

Lanthanide(III) complexes of N-salicylideneglycine and N-(2-hydroxy-1-naphthylidene)glycine

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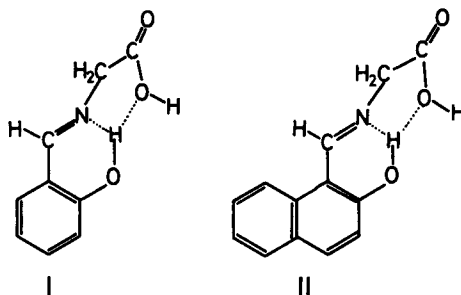
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Abstract. New lanthanide(III) complexes of N-salicylideneglycine and N-(2-hydroxy-1-naphthylidene)glycine have been prepared and characterized by elemental analytical, molar conductance, and IR and UV-visible spectral data. Both the ligands (H_2L) have been found to act as monobasic tridentate towards lanthanide ions, yielding complexes of the type $[Ln(HL)_2(NO_3)]$ and $[Ln(HL)_2(Cl)(H_2O)]$. The spectral data reveal that the HL moiety is bonded to the central atom through its phenolic oxygen, imine nitrogen and a carboxylate oxygen, and that the nitrate group acts as bidentate. From the observed pattern of hypersensitive $f-f$ bands, octacoordination is construed.

Keywords. Lanthanides; N-salicylideneglycine; N-(2-hydroxy-1-naphthylidene)glycine; hypersensitive visible bands.

1. Introduction

Although tridentate Schiff base complexes of d -block elements have been extensively investigated (Holm *et al* 1964; Csaszar 1982), reports on those of f -block elements are sparse and sporadic. The present paper describes synthesis and characterization of a few lanthanide complexes of N-salicylideneglycine (I) and N-(2-hydroxy-1-naphthylidene)glycine (II).



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2. Materials and methods

2.1 Materials

Chemicals used were either BDH 'AnalaR' or E. Merck GR quality. Lanthanide oxides (99.9% pure) used were from Indian Rare Earths. Commercial solvents were distilled and used for synthesis, but for physiochemical measurements, these were purified by standard methods.

2.2 Lanthanide salts

Lanthanide nitrate/chloride was prepared from the corresponding oxide by a reported method (De Sa *et al* 1975).

2.3 Synthesis of ligands

Potassium salts of the ligands were isolated by reported methods (Heinert and Martell 1962; Thankarajan and Mohanan 1986).

2.4 Synthesis of complexes

To a warmed and magnetically stirred ethanolic solution (100 ml) of potassium salt of the ligand (0.01 mol, pH adjusted to ~ 6) was added an ethanolic solution (10 ml) of lanthanide(III) salt hydrate (0.005 mol) and the pH of the mixture adjusted to 7 by adding ammonium hydroxide (1:20). After continued stirring for 7 h, the mixture was kept overnight, before filtering the powdery precipitate, which was washed successively with water, ethanol and acetone and dried *in vacuo*.

2.5 Analysis

The metal content of the complexes was determined through ignition to the metal oxide. Carbon, hydrogen and nitrogen percentages were obtained microanalytically (tables 1 and 2).

2.6 Physical methods

Infrared spectra in the range $4000\text{--}400\text{ cm}^{-1}$ were recorded on a Pye Unicam SP3-300 Infrared Spectrophotometer from both KBr disc and Nujol mull. A polytec FIR 30 Fourier Far IR spectrometer, and a Pye Unicam SP-1800, UV-Visible Spectrophotometer were used for far-IR and UV-visible spectral measurements respectively. Molar conductances of 10^{-3}M solutions were measured using a Toshniwal conductivity bridge at $28 \pm 0.2^\circ\text{C}$.

3. Results and discussion

Details regarding lanthanum(III), neodymium(III), cerium(III), samarium(III), gadolinium(III) and erbium(III) complexes prepared pure are presented in tables 1 and 2. All the complexes are stable except those of cerium(III) which are found to decompose on long exposure to air.

Table 1. Analytical data of lanthanide complexes of N-salicylidene glycine.

Complex	Yield (%)	Metal (%) found (calc)	Carbon (%) found (calc)	Hydrogen (%) found (calc)	Nitrogen (%) found (calc)
[La(HL) ₂ (NO ₃)]	62	24.57 (24.94)	38.65 (38.80)	2.71 (2.89)	7.57 (7.54)
[La(HL) ₂ (Cl)(H ₂ O)]	61	25.17 (25.32)	39.17 (39.38)	3.42 (3.31)	5.23 (5.10)
[Ce(HL) ₂ (NO ₃)]	59	25.39 (25.10)	38.79 (38.69)	2.68 (2.89)	7.45 (7.52)
[Nd(HL) ₂ (NO ₃)]	58	25.33 (25.65)	38.30 (38.41)	2.70 (2.87)	7.30 (7.47)
[Nd(HL) ₂ (Cl)(H ₂ O)]	61	25.73 (26.04)	39.22 (39.00)	3.37 (3.28)	5.19 (5.06)
[Sm(HL) ₂ (NO ₃)]	63	26.18 (26.45)	38.20 (38.00)	2.79 (2.84)	7.40 (7.39)
[Gd(HL) ₂ (NO ₃)]	65	27.19 (27.33)	37.68 (37.54)	2.72 (2.80)	7.40 (7.30)
[Er(HL) ₂ (NO ₃)]	60	28.71 (28.57)	36.85 (36.90)	2.65 (2.76)	7.05 (7.18)

Table 2. Analytical data of lanthanide complexes of N-(2-hydroxy-1-naphthylidene)glycine.

Complex	Yield (%)	Metal (%) found (calc)	Carbon (%) found (calc)	Hydrogen (%) found (calc)	Nitrogen (%) found (calc)
[La(HL) ₂ (NO ₃)]	66	21.31 (21.14)	47.31 (47.48)	3.15 (3.07)	6.29 (6.39)
[La(HL) ₂ (Cl)(H ₂ O)]	65	21.19 (21.42)	48.32 (48.11)	3.57 (3.41)	4.37 (4.32)
[Ce(HL) ₂ (NO ₃)]	57	21.10 (21.28)	47.27 (47.40)	3.01 (3.06)	6.30 (6.38)
[Nd(HL) ₂ (NO ₃)]	64	21.57 (21.78)	47.09 (47.10)	3.09 (3.04)	6.27 (6.34)
[Nd(HL) ₂ (Cl)(H ₂ O)]	62	22.33 (22.06)	47.61 (47.72)	3.48 (3.39)	4.37 (4.28)
[Sm(HL) ₂ (NO ₃)]	59	22.30 (22.49)	46.40 (46.67)	3.13 (3.02)	6.19 (6.28)
[Gd(HL) ₂ (NO ₃)]	60	23.51 (23.28)	46.10 (46.19)	2.89 (2.99)	6.20 (6.22)
[Er(HL) ₂ (NO ₃)]	59	24.79 (24.40)	45.33 (45.52)	2.90 (2.94)	6.17 (6.13)

The complexes could not be recrystallized owing to their poor solubility in suitable solvents. Yet, their analytical data are in good accord with their formulation as [Ln(HL)₂(NO₃)] and [Ln(HL)₂(Cl)(H₂O)]. From the observed conductances in DMF ($2.0 \pm 0.3 \text{ ohm s}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) these are evidently nonelectrolytes (Geary 1971).

Lanthanides show great affinity for chloride ions and water, which are avidly accommodated in the coordination sphere. Thus, no loss in weight was observed on heating the aqua complexes at 100°C *in vacuo* over P₄O₁₀.

Crystallographically, nitrate is invariably bidentate towards lanthanide ions (Bullock and Riahi 1980). Shortbite ligands like nitrate (bidentate) minimize

ligand-ligand repulsion, and are ideally suited to lanthanides because of their pronounced tendency to attain high coordination numbers. Eight is possibly the most characteristic coordination number of lanthanides (Moeller 1972). Since the composition of the complexes reported herein also demands this coordination number, these are presumably octacoordinate.

Intensity and shape of visible spectral (*f-f*) bands of lanthanide complexes are markedly affected by environment, and Karraker (1967) has shown that the pattern is indicative of coordination number. The hypersensitive bands of the Nd^{3+} complexes (at ≈ 560 nm) recorded in DMF, resembled closely the reported band shape of $(\text{CH}_3)_4\text{NH}[\text{Nd}(\text{Hfaa})_4]$, which is provenly octacoordinate. The nitrate complexes showed almost identical spectra as the aquahalo complexes, thus indicating the bidentate bonding of the nitrate group. Also, since the Nujol mull spectrum resembled the solution spectrum of each complex, the coordination number seems to remain unchanged in the solid state also. From the occurrence of a chloro or nitrate group in these neutral complexes, it is evident that the ligands (H_2L) are acting as monobasic (HL). Similar complexes of potentially dibasic tridentate ligands have been reported (De Sa *et al* 1975).

In agreement with the phenolimine-N-acetate tautomeric structure of the N-salicylidene-glycinate moiety (Burrows and Bailar 1966), the infrared spectra of its complexes showed a medium intense $\nu(\text{C}=\text{N})$ band at ≈ 1630 cm^{-1} , very strong bands at ≈ 1610 , and 1390 cm^{-1} for $\nu_a(\text{COO})$ and $\nu_s(\text{COO})$, respectively, and a strong broad $\nu(\text{O}-\text{H})$ band at ≈ 3400 cm^{-1} (nitrate complexes). In the spectra of the aqua complexes, the last mentioned band is overlapped by bands of coordinated water, so that a broad band with peaks at ≈ 3540 and 3410 cm^{-1} is observed in the 3600 – 3200 cm^{-1} region.

Infrared spectral data of complexes of N-(2-hydroxy-1-naphthylidene)glycine are closely similar to those of the N-salicylidene-glycine complexes, indicating thereby that the former ligand moiety exists as quinolimine-N-acetate. This is at first sight surprising, since in its transition metal complexes the N-(2-hydroxy-1-naphthylidene)glycinate(2-) moiety is present predominantly in the quinoneamine tautomeric form (Thankarajan and Mohanan 1986), unlike the N-salicylidene-glycinate(2-) moiety which exists in the phenolimine form in those complexes also (Burrows and Bailar 1966). It is generally accepted that interaction of the lanthanide ion with phenolic oxygen or amine nitrogen does not increase the acidity sufficiently for ionisation of the proton (De Sa *et al* 1975). In such a situation the positively polarized hydrogen atom should prefer the more electronegative oxygen atom, thus causing a shift in the tautomeric equilibrium from quinoneamine to quinolimine. Accordingly, the electronic spectra of complexes of both the ligands showed a strong band at ≈ 335 nm characteristic of the phenolimine form, and no band at ≈ 400 nm for the quinoneamine form (Thankarajan and Mohanan 1986). ^1H NMR spectra, which could have been instructive in this regard, however, could not be recorded due to low solubility in suitable solvents.

As expected for bidentate bonding by nitrate group, bands are observed in the infrared spectra of the nitrate complexes at 1475 , 1290 and 1025 cm^{-1} assignable to $\nu(\text{N}=\text{O})$, $\nu_a(\text{NO}_2)$ and $\nu_s(\text{NO}_2)$, and the separation of the first two bands is 185 cm^{-1} , as against ≈ 115 cm^{-1} expected for monodentate bonding (Gatehouse *et al* 1957). Comparison of the spectra with those of the corresponding aquachloro complexes, has been helpful in identifying the above bands amidst

bands due to phenolic ν (C–O), ν_s (COO) and δ (C–H) modes. From the $\Delta\nu$ (COO) observed in the spectra of the complexes ($> 200 \text{ cm}^{-1}$) it is evident that the carboxylate is acting as a monodentate ligand (Nakamoto 1978). Ranges observed for ν (M–N), ν (M–O) and ν (M–Cl) in the far IR spectra of the complexes of either ligand, are $235\text{--}245 \text{ cm}^{-1}$, $220\text{--}230 \text{ cm}^{-1}$ and $200\text{--}210 \text{ cm}^{-1}$ respectively, and are fully in agreement with those reported for similar complexes (Agarwal and Tandon 1979).

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