

## Synthesis and Characterization of some Lanthanide(III) Chelates of some Schaffer Acid Azo Dyes

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**Summary.** A series of trivalent lanthanide chelates of the type  $[Ln(PHNSA)(H_2O)_n](2Cl)$  (where  $Ln^{3+} = Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb$  or  $Lu$ ;  $PHNSA = 2-(X)$ -phenylazo-2-hydroxynaphthalene-6-sulphonic acid;  $X = H, Cl, OCH_3, CH_3$  and  $SO_3H$ ) have been synthesized and characterized by elemental and thermal analysis, molar conductance, IR,  $^1H$  NMR (for diamagnetic complexes), electronic spectra and magnetic susceptibility measurements. IR data along with those of the  $^1H$  NMR unequivocally proved that the coordination of the ligands to the metal ions took place in a bidentate fashion through the oxygen of the hydroxyl group and the nitrogen of the azo group. The magnetic moment values showed little deviation from Van Vleck values.

**Keywords.** Lanthanide(III) chelates; Schaffer acid azo dyes;  $^1H$  NMR; IR; Electronic spectra.

### Synthese und Charakterisierung einiger Lanthaniden(III)-Chelate von Schaffersäure-Azofarbstoffen

**Zusammenfassung.** Es wurde eine Reihe von dreiwertigen Lanthanidenchelaten des Typs  $[Ln(PHNSA)(H_2O)_n](2Cl)$  (mit  $Ln^{3+} = Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb$  oder  $Lu$  und  $PHNSA = 2-(X)$ -Phenylazo-2-hydroxynaphthalin-6-sulphonsäure,  $X = H, Cl, OCH_3, CH_3$  und  $SO_3H$ ) synthetisiert und mittels Elementar- und thermischer Analyse, molarer Leitfähigkeit, IR,  $^1H$ -NMR (für diamagnetische Komplexe), Elektronenspektren und Messungen der magnetischen Suszeptibilität charakterisiert. Die IR-Daten zusammen mit  $^1H$ -NMR-Befunden zeigten eindeutig, daß die Koordinierung der Liganden zum Metallion zweizählig durch den Sauerstoff der Hydroxylgruppe und den Stickstoff der Azo-Gruppe erfolgt. Die magnetischen Momente zeigten nur eine geringe Abweichung von den Van Vleck-Werten.

### Introduction

The chemistry of the azo derivatives of 2-hydroxynaphthyl-6-sulphonic acid (Schaffer acid) has attracted special interest due to their use as food dyestuffs and as chromophoric reagents for many metal ions [1–3]. While there are some informations about transition metal complexes with Schaffer acid azo dyes [4–6], little is known about lanthanide complexes with such ligands. In this paper we wish to report the synthesis and characterization of some lanthanide ions complexes of *PHNSA*.

## Experimental Part

All chemicals used were pure BDH or Merck products and were used without further purification. The Schaffer acid azo dyes 1–5 were prepared as previously recommended [7] by coupling the corresponding amines in sodium hydroxide medium. After recrystallization from ethanol, their purities were confirmed by elemental analysis, IR and  $^1\text{H}$  NMR spectra.

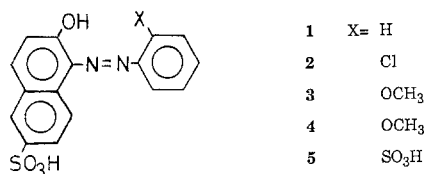
The lanthanide(III) chelates were prepared by refluxing an ethanolic mixture of lanthanide(III) chloride (1 mmol) and the ligand (1 mmol) for about 6 h. On cooling the solution mixture to room temperature, a crystalline solid was obtained, filtered, washed with ethanol and dried in vacuo over  $\text{P}_2\text{O}_5$ . Analytical data along with the electrolytic conductance in *DMF* are given in Table 1.

*Analysis.* Carbon, hydrogen and nitrogen analysis were carried out in the Micro analytical laboratory, Cairo University, Cairo, Egypt. Lanthanides were analysed by *EDTA* titration after decomposition of the chelates according to a reported procedure [8].

*Physical Methods.* Conductance measurements were carried out using a YSI Model 32 conductance meter of cell constant  $K=1$ . The IR spectra ( $200-4000\text{ cm}^{-1}$ ) were recorded as KBr discs using a Beckman IR 4200 double beam spectrophotometer.  $^1\text{H}$  NMR spectra were run on a Varian T-60 A 90 MHz spectrometer in *DMSO-d*<sub>6</sub>, chemical shifts are reported relative to *TMS* as internal standard. Thermogravimetric analysis (TGA-DTA) were recorded on a STA-409 Netzsch DTA-TGA analyzer in the range  $25-1000^\circ\text{C}$  with  $10^\circ\text{C}/\text{min}$  heating rate using air as atmosphere. UV-visible spectra of the solid complexes were recorded in solution (*DMF*) and in the solid state (nujol mull) using a Perkin-Elmer  $\lambda_{3B}$  spectrophotometer. Magnetic susceptibilities of the chelates at room temperature were measured on a standard Faraday balance, using  $\text{HgCo}(\text{NCS})_4$  as susceptibility standard. Diamagnetic corrections were estimated using Pascal's constants.

## Results and Discussion

The analytical data for all the isolated complexes gave a satisfactory agreement with the expected formula. Almost all the chelates are quite hygroscopic, and all are soluble in *DMF* but insoluble in other common organic solvents. Molar conductance values in *DMF* indicate the ionic nature of the chelates and the presence of anions outside the coordination sphere which is confirmed by the precipitation of  $\text{AgCl}$  by addition of  $\text{AgNO}_3$  to the solubilized chelates in *DMF*.



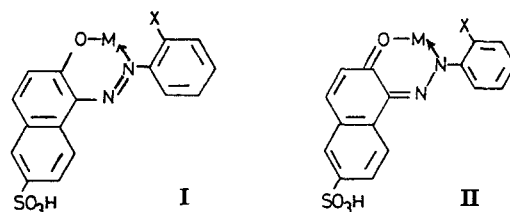
TGA data of some selected chelates show that they lose their water of coordination within the range  $120-150^\circ\text{C}$  followed by the removal of chloride ions from the solid chelates in the temperature range  $180-195^\circ\text{C}$ . All the anhydrous complexes show thermal stability up to  $450^\circ\text{C}$  above which decomposition of the complex species takes place leading to the formation of  $\text{Ln}_2\text{O}_3$  as a final product. The number of coordinated water molecules, chloride ions as well as the percent of  $\text{Ln}^{3+}$  were calculated from the corresponding inflections on the TG curves whose values were in satisfactory agreements with those obtained from elemental analysis.

The paramagnetic behaviour of the lanthanide(III) ions is consistent with the presence of unpaired 4f electrons. Since these electrons are well-shielded by  $5s^2$

**Table 1.** Analytical, molar conductance and magnetic data for some lanthanide(III) chelates (coordination sphere derived from molar conductance and elemental analysis)

Compound	Analysis [Calc. (found)] %				M	$\mu_{\text{eff.}}$ (298 K)
	C	H	N	M		
[Pr <sub>2</sub> ·6 H <sub>2</sub> O] <sup>2+</sup> ·2 Cl <sup>-</sup>	28.091 (27.81)	3.66 (3.71)	4.10 (4.02)	20.62 (20.42)	131.3	3.59
[Nd <sub>2</sub> ·5 H <sub>2</sub> O] <sup>2+</sup> ·2 Cl <sup>-</sup>	28.71 (28.50)	3.44 (3.20)	4.19 (3.99)	21.57 (21.88)	98.40	3.51
[Sm <sub>2</sub> ·6 H <sub>2</sub> O] <sup>2+</sup> ·2 Cl <sup>-</sup>	29.23 (29.40)	3.81 (29.40)	4.26 (4.42)	22.89 (22.60)	151.20	1.80
[Eu <sub>2</sub> ·6 H <sub>2</sub> O] <sup>2+</sup> ·2 Cl <sup>-</sup>	27.65 (27.50)	3.60 (4.00)	4.03 (4.13)	21.88 (21.60)	150.80	
[Gd <sub>2</sub> ·6 H <sub>2</sub> O] <sup>2+</sup> ·2 Cl <sup>-</sup>	26.06 (26.00)	3.57 (3.66)	4.00 (4.13)	22.47 (22.55)	143.13	7.86
[Dy <sub>2</sub> ·5 H <sub>2</sub> O] <sup>2+</sup> ·2 Cl <sup>-</sup>	27.95 (28.01)	3.35 (3.50)	4.08 (4.21)	23.65 (23.55)	188.34	10.22
[Er <sub>2</sub> ·5 H <sub>2</sub> OCl] <sup>+</sup> ·Cl <sup>-</sup>	27.76 (27.50)	3.33 (3.38)	4.05 (4.17)	24.18 (24.30)	62.43	
[Yb <sub>2</sub> ·6 H <sub>2</sub> OCl]Cl <sup>-</sup>	26.83 (26.70)	3.49 (3.60)	3.91 (4.00)	24.18 (24.00)	72.18	4.20
[Lu <sub>2</sub> ·6 H <sub>2</sub> O] <sup>2+</sup> ·2 Cl <sup>-</sup>	26.76 (26.70)	3.49 (3.60)	3.90 (3.81)	24.39 (24.50)	120.41	diamagnetic
[Nd <sub>3</sub> ·5 H <sub>2</sub> O] <sup>2+</sup> ·2 Cl <sup>-</sup>	30.71 (30.60)	3.91 (4.00)	4.22 (4.10)	21.72 (21.66)	114.32	3.49
[Sm <sub>3</sub> ·6 H <sub>2</sub> O] <sup>2+</sup> ·2 Cl <sup>-</sup>	29.64 (30.00)	4.07 (4.15)	4.07 (4.02)	21.84 (21.70)	135.81	1.56
[Gd <sub>3</sub> ·5 H <sub>2</sub> OCl] <sup>+</sup> ·Cl <sup>-</sup>	30.12 (30.22)	3.84 (3.70)	4.13 (4.20)	23.22 (23.12)	55.31	7.88
[Dy <sub>3</sub> ·6 H <sub>2</sub> O] <sup>2+</sup> ·2 Cl <sup>-</sup>	30.70 (30.60)	4.21 (4.11)	4.21 (4.25)	24.46 (24.50)	131.6	10.24
[Er <sub>3</sub> ·6 H <sub>2</sub> O] <sup>2+</sup> ·2 Cl <sup>-</sup>	28.93 (29.03)	3.97 (3.87)	3.97 (4.00)	23.72 (23.60)	140.20	
[Yb <sub>3</sub> ·5 H <sub>2</sub> OCl] <sup>+</sup> ·Cl <sup>-</sup>	29.44 (29.30)	3.75 (3.60)	4.04 (4.14)	24.97 (24.80)	70.14	4.35
[Lu <sub>3</sub> ·6 H <sub>2</sub> O] <sup>2+</sup> ·2 Cl <sup>-</sup>	28.16 (28.20)	3.93 (3.99)	3.93 (3.82)	24.54 (24.40)	98.17	diamagnetic
[Pr <sub>4</sub> ·6 H <sub>2</sub> O] <sup>2+</sup> ·2 Cl <sup>-</sup>	30.77 (30.52)	4.22 (4.15)	4.22 (4.30)	21.26 (21.30)	115.20	3.61
[Nd <sub>4</sub> ·6 H <sub>2</sub> O] <sup>2+</sup> ·2 Cl <sup>-</sup>	30.62 (30.70)	4.20 (4.15)	4.20 (4.31)	21.65 (21.41)	142.72	3.49
[Sm <sub>4</sub> ·5 H <sub>2</sub> O] <sup>2+</sup> ·2 Cl <sup>-</sup>	31.18 (31.23)	3.97 (4.03)	4.28 (4.18)	22.98 (23.10)	173.10	1.88
[Eu <sub>4</sub> ·6 H <sub>2</sub> O] <sup>2+</sup> ·2 Cl <sup>-</sup>	30.27 (30.30)	4.16 (4.09)	4.16 (4.18)	22.55 (22.40)	162.41	
[Gd <sub>4</sub> ·6 H <sub>2</sub> O] <sup>2+</sup> ·2 Cl <sup>-</sup>	30.03 (30.25)	4.12 (4.19)	4.12 (4.20)	23.15 (23.60)	161.32	7.86
[Dy <sub>4</sub> ·4 H <sub>2</sub> O] <sup>2+</sup> ·2 Cl <sup>-</sup>	31.46 (31.70)	3.70 (3.82)	4.31 (4.12)	25.06 (25.15)	162.1	9.81
[Er <sub>4</sub> ·5 H <sub>2</sub> OCl] <sup>+</sup> ·Cl <sup>-</sup>	30.39 (30.45)	3.87 (3.70)	4.17 (4.22)	24.92 (24.80)	47.33	
[Lu <sub>4</sub> ·6 H <sub>2</sub> O] <sup>2+</sup> ·2 Cl <sup>-</sup>	29.27 (29.38)	4.02 (4.12)	4.02 (4.17)	25.10 (25.18)	113.71	diamagnetic

5 p<sup>6</sup> octet both in their spin and orbital motion, the magnetic movement of a chelate should indicate whether these 4f electrons take part in bond formation or not. The magnetic moments of the present lanthanide(III) chelates, recorded in Table 1, show little deviation from the Van Vleck values [9] and those reported for 8-hydrated sulphates [10], suggesting thereby that 4f electrons do not participate in bond formation. On the other hand, the values of the corrected gram susceptibilities



of Lu-complexes amounted to  $\approx 1.33 \cdot 10^{-6}$  emu/gm indicating the diamagnetic character of these complexes, the fact which is expected since elemental analysis and molar conductance measurements showed that Lu interacts in chelate formation via its (+III) oxidation state.

The  $^1\text{H-NMR}$  spectra of the organic ligands in  $\text{DMSO-}d_6$  are compared with those of the diamagnetic Lu(III) complexes in the same solvent and at the same temperature. The most interesting signal is that appearing at very low field, i. e. at  $\delta = 11.60 - 11.82$  ppm, which disappears in presence of  $\text{D}_2\text{O}$ ; it is attributed to the hydrogen-bonded hydroxyl group in *o*-position to the azo linkage. In all Lu(III) complexes this signal completely disappeared indicating that complex formation takes place through proton elimination from the azo form I and not the hydrazo form II. This is also supported by IR data.

The signals of the aromatic protons (7.30 – 8.25 ppm) of the free ligands show some shifts downfields in the spectra of the solid chelates due to the deshielding effect of the metal ion on the ligand protons as a results of coordination process. The shift of the aromatic signals is expected since the formation of the *M-N* or *M-O* bond withdraws electrons from the aromatic ring resulting in a deshielding of the proton on the carbon atom adjacent to the azo group.

In case of the Lu-5 complex, the strong signal found at 4.7 ppm due to the  $\text{SO}_3\text{H}$  proton in the free ligand completely disappeared indicating the dibasic character of the ligand. On the other hand, the signal at 3.55, and 2.7 ppm for ligands 3 and 4 (corresponding to the  $\text{OCH}_3$  and  $\text{CH}_3$  protons) shifted slightly to lower field in the spectra of their Lu-complexes indicating some sort of deshielding due to complex formation.

In the UV-visible region (200 – 500 nm), the free ligands exhibit three absorption bands within the ranges 205 – 220, 230 – 265 and 320 – 400 nm which can be assigned to the moderate energy  $\pi - \pi^*$  transition corresponding to the ( $^1\text{L}_a \leftarrow ^1\text{A}$ ) state, the low energy  $\pi - \pi^*$  transition due to the ( $^1\text{L}_b \leftarrow ^1\text{A}$ ) state within the aromatic moieties and finally to the charge transfer interaction within the whole molecule. However, the electronic spectra of lanthanide(III) chelates are dominated by ligand absorption bands with a hyperchromic effect. The domination of the ligand absorption bands could be related to the high absorption coefficient of the ligands as compared to  $\text{Ln}^{3+}$  ions which masks any splitting of the band [11].

The IR spectra of the dehydrated solid complexes are recorded and compared with those of the free ligands. Such comparison showed that the broad band within the range  $3300 - 3425 \text{ cm}^{-1}$  corresponding to  $\nu \text{ OH}$  disappears on complex formation; the  $\nu \text{ N}=\text{N}$  band of the free ligands found at  $1437 - 1410 \text{ cm}^{-1}$  shifts to lower frequencies by  $\approx 20 - 30 \text{ cm}^{-1}$  on complex formation suggesting that complex formation takes place through simple covalent and coordinate bonds with the oxygen atom of the hydroxyl group and the nitrogen atom of the azo group, respectively. This also confirms that the azo structure and not the hydrazo form of the ligand is involved in complex formation. The IR spectra of all compounds under investigation show two bands within the range  $1620 - 1580 \text{ cm}^{-1}$  which can be attributed to the  $\text{C}=\text{C}$  ring absorption suffering a very small shift on complex formation. In the far IR region, all  $\text{Ln(III)}$  chelates show bands of varying intensity at  $240 \text{ cm}^{-1}$  and  $215 \text{ cm}^{-1}$  due to ( $\text{Ln-N}$ ) and ( $\text{Ln-O}$ ), respectively [11].

Thus the analytical and conductivity data, as well as the IR and electronic spectral data suggest that the lanthanide(III) ions are surrounded by coordinated

water molecules and one ligand molecule bound in a bidentate O, N fashion forming a coordination number of eight.

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