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Infrared and Raman spectra of complexes about rare earth nitrate with Schiff base from o-vanillin and 1-naphthylamine

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Abstract

Infrared and Raman spectra are reported for 10 complexes of rare earth nitrate with Schiff base from o-vanillin (2-hydroxy-3-methoxy-benzaldehyde) and 1-naphthylamine in the range 100–4000 cm^{-1} and 100–1799 cm^{-1}. Some absorption bands are assigned and the results of them are used to discuss the coordinated structure of the complexes. © 1997 Elsevier Science B.V.

Keywords: Infrared spectrum; Raman spectrum; Rare earth complex; Schiff base; o-Vanillin

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1. Introduction

Schiff base complexes may use as catalyzer, anti-cancerous medicant and model compounds imitating enzymes [1–3]. There have been a number of reports about metal ion complexes with Schiff bases. The complexes of rare earth ions with Schiff bases derived from vanillin (3-methoxy-4-hydroxy-benzaldehyde) and p-toluidine [4,5], o-vanillin (2-hydroxy-3-methoxy-benzaldehyde) and 2-naphthylamine [6], o-vanillin and p-toluidine [7], bis-o-vanillon and ethylenediamine [8], have been reported, but vibration spectra of these complexes were rarely investigated. In the present work infrared and Raman spectra of complexes about rare earth nitrate with Schiff base from o-vanillin and 1-naphthylamine were discussed.

2. Experimental

2.1. Preparation of Schiff base

The mixture of o-vanillin with equimolar 1-naphthylamine in absolute ethanol was refluxed for 2 h and then cooled to room temperature. The resulting precipitate was filtered and washed with absolute ethanol. The crude product was recrystallized from absolute ethanol. Yield 92%.

2.2. Preparation of the complexes

The complexes were prepared by the reaction of rare earth nitrate with Schiff base ligand in absolute ethanol according to Ref. [9]. The general formula of the complexes $(ML_2(NO_3)_2)NO_3$ (M = La, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Tm and Yb) is given.

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Table 1
Observed infrared frequencies of the complexes and ligands (cm^{-1})

Ligand	La	Pr	Nd	Sm	Eu	Tb	Dy	Ho	Tm	Yb	Assignment
	406m	408m	409m	411m	412m	414m	415m	417m	418m	419m	
424m	420w	420m	420w	445w	441w	421m		448w			
	476m	477m	477m	477m	477m	477m	477m	478m	477m	477m	M–O stretch
	493m	493m	493m	494m	494m	494m	494m	494m	494m	494m	M–O stretch
	508w	509w	509w	509w	509w	510w	510w	508w	508w	509w	
	520w	520w	521w	522w		514w					
	530m	531m	531m	532m	532m	532m	532m	531m	532m	532m	
552m	553m	553m	553m	553m	553m	553m	553m	553m	553m	553m	
565w	604w	576m	576w	578w	582w	582w	583w	584w	593w		
590w	616w	605w	604w	606w	606w	607w	606w	606w	607w	607w	
	634w	634w	634w	634w	634w	634w	634w	634w	634w	634w	
713m											
713m	716m	716m	716m	717m	717m	716m	717m	717m	717m	717m	$NO_3^-(\nu_5)$
735m	732m	734m	736m	738m	740m	743m	742m				
	753m	753m	753m	753m	753m	753m	753m	753m	753m	753m	$NO_3^-(\nu_3)$
769s	768s	768s	768s	768s	768s	767s	767s	768s	767s	767s	C–H out of plane bend (benzene)
	792m	792m	792m	792m	792m	792m	792m	792m	792m	792m	$NO_3^-(\nu_2)$
797w	818w	817w	817w	817w	816w	816w	816w	815w	814w	813w	
841w	853w	854w	853w	854w	853w	852w	853w	853w	853w	853w	C–H out of plane bend (a-naphthalene)
883w	880w	880w	880w	879w	880w	879w	879w	879w	879w	877w	
	902w	902w	902w	902w	902w	902w	902w	902w	902w	902w	
927m	959m	960m	960m	961m	961m	961m	961m	962m	962w	962w	
1015m	1018m	1018m	1018m	1017m	1017m	1017m	1016m	1015m	1015m	1014m	
	1030m	1033m	1033m	1035m	1035m	1035m	1035m	1037m	1037m	1032m	$NO_3^-(\nu_2)$
1040	1069m	1069m	1069m	1069m	1068m	1068m	1068m	1068m	1068m	1068m	
1090m	1092m	1093m	1093m	1094m	1094m	1094m	1094m	1094m	1095m	1094m	
1154w											
1177m	1170s	1170s	1171s	1171s	1171s	1171s	1171s	1171s	1171s	1171s	
1223s	1211s	1211s	1211s	1212s	1212s	1212s	1212s	1213s	1213s	1213s	=C–O stretch (phenol)
	1234m	1234m	1234m	1234m	1234m	1234m	1234m	1234m	1235m	1236m	
1252s	1249m	1249m	1249m	1249m	1249m	1249m	1249m	1249m	1249m	1249m	=C–O–C antisymmetric stretch (aryl ether)
1281m											
	1300vs	1300vs	1300vs	1303vs	1304vs	1306vs	1305vs	1307vs	1308vs	1307vs	$NO_3^-(\nu_1)$
1334w											
1364w	1372m	1371m	1371m	1370m	1371m	1371m	1371m	1371m	1371m	1371m	=N–C stretch
1391m	1384m	1385m	1384m	1384m	1385m	1385m	1385m	1385m	1385m	1386m	O–H in plane bend (phenol)
	1398m	1399m	1399m	1399m	1399m	1400m	1400m	1399m	1398m	1399m	
	1460s	1459s	1459s	1460s	1459s	1459s	1460s	1461s	1461s	1460s	
1466s	1468s	1470s	1469s	1470s	1471s	1468s	1470s	1471s	1469s	1469s	
	1493s	1493s	1493s	1494s	1494s	1495s	1494s	1495s	1496s	1496s	
1511											
1511w	1520m	1520m	1520m	1520m	1519m	1520m	1519m	1518m	1518m		$NO_3^-(\nu_4)$
1562m	1547m	1548m	1548m	1548m	1548m	1549m	1549m	1550m	1550m	1551m	
	1575w	1574w	1574w	1574w	1575w	1577w	1574w	1575m	1574m	1575m	

Table 1 continued

Ligand	La	Pr	Nd	Sm	Eu	Tb	Dy	Ho	Tm	Yb	Assignment
1599m	1598m	1598m	1598m	1598m	1598m	1598m	1598m	1598m	1598m	1598m	C=C stretch (aryl ring)
1608s											
	1641s	1642s	1642s	1642s	1642s	1642s	1643s	1642s	1643s	1642s	C=N stretch
	1737w	1737w	1737w	1738w	1737w	1737w	1737w	1737w	1745w	1737w	$NO_3^-(\nu_1 + \nu_4)$
	1769w	1769w	1770w	1770w	1776w	1778w	1778w	1770w	1778w	1770w	$NO_3^-(\nu_1 + \nu_4)$
2834w	2853w	2837w	2845w	2845w	2844w	2845w	2837w	2837w	2845w	2845w	
2857w	2943w	2943w	2943w	2493w	2943w	2943w	2943w	2944w	2943w	2943w	C–H stretch (OCH_3)
	2984w	2976w	2975w	2977w	2976w	2976w	2976w	2976w	2976w		
3005w	3057w	3050w	3057w	3050w	3049w	3050w	3050w	3041w	3049w	3050w	
3047w	3090w	3091w	3091w	3090w	3090w	3091w	3092w	3094w	3091w	3092w	C–H (aryl)
3443m	3419m	3416m	3418m	3402m	3402m	3402m	3402m	3394m	3402m	3402m	O–H stretch (phenol)
3465m	3469m	3484m	3468m	3468m	3476m	3468m	3468m	3468m	3468m	3460m	

2.3. Measurements of spectra

Infrared spectra were recorded on a Nicolet FTIR-5PC spectrometer in the region 400–4000 cm^{-1} using KBr pellets. Raman spectra were recorded on a Spex 1403 Ramanor spectrometer in the range 100–1700 cm^{-1} region. The excitation wavelength was 6471 Å. The resolution of infrared and Raman spectra is 2 and 1 cm^{-1} respectively.

3. Results and discussion

3.1. Infrared spectra

The infrared absorption frequencies of Schiff base ligand and its complexes are presented in Table 1. The spectrum of Nd complex is illustrated in Fig. 1. The –C=N stretching vibration frequency of free Schiff base is at 1608 cm^{-1} but the band of the complexes

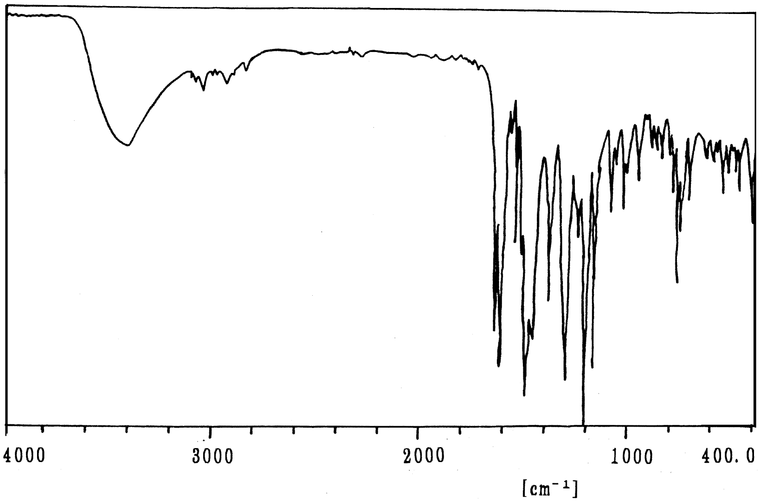


Fig. 1. Infrared spectrum of Nd complex.

Table 2
Infrared frequencies, activity and assignment for the NO_3^- ion

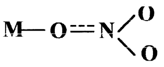
Type	Activity	Frequencies (cm^{-1})	Assignment
A'_1	ia	ν_1 ca. 1050	N–O stretching
A''_2	a	ν_2 ca. 831	NO_2 deformation
E'	a	ν_3 ca. 1390	NO_2 antisymmetric stretch
E'	a	ν_4 ca. 720	ONO_2 planar rocking

a = active ia = inactive

is in the range 1641–1643 cm^{-1}. This band is shifted to higher wavenumbers in the complexes. It shows that the nitrogen of the azomethine group is coordinated to the rare earth ion. The phenolic OH stretching vibration frequency of the Schiff base in at 3443 cm^{-1}. In the complexes this band is in the range 3394–3419 cm^{-1}. The absorption band shifted to the lower frequencies, indicating that oxygen of the phenolic OH is coordinated to the rare earth ion. The absorption bands, near 477 and 496 cm^{-1}, are due to symmetrical and antisymmetrical stretching vibrations of M–O [10]. There are two M–O bands, since the nitrate group is coordinated in a bidentate fashion [11].

The =C–O stretching vibration of phenol and phenolic OH deformation in-plane are all shifted to the lower frequencies, since the phenolic OH is coordinated to rare earth ion (Table 1) [12]. The C=C stretching vibration of aryl ring, the C–H out-of-plane bend vibration of naphthalene and the =C–O–C antisymmetric stretching vibration of aryl ether do not basically change [12,13]. The bands in the range 2834–2984 cm^{-1} are assigned to C–H stretching mode of methoxy group, therefore, in the range 3005–3094 cm^{-1} to aryl group.

The ν_1–ν_6 absorption bands in Table 1 are due to the coordinated nitrate group. The infrared absorption frequencies for NO_3^-, which belongs to the point group D_{3h}, are listed in Table 2 with the vibration types, activity and assignments. Its infrared spectrum shows four absorption bands, where three (ν_2, ν_3 and ν_4) are active, one (ν_1) normally is inactive, but sometimes becomes weakly active through crystal field interactions. ν_3 (E') and ν_4(E') are doubly degenerate. In the complexes the nitrate ion acts as a monodentate or bidentate coordination, and they both belong to the point group C_{2v}. Their vibration types and properties are listed in Table 3. Under C_{2v} symmetry the $\nu_1(A'_1)$ mode becomes active $\nu_2(A_1)$ mode and the E(ν_3, ν_4) mode splits into A_1(ν_1, ν_3) and B_1(ν_4, ν_5) components, so that the spectrum now ideally have six bands, all being active in the infrared spectrum. Under C_{2v} symmetry, three of the modes belong to the totally symmetric irreducible representation $3A_1$, and remain three are no totally symmetric ($2B_1 + B_2$). The band splittings for the bidentate coordination are larger in magnitude than those for monodentate coordination. The ν_1 and ν_4, ν_3 and ν_5 absorption bands in Table 3 are splitting bands. The magnitude of $\nu_4 - \nu_1$ for the bidentate mode is in general more than 180 cm^{-1} and



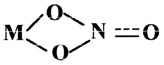


Table 3
Infrared frequencies, activity and assignment for the coordination nitrate group

Type	Activity	Frequencies (cm^{-1})	Assignment
A_1	a	ν_3 ca. 753	NO_2 bending
A_1	a	ν_1 ca. 1306	NO_2 symmetric stretch
A_1	a	ν_2 ca. 1035	N–O stretch
B_2	a	ν_6 ca. 792	ONO_2 nonplanar rocking
B_1	a	ν_4 ca. 1520	NO_2 antisymmetric stretch
B_1	a	ν_5 ca. 717	ONO_2 planar rocking

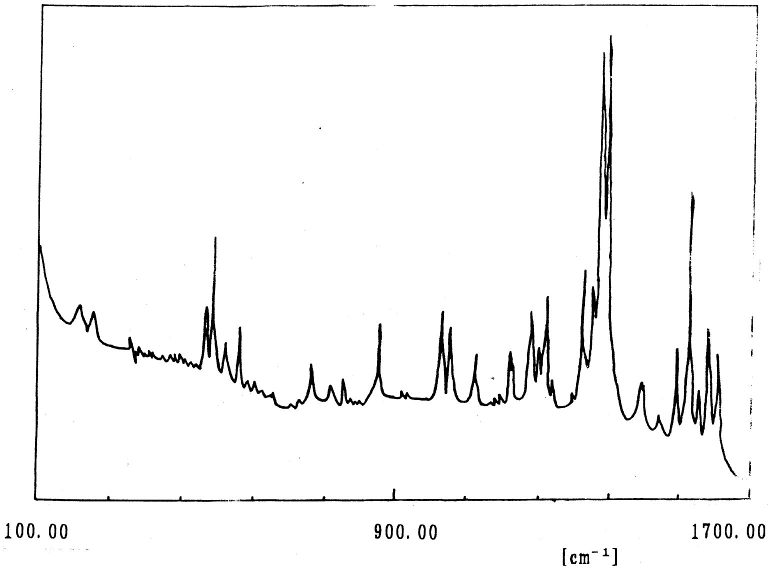


Fig. 2. Raman spectrum of Nd complex

that of $\nu_3 - \nu_5$ near 40 cm^{-1}. The magnitude of $\nu_4 - \nu_1$ for monodentate mode is in general in the region 100–120 cm^{-1} and that of $\nu_3 - \nu_5$ near 15 cm^{-1} [14,15].

The ν_1, ν_3, ν_4 and ν_5 values in our experiment are in the regions 1300–1308, 752–753, 1518–1520 and 716–717 cm^{-1} respectively. The $\nu_4 - \nu_1$ and $\nu_3 - \nu_5$ values are in the regions 212–218 and 36–39 cm^{-1}. The separation of two ($\nu_1 + \nu_4$ combination) bands in the 1700–1800 cm^{-1} region is in the 32–41 cm^{-1} range (Table 1).

These results indicate that the nitrate group is coordinated in a bidentate fashion.

3.2. Raman spectra

Table 4 gives Raman band frequencies of Schiff base ligand and its complexes. Fig. 2 shows Raman spectrum of the complex Nd. The –C=N stretching vibration of the Schiff base is at 1608 cm^{-1}. This band is shifted to 1640–1644 cm^{-1} in the complexes. It shows that the nitrogen of azomethine group is coordinated to the rare earth ion. The M–O symmetrical and antisymmetrical stretching vibration of the complexes are in the regions 476–479 and 493–495 cm^{-1} respectively.

The relative intensity sequence of the three highest frequency N–O stretching vibration bands for bidentate coordination differs from that for monodentate. For monodentate coordination, the medium frequency band is generally fairly strong. In contrast, for bidentate species the medium frequency is weak [11]. There are three bands, near 1017, 1264 and 1546 cm^{-1}, in our experiment. The medium frequency band, near 1264 cm^{-1}, is medium strong (Table 4) and the Raman band around 1550 cm^{-1} is polarized. It indicated that nitrate group is coordinated in a bidetate fashion.

4. Conclusion

In the complexes two Schiff bases and two nitrate group are all bound to the rare earth ion in a bidentate

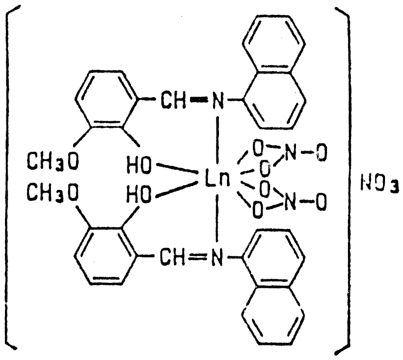


Fig. 3. Structure of the complexes. Ln: Lanthanide ions.

Table 4
Observed Raman freqencies of the complexes and ligands (cm^{-1})

Ligand	La	Pr	Nd	Sm	Eu	Tb	Dy	Ho	Tm	Yb	Assignment
469w											
	476m	476m	478m	479m	479m	479m	478m	478m	479m	479m	M–O stretch
	495s	493s	495s	495s	495s	495s	494s	495s	495s	495s	M–O stretch
501w	519m	521m	520m	522m	522m	523m	522m	522m	526m	527m	
550w	553m	553m	553m	553m	553m	554m	552m	554m	554m	553m	
718w	719w	717w	719w	720w	721w	720w	720w	719w	720w	719w	
766w	764w	765w	763w	762w	766w	766w	762w	764w	762w	765w	C–H out of plane band (benzene)
813m	791w	791w	791w	792w	790w	788w	792w	793w	795w	793w	
875w	874w	872w	874w	872w	873w	873w	874w	873w	871w	873w	C–H out of plane bend(naphthalene)
	1016m	1018m	1017m	1017m	1016m	1018m	1018m	1015m	1017m	1017m	N–O stretch (NO$_3^-$)
1032w	1033m	1034m	1036m	1036m	1035m	1038m	1036m	1035m	1036w	1035w	
1094m	1092m	1092m	1092m	1092m	1092m	1093m	1093m	1092m	1092m	1092m	
1161w	1165w	1169w	1168w	1164w	1168w	1169w	1165w	1167w	1168w	1168w	
1173w	1175w	1174w	1174w	1173w	1173w	1174w	1174w	1175w	1175w	1171w	
1215m	1214m	1215m	1216m	1217w	1216w	1216w	1218w	1217w	1221w	1221w	=C–O–C stretch (phenol)
1240w	1233m	1233m	1233m	1233m	1232m	1233m	1232m	1236m	1235m	1234m	
1250m	1248m	1251m	1250m	1249m	1250m	1251m	1250m	1247m	1249m	1250m	=C–O–C antisymmetric stretch (aryl ether)
	1262w	1262w	1263w	1265w	1265w	1264w	1264w	1265w	1265w	1267w	N–O stretch(NO$_3^-$)
1330w	1329w	1332m	1331m	1331m	1333m	1332m	1331m	1331m	1330m	1330m	
1356w	1351w	1352w	1352w	1354w	1353w	1353w	1352w	1351w	1354w	1355w	
1374s	1369s	1368s	1368s	1369s	1369s	1369s	1368s	1367s	1371s	1369s	N–C–
1390s	1383s	1384s	1385s	1385s	1385s	1386s	1385s	1387s	1387s	1387s	O–H in plane bend (phenol)
1443m											
1468m	1467w	1466w	1467w	1467w	1467w	1469w	1465s	1462s	1463s	1466s	
1510m		1502w	1498w	1494w	1503w	1502w	1496w	1492w	1498w	1495w	
	1544m	1545m	1545m	1547m	1545m	1547m	1547m	1546m	1547m	1548m	N–O stretch (NO$_3^-$)
1565m											
1574s	1572s	1573s	1574s	1571s	1576s	1574s	1575s	1575s	1574s	1575s	
1600m	1598m	1597m	1597m	1597m	1598m	1596m	1597m	1597m	1596m	1597m	C=C stretch (aryl ring)
1605s	1618s	1618s	1618s	1619s	1618s	1617s	1616s	1618s	1619s	1619s	C=N stretch
1617s	1641m	1641m	1641m	1641m	1641m	1642m	1640m	1644m	1640m	1640s	C=N stretch
1676w	1666w			1674w		1683w	1665w	1670w		1689	
1690w											

fashion, the other one nitrate group is at outer coordination sphere, which is proved by molar conductance measurement (1:1 electrolytic behaviour).

The probable structure of the complexes is shown in Fig. 3.

Acknowledgements

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References

[1] M. Melnik, Coord. Chem. Rev., 42 (1982) 259.
[2] H. Beinert, Coord. Chem Rev., 33 (1980) 259.
[3] E.I. Solornor, Pure Appl. Chem., 55 (1983) 1069.

[4] G.F. Liu, C.W. Na and B. Li, Kexue Tongbao, 34 (1989) 111.

[5] G.F. Liu, C.W. Na and B. Li, Jilin Daxue Ziran Kexue Xuebao, 1 (1991) 109.

[6] G.F. Liu, C.W, Na and B. Li, Synth. React. Inorg. Met.—Org. Chem., 20 (1990) 1387.

[7] G.F. Liu, C.W. Na and B. Li, Polyhedron, 9 (1990) 1387.

[8] B. Li, G.L. Zhao and G.F. Liu, Chinese J. Appl. Chem., 7 (1990) 70.

[9] G.F. Liu, Y.N. Zhao and X.X. Liu, Huaxue Xuebao, 50 (1992) 473.

[10] G.F. Liu and Y.F. Zhang, Gaodeng Xuexiao Huaxue Xuebao, 4 (1983) 82.

[11] C.C. Addison, N. Logan and S.C. Walwork, Quart Rev., 25 (1971) 289.

[12] R.M. Silverstein, G.C. Bassler and T.C. Morrill, Spectrometric Identification of Organic Compounds, John Wiley, 1974.

[13] K. Nakanshi and P.H. Sdomon, Infrared Absorption Spectroscopy, Holden-Dag, 1977.

[14] B.M. Gatehouse, S.E. Livingstone and R.S. Nyholm, J. Chem. Soc., (1957) 4222.

[15] N.F. Curtis and Y.M. Curtis, Inorg. Chem., 4 (1965) 804.