta\nu=\nu_{coo^-}^{as}-\nu_{coo^-}^{s})$ from 212 cm^{-1} in proline to about 167 cm^{-1} in the complexes . The peak mean 405cm^{-1} in the Raman spectra varies with the total orbital angular momentum of the lanthanide ions in the ground states , exhibiting a profile of an "inclined w". These spectral features in the IR and Raman spectra were regarded as strong evidences of Ln-O bonding. The peak near 405cm^{-1} was assigned as the Ln-O stretch modes.

INTRODUCTION

Recently, the lanthanide complexes with amino acids have attracted many researchers attention because of the role of lanthanide ions in studies of biological systems and because of their importance in spectroscopy probes. A variety of lanthanide complexes coordinating

with amino acids have been synthesized and their spectroscopic properties, bonding modes, and crystal structures have been extensively studied by our group and others[1-12]. However, there are no reports of the IR and Raman spectra of a series of lanthanide complexes with proline. Thus this series of lanthanide complexes (excepting the Ce and Pm) have been synthesized and their IR and Raman spectra been studied.

EXPERIMENTAL

A series of lanthanide complexes with proline was obtained by dissolving 0.1-0.4g of Ln_2O_3 in a stoichiometric amount of 5M perchloric acid, isolating the solid, then refluxing the lanthanide perchlorate with proline(mole ratio 1:2) in about 40ml of methanol for 3hr. Evaporation of the solvent produced a solid product which was isolated, washed with a small portion of methanol, and recrystallized from an acidic aqueous solution(pH=4) by slow evaporation. Rod-like crystals were obtained.

The concentration of La^{3+} in the crystals was determined by chemical analysis. The proline content was calculated from carbon and nitrogen analyses obtained using a Perkin-Elmer 2400. Water was determined by thermal analysis using a Rigaku PTC-10A. The results of component analysis and electrical conductivity measurement of the complexes are tabulated in Table 1. The infrared spectra were measured from 4000 to 400cm^{-1} using a Nicolet Sx-170 FT-IR spectrophotometer. The spectra were recorded for samples in NaBr pellets and the spectra were measured employing Spex model 1403 laser-raman spectrometer with an Ar laser as the excitation source (power 120 mW at 514.5nm) .

RESULTS AND DISCUSSION

The analytical results indicate that we have prepared a series of lanthanide complexes with proline with the general formula$[Ln(Pro)_2(H_2O)](ClO_4)_3$. The TG-DTA analysis of proline and of the Ln(III) complexes with proline showed that the complexes and proline all have no definite melting points. The TG-DTA curves for all complexes are similar and are

Table 1. Elemental analysis and conductivity for lanthanide complexes with proline

Complexes	Color	Ln%		Pro%		H_2O%		Λ_m
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	[s · cm^2 · mol^{-1}]
$[La(Pro)_2(H_2O)_4](ClO_4)_3$	colorless	18.78	18.90	31.13	31.69	9.74	9.85	389[1.020×10^{-3}*]
$[Pr(Pro)_2(H_2O)_4](ClO_4)_3$	pale green	19.00	18.63	31.10	31.78	9.71	9.82	387[9.862×10^{-4}]
$[Nd(Pro)_2(H_2O)_4](ClO_4)_3$	pale red-violet	19.37	18.98	30.91	30.20	9.67	9.72	386[1.104×10^{-3}]
$[Sm(Pro)_2(H_2O)_4](ClO_4)_3$	colorless	20.02	19.40	30.66	30.36	9.59	9.69	387[1.108×10^{-3}]
$[Eu(Pro)_2(H_2O)_4](ClO_4)_3$	colorless	20.19	19.92	30.59	30.78	9.57	9.59	375[1.076×10^{-3}]
$[Gd(Pro)_2(H_2O)_4](ClO_4)_3$	colorless	20.75	20.02	30.38	30.69	9.50	9.56	367[1.105×10^{-3}]
$[Tb(Pro)_2(H_2O)_4](ClO_4)_3$	colorless	20.93	20.10	30.31	29.96	9.48	9.58	384[9.973×10^{-4}]
$[Dy(Pro)_2(H_2O)_4](ClO_4)_3$	colorless	21.30	21.98	30.19	29.87	9.44	9.39	369[9.892×10^{-4}]
$[Ho(Pro)_2(H_2O)_4](ClO_4)_3$	colorless	21.55	21.00	30.07	29.85	9.41	9.48	376[1.102×10^{-3}]
$[Er(Pro)_2(H_2O)_4](ClO_4)_3$	pale red	21.78	21.03	29.98	29.70	9.38	9.49	374[1.130×10^{-3}]
$[Tm(Pro)_2(H_2O)_4](ClO_4)_3$	colorless	21.95	21.04	29.92	29.30	9.36	9.60	367[1.115×10^{-3}]
$[Yb(Pro)_2(H_2O)_4](ClO_4)_3$	colorless	22.37	21.99	29.76	29.20	9.31	9.63	359[1.083×10^{-3}]
$[Lu(Pro)_2(H_2O)_4](ClO_4)_3$	colorless	22.56	21.97	29.68	29.89	9.28	9.70	384[1.105×10^{-3}]

*Solution concentration

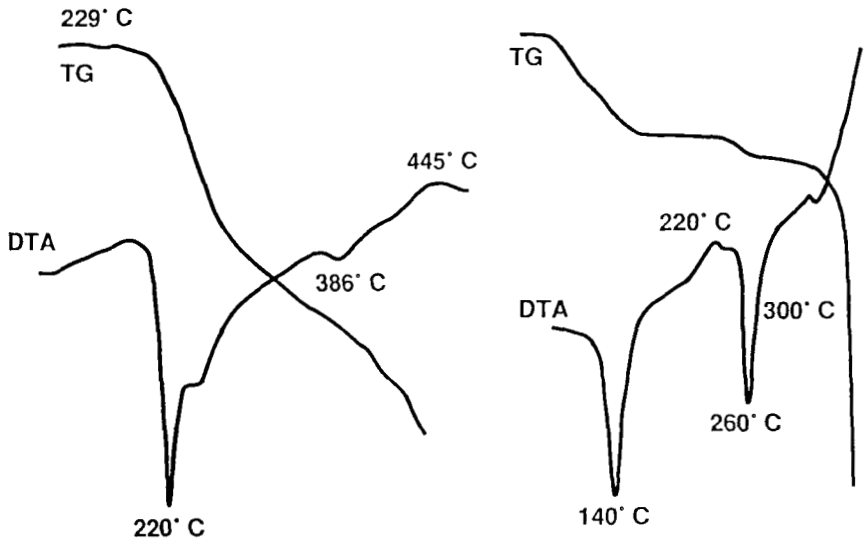

Figure 1 TG-DTA curves of proline and the Tm^{III} complex with proline

different from that of proline. The TG-DTA curves of the Tm(III) complex with proline, as an example, and of proline are shown in Figure 1. The complexes exhibit an endothermic dehydration process in the range 80-140°C. The loss of weight in the TG curves corresponds to 4 water molecules, which is consistent with the result of elemental analysis. Characteristic infrared and Raman spectral features of proline and its Pr(III) couplexes are reported in Table 2. The features reported for the Pr(III) complex are characteristic of all of the lanthanide complexes with proline.

Proline belongs to the trivial point group C_1 and all vibration modes are both infrare and Raman active. The spectrum of proline is sensitive to hydrogen-bonding effects, and the

Table 2. Some characteristic IR and Raman spectral features of proline and its Pr^{III} complex (cm^{-1})

Proline		Pr-Pro		assignment
IR	Raman	IR	Raman	
3064 - 2958 (vs)		2943 (s)	2996 (vs)	$\nu\ NH_2^+$
2958 (vs)				
1619 (vs)	1618 (m)	1598 (vs)	1598 (m)	$\nu_{as}\ COO^-$
1555 (sh)	1550 (m)	1541 (s)	1552 (s)	NH_2^+ scissoring
1407 (s)	1409 (w)	1437 (vs)	1426 (w)	$\nu_{s}\ COO^-$
1379 (s)	1373 (s)	1372 (w)		NH_2^+ twisting
1168 (s)	1176 (vw)	1179 (w)	1162 (m)	NH_2^+ wagging
900 (w)	900 (vs)	900 (m)		NH_2^+ rocking
848 (vs)	842 (s)	856 (w)	856 (m)	H_2O wagging
642 (s)	644 (m)	627 (vs)	626 (vs)	COO^- wagging
		412 (s)	405 (w)	Ln – O stretch

vs, very strong; s, strong; m, medium; w, weak;
vw, very weak; sh, shoulder

assignments listed in Table 2 are those for the zwitterionic form. The frequencies of the asymmetric and symmetric NH_2^+ stretches are found in the range of frequencies from 3064 to 2958cm^{-1}. The frequencies 1379,1168 and 900cm^{-1} are attributable to NH_2^+ motions and may be described as NH_2^+ twisting, wagging and rocking respectively. The frequencies 1619, 1407 and 642cm^{-1} are attributable to coo^- motions and may be described as the asymmetric carboxylate stretch, symmetric carboxylate stretch and the coo^- wagging.

The peaks which are associated with the zwitterionic form of the free acid are maintained in the spectra of our lanthanide complexes with proline. This suggests proline is

present as a zwitterion in these compounds. The frequencies of the asymmetric and symmetric coo⁻ stretches observed for proline and the lanthanide complexes with the proline are listed in Table 3. We find that the peak attributable to the asymmetric coo⁻ stretch is shifted to lower energies in the complexes, but the peak attributable to the symmetric coo⁻ stretch is shifted to higher energies in the complexes. The values of $\Delta\nu$ ($\Delta\nu=\nu_{coo^-}^{as}-\nu_{coo^-}^{s}$) decrease from 212cm^{-1} in proline to about 167cm^{-1} in complexes. This indicates that the lanthanide ions form mainly ionic bonds with the carboxylate group in these compound[9].

Krishnan K.et al[1] studied the Raman spectra of complexes with glycine and suggested that that the frequencies associated with the M-O stretch is near 395cm^{-1}. We found that the frequencies near 405cm^{-1} in the proline complexes are sensitive to different lanthanide ions(Table 4), and we assign these frequencies to Ln-O stretching modes. Sinha S.P.[13] proposed plotting the properties(P_i) of f-ions vs the free ion orbital angular angular quantum numbers(L) of their ground states. Such plots show linear variation of P_i within each of four tetrad, often exhibiting the profile of an inclined w. Subsequently, a wide variety of properties for the lanthanide and the actinide in different oxidation states have been examined and confirm the general validity of the "inclined W" relationship[13-16]. Plotting the Ln-O frequencies near 405cm^{-1} versus the total orbital angular momentum of the lanthanide ion ground states gives a plot with profile of an inclined w(Figure 2). If we use th approximate relation.

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{k/\mu}$$

where $\bar{\nu}$ is the frequency; μ, the reduced mass of lanthanide atom and oxygen atom, and k, the force constant (k'values use d^2x10^6 as unit,where $d=2\pi C$); and plot calculated the force constant (Table 4) versus the total orbital angular momentum of lanthanide ion ground state,

Table 3. $\nu^{as}_{coo^-}$, $\nu^{s}_{coo^-}$, and $\Delta\nu$ in lanthanide complexes with proline (cm^{-1})

	proline	complexes												
		La	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
$\nu^{as}_{coo^-}$	1619	1602	1598	1597	1599	1606	1605	1608	1608	1607	1607	1608	1599	1599
$\nu^{s}_{coo^-}$	1407	1428	1437	1439	1432	1435	1437	1437	1438	1438	1438	1436	1436	1436
$\Delta\nu$	212	174	161	158	167	171	168	171	170	169	169	172	163	163

Table 4. Raman frequencies for the Ln-O stretch (ν), force constant (k), and total angular momentum (L) of the lanthanide ions

	La	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
$\nu_{Ln\text{-}O}$ (cm^{-1})	405.0	405.5	406.0	406.5	407.5	408.5	409.0	409,5	409.5	410.5	410.5	413.5	416.5
k ($d^2 \cdot 10^6$)	2.354	2.363	2.374	2.389	2.404	2.423	2.432	2.443	2.443	2.460	2,476	2.504	2.562
L	0	5	6	5	3	0	3	5	6	6	5	3	0

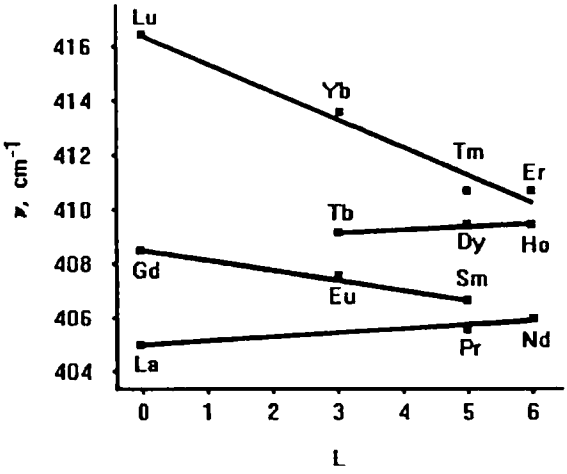

Figure 2 Plot of the frequencies (ν) near 405 cm^{-1} for different complexes against the total orbital angular momentum (L) of the lanthanide ion in the complex

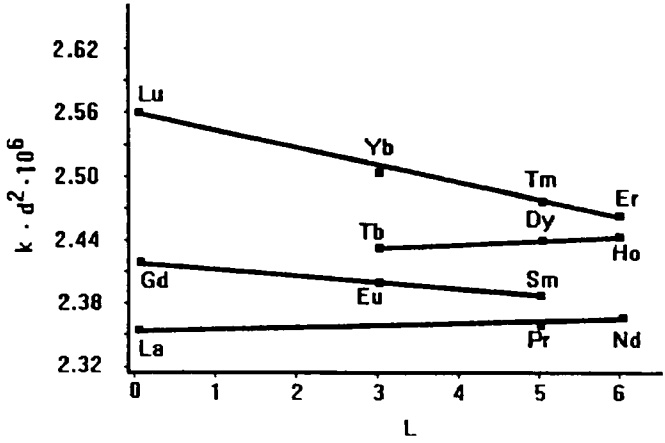

Figure 3 Plot of force constants k for Ln-O stretching modes against total orbital angular momentum L of lanthanide ions

we also observe the "inclined W" effect(Figure 3). In accordance with this analysis, we believe that the change in the frequency of the peak near 405cm^{-1} was the different lanthanide ions with oxygen of the carboxlate group.

ACKNOWLEDGMENT

We thank the School of Science and the Chemistry Department, Purdue University and the School of Science, University of Science and Technology of China, for providing an opportunity of cooperative work. This work was supported by grants from the Natural Science Foundation of China.

REFERENCES

1. Krishnan K.,Plane P.A., Inorg.Chem.,1967;6:55.

2.Herlinger A.W. and Long T.V., J.Am.Chem.Soc.,1970;92:6481.

3.Nakamoto K.,Infrared and Raman Spectra of Inorganic and Coordination cmpounds, Wiley,New york,1978(3rd ed).

4.Zheng N.W..Pan L.,Xu Z.L.,Jing X.L.,JIEGOU HUAXUE,1993;5:387.

5.Legengendziewcz J.,Glowiak T.,Huskowskaand E.et al.,Polyhedron,7(1988)2495.

6.JinT.Z.,Gao S.,Huang C.H.,HanY.Z.,Xu G.X., Journal of the Chinese Rare Earth Society,1978;5:1.

7. Zeng H.D., Pan K.Z.,JIEGOU HUAXUE,1992;11:388.

8. Rastogl R.,Kapoor R.N.,Indian J.Chem.,1993;22A:78.

9. Wang Z.L.,Niu C.J,Hu N.H.,Ni J.Z.,Acta Chimica Sinica,1993;5:257.

10.Nath B.B., Indian J.Biochem.Biophys.,1982;19:32.

11.Legndziewicz J.,et al,J.Less-Common Metals,1991;168:32.

12.Legendziewicz J.,et al,Inorg.Nucl.Chem.Lett.,1981;17:57.

13.S.P.Sinha,Helv.Chim.Acta,1975;58:1978.

14.S.P.Sinha,Inorg.Chim.Acta,1977;22:L5.

15.S.P.Sinha,Inorg.Chim.Acta,1978;27:253.

16.Zheng N.W.,et al,J.Phys.B:At.Mol.Opt.Phys.,1991;24:1187.

Received: June 7, 1996
Accepted: July 19, 1996