

Study of Y(III), La(III) and Ce(III) solid compounds of 1-phenylazo-2-naphthol-3,6-disulphonic acid and its *p*-nitroderivative

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Abstract. The solid compounds of Y(III), La(III) and Ce(III) with 1-phenylazo-2-naphthol-3,6-disulphonic acid (disodium salt) and its *p*-nitroderivative were synthesized. The nature, composition and structure of the isolated solids have been elucidated by elemental analysis, conductometric titrations, UV-Vis and IR. It may be assumed that in both reagents the bond is only due to the sulphonic groups.

Keywords. 1-phenylazo-2-naphthol-3,6-disulphonic acid; *p*-nitrophenylazo-2-naphthol-3,6-disulphonic acid; rare earth metals; azo dyes.

1. Introduction

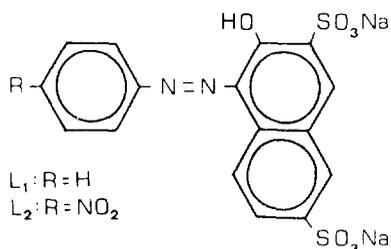
The chemical literature provides ample information on the complex combinations of rare earth metal ions with azo dyes, but there is considerable disagreement in regard to which groups are coordinated to the metal ion (Manku *et al* 1971; Pesavento *et al* 1979; Buděšínský 1968; Zenki 1976).

The rare earth metal ions, which contain pairs of nonbonding 4*f* electrons, are effectively shielded from interaction with ligand orbitals by electrons in the 5*s* and 5*p* orbitals. If hybridization is to occur, it must involve normally unoccupied higher-energy orbitals and hybridization of this type can only be expected with ligands containing highly electronegative donor atoms (e.g., oxygen) (Moeller 1963). These cations are thus of the A-type (i.e. hard Lewis acids) (Ahrland *et al* 1958) and therefore, they have an affinity for hard Lewis bases. Since the sulphonated azo dyes are ligands which include in their molecules nitrogen and oxygen donor atoms, they are in fact hard Lewis bases (Pearson 1963).

In a previous paper (Capitán *et al* 1984) we investigated the reduction of 1-phenylazo-2-naphthol-3,6-disulphonic acid (disodium salt) on a mercury electrode. This reduction can be applied to the polarographic determination of Ba(II) (Capitán *et al* 1986). Later we studied the combinations of Sr(II) and Pb(II) with this reagent (Capitán *et al*, 1988). Here, we present the results of our research on the solid compounds of Y(III), La(III) and Ce(III) with two

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sulphonated azo dyes, 1-phenylazo-2-naphthol-3,6-disulphonic acid (disodium salt) (L_1) and its *p*-nitro derivative (L_2).



2. Experimental

2.1 Material and solutions

All reagents used were of analytical grade. Sulphonated azo dyes were prepared and purified by methods described earlier (Capitán *et al* 1985, 1988).

2.2 Synthesis and analysis of the solids

Solid compounds were prepared by mixing aqueous solutions of the azo dyes (disodium salts) and the metal salts (nitrates) containing the appropriate quantities of the reactants in molar ratios (reagent:metal = 2:1). The products were filtered, washed with distilled water and dried in vacuum over $CaCl_2$. The compounds obtained are solid substances, coloured in various shades of red depending on the metal. They are insoluble in organic solvents, with the exception of dimethylsulphoxide and dimethylformamide.

Results of the elemental chemical analyses carried out on these compounds are given in table 1. These results suggest ML_2 stoichiometry in all cases and agree with

Table 1. Properties and analytical data of azo dyes solid compounds

Compound	Decomposition temperature (°C)	% Found (Calcd.)				
		C	H	N	Me	Na
YNa $(C_{16}H_{10}N_2O_7S_2)_2 \cdot 8H_2O$	280	35.72 (35.95)	3.20 (3.37)	5.14 (5.24)	8.13 (8.32)	2.23 (2.15)
LaNa $(C_{16}H_{10}N_2O_7S_2)_2 \cdot 8H_2O$	290	33.54 (34.35)	3.18 (3.22)	5.15 (5.01)	12.27 (12.42)	1.97 (2.05)
CeNa $(C_{16}H_{10}N_2O_7S_2)_2 \cdot 8H_2O$	280	35.06 (34.32)	3.20 (3.22)	4.90 (5.00)	12.30 (12.51)	1.94 (2.05)
YNa $(C_{16}H_9N_3O_9S_2)_2 \cdot 8H_2O$	280	33.25 (33.16)	3.00 (2.93)	7.00 (7.25)	7.78 (7.68)	1.88 (1.98)
LaNa $(C_{16}H_9N_3O_9S_2)_2 \cdot 8H_2O$	280	31.77 (31.79)	2.80 (2.81)	7.19 (6.95)	12.00 (11.50)	2.00 (1.90)
CeNa $(C_{16}H_9N_3O_9S_2)_2 \cdot 8H_2O$	280	30.78 (31.76)	2.76 (2.81)	6.92 (6.95)	12.02 (11.58)	1.80 (1.90)

the determination of its composition by conductometric titrations of the metal ions with reagents. All of them are in the ratio 2:1 (reagent:metal).

2.3 Apparatus and methods

Conductometric titrations were carried out with a Radiometer CDM-2e conductimeter at $25 \pm 0.1^\circ\text{C}$. A Carlo Erba 1106 Elemental Analyzer was used.

Infrared spectra of samples in KBr pellets were recorded in the region of $4000\text{--}200\text{ cm}^{-1}$, using a Perkin Elmer 983 IR spectrophotometer and the spectra of samples in polyethylene pellets were similarly recorded in the region of $600\text{--}200\text{ cm}^{-1}$.

The electronic spectra were recorded with a UV-Vis Bausch-Lomb Spectronic 2000 spectrophotometer using 1 cm quartz cells.

3. Results and discussion

3.1 IR spectra

The characteristic infrared frequencies assigned to reagents and their solid compounds are given in table 2. A strong and broad band is found in the region $3500\text{--}2900\text{ cm}^{-1}$ in the IR spectra of the reagents and their solids. This band can be assigned to the stretching vibration of the OH group.

The band which appears both in the reagents and their respective solids around $1598\text{--}1615\text{ cm}^{-1}$ may be due to the carbonyl group, so that all compounds are in the phenylhydrazone form (Hadzi 1956), and this suggests that the oxygen atom of the phenolic group has not taken part in the reaction (Ueno 1957). The band around 1480 cm^{-1} is attributed to a combined vibration, involving the NH bending and some skeletal stretching motion (Hadzi 1956). A weak intensity band appears in reagents in the region $1450\text{--}1390\text{ cm}^{-1}$, which is attributable to the $\text{N}=\text{N}$ stretching vibration, and persists in the solid compounds which shows that coordination has not taken place through the azo nitrogen (Ueno 1957).

Changes in the IR spectra appear in the bands attributable to the sulphonic groups: disappearance of the band at 1055 cm^{-1} , appearance of the bands around 1230 , 1170 and 1150 cm^{-1} and the band at 1190 cm^{-1} is reduced in intensity. It suggests that the oxygen atom of this group is a bonding site of the reagents. Furthermore, new absorption bands around 610 , 580 and 430 cm^{-1} for the solid combinations of L_1 and around 430 and 415 cm^{-1} for the solid combinations of L_2 were observed in these IR spectra. They were assigned to the stretching vibration of the metal atom with the oxygen atom of the sulphonic groups (Ferraro 1971).

3.2 UV-visible spectra

The electronic spectra of L_1 in dimethylsulphoxide show three bands (486 , 420 and 320 nm) whereas L_2 has four bands (495 , 450 , 333 and 300 nm). The maximum wavelength band of both reagents ($\log \epsilon = 4.13$ for L_1 and $\log \epsilon = 4.37$ for L_2) was assigned to the forbidden transition $n \rightarrow \pi^*$ and is attributed to the hydrazone form. The shoulders noticed at 420 nm ($\log \epsilon = 3.91$) and 450 nm ($\log \epsilon = 4.18$) respectively were assigned to the allowed transition $\pi \rightarrow \pi^*$ and are due to the azo form. The bands located at 320 nm ($\log \epsilon = 3.88$) and 333 nm ($\log \epsilon = 3.94$) were

Table 2. Some characteristic IR frequencies of sulphonated azo dyes and their solid compounds (cm^{-1})

Compound	νOH	$\nu\text{C}=\text{O}$	δNH	$\nu\text{N}=\text{N}$	νSO_3	$\nu\text{Me}-\text{O}-\text{SO}_2$	νNO_2
$\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_7\text{S}_2\text{Na}_2$ (L_1)	3462 s	1615 m	1476 m	1450 w	1190 s, 1055 m 1039 s		
YNa ($\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_7\text{S}_2$) ₂	3400 s	1614 m	1476 m	1450 w	1232 w, 1192 m 1039 s, 1172 m	613 w, 581 m 435 w	
LaNa ($\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_7\text{S}_2$) ₂	3390 s	1612 m	1476 m	1450 w	1232 w, 1196 m 1038 s, 1170 m, 1152 m	612 w, 579 m 430 w	
CeNa ($\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_7\text{S}_2$) ₂	3388 s	1612 m	1476 m	1450 w	1232 w, 1190 m 1036 s, 1170 m, 1154 m	613 w, 579 m 430 w	
$\text{C}_{16}\text{H}_9\text{N}_3\text{O}_9\text{S}_2\text{Na}_2$ (L_2)	3432 s	1598 m	1480 m	1391 w	1192 s, 1055 m 1037 s		1550 m, 1341 s
YNa ($\text{C}_{16}\text{H}_9\text{N}_3\text{O}_9\text{S}_2$) ₂	3410 s	1598 m	1480 m	1388 w	1225 w, 1193 m 1040 s, 1158 m	430 m	1550 m, 1340 s
LaNa ($\text{C}_{16}\text{H}_9\text{N}_3\text{O}_9\text{S}_2$) ₂	3417 s	1598 m	1480 m	1389 w	1225 w, 1193 m 1039 s, 1158 m	428 m, 415 w	1550 m, 1347 s
CeNa ($\text{C}_{16}\text{H}_9\text{N}_3\text{O}_9\text{S}_2$) ₂	3414 s	1598 m	1480 m	1388 w	1225 w, 1192 m 1038 s, 1158 m	418 m	1550 m, 1346 s

Abbreviations: s-strong; m-medium; w-weak

assigned to the allowed transition $\pi \rightarrow \pi^*$, ascribed to conjugation between the $-\text{N} = \text{N}-$ group and the aromatic nucleus. The band at 300 nm ($\log \epsilon = 3.93$), present only in the *p*-nitro derivative, is assigned to a $n \rightarrow \pi^*$ type transition and is attributed to the nitro group. These assignments have been discussed previously (Capitán *et al* 1985, 1988). For the present purpose, it is noteworthy that the electronic spectra of the solid compounds do not undergo bathochromic shifts; it indicates that neither the azo nitrogen nor the oxygen atom of the phenolic group are bonding sites of reagents (Yagi 1964). It also supports the conclusions reached from the infrared data.

4. Conclusions

The presence of a carbonyl group and an NH group in the IR spectra proves that the compounds are in the hydrazone form in the solid state. The electronic absorption indicates that the azo form is also present in the solid and in substantial amounts; the presence of both forms in the solid implies a significant contribution of a zwitterionic form (Hadzi 1956).

The present research shows that the metal ion binds with the reagents only through the sulphonic groups. It proves that the solid species formed by rare earth metal ions resemble those derived from alkaline earth metal ions (Moeller 1963; Capitán *et al* 1986, 1988).

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