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Rare Earth Complexes of 1-(2-Pyridylazo)-2-naphthol

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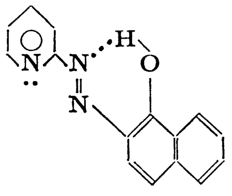
The rare earth complexes of 1-(2-pyridylazo)-2-naphthol (PAN=Hpan) are prepared in the solid state. The analytical, molecular weight and differential thermal analysis data of the complexes indicated the metal-ligand ratio as 1:3 with the general formulae $Ln(pan)_3 \cdot H_2O$ ($Ln=Pr^{3+}$, Nd^{3+}, and Sm^{3+}) and $Ln(pan)_3$ ($Ln=La^{3+}$, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, and Yb^{3+}). Based on IR, UV, and visible absorption spectra, electrical conductance and magnetic susceptibility data, an octahedral structure having the metal ion bonded through nitrogen of azo and oxygen of carbonyl groups of the ligand has been postulated to these complexes.

The solvent extraction and the potentiometric studies of the complexes of lanthanoids with 1-(2-pyridylazo)-2-naphthol(I), (hereafter referred as PAN=Hpan) have been reported in the literature.[1-4] Besides, PAN has also been used for the detection and the spectrophotometric determination of a large number of metal ions.[5-11] But the synthesis and the characterization of its rare earth metal complexes in the solid state have not so far been reported. In this communication we report the preparation of the lanthanoid complexes of PAN in the solid state. Their probable structures have been established using analytical, IR, UV, and visible spectra, magnetic moment, conductivity, differential thermal analysis, and molecular weights data.



I

Experimental

All the chemicals used are of Analar or chemically pure grade. PAN (Riedel) was recrystallised from ethanol.[12]

Preparation of the Complexes. On slowly mixing a solution of 1 mmol of rare earth chloride in ethanol (10 ml) with a solution of 1 mmol of PAN in ethanol (40 ml) and adjusting its pH between 8 and 10 by dropwise addition of NaOH solution(0.1 M),** a dark red coloured thick precipitate was obtained. The slurry was then cooled to about 3—4 °C and kept at this temperature for 24 h. The precipitate was separated by centrifugation and it was then extracted several times with ether until the ether layer acquired no colour. The combined ethereal extract was evaporated to dryness whereby the red coloured complex of the lanthanoid was obtained. It was then kept in vacuum desiccator for about 24 h and analysed. Yield 20—25%.

In the above preparation the amount of PAN added to the metal ion solution was always less than the stoichiometric amount (1:1, in place of 3:1). If excess PAN was used, it gets extracted along with the complex into the ether layer which was difficult to remove. By using excess lanthanoid salt, its hydroxide which precipitates along with the metal complex remained unextracted in the ethereal layer.

Analysis. The analyses of the metal ions were carried out gravimetrically by the standard oxalate method.[13,14)]

Carbon, hydrogen and nitrogen analyses were performed by the Micro Analytical Section of the Indian Institute of Technology, Kanpur. The analytical results are given in Table 1.

Measurements. The molecular weights of the complexes were determined cryoscopically. The measurements were carried out in purified benzene. The results are given in Table 1.

Magnetic susceptibility measurements were made using a Gouy balance at room temperature (28 °C). Mercury tetrathiocyanatocobaltate(II) was used as a calibrant. The results are given in Table 1.

The conductivity of the complexes were measured in *N,N'*-dimethyl formamide using Philips PR 9500/90 type Conductivity Measuring Bridge. The results are given in Table 2.

The electronic spectra of the ligand and the complexes were obtained in chloroform solutions using a Cary Model 14 Recording spectrophotometer. Their IR spectra were recorded with a Perkin-Elmer 521 Infrared Diffraction Grating spectrophotometer in 4000—250 cm^{-1} range. The samples were prepared as KBr pellets. Positions and assignments of the IR spectral bands of the ligand and the complexes are given in Table 3.

The differential thermal analytical curves were taken on DTA-02 UNIVERSAL (VEB Laborelektronik, Halle, DDR).

Results and Discussion

The analytical data of the complexes indicate the metal ligand ratio as 1:3 with the general formulae $Ln(C_{15}H_{10}N_3O)_3 \cdot H_2O$ ($Ln=Pr^{3+}$, Nd^{3+}, and Sm^{3+}) and $Ln(C_{15}H_{10}N_3O)_3$ ($Ln=La^{3+}$, Eu^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Yb^{3+}, and Gd^{3+}). Their monomeric nature in solution is confirmed by the experimental values of the molecular weights (Table 1).

The equivalent conductance values of the complexes in DMF at 28 °C when compared with those already reported[15] indicate that they are non-electrolytes. This is further supported by their insolubility in water, and high solubility in most of the non-aqueous solvents like $CHCl_3$, CCl_4, ether, C_6H_6, *etc.* These complexes when dissolved in organic solvents are not very stable and the deep red coloured solution gradually changes to orange yellow.

PAN has been reported to be a tridentate ligand where the bonding sites to the metal ion are oxygen of the hydroxyl group after deprotonation, azo and the pyridine nitrogen atoms.[8,16-18] In order to investigate the bonding sites in the complexes the spectral and the magnetic studies have been carried out.

** 1 M=1 mol/dm³.

TABLE 1. ANALYTICAL DATA, MOLECULAR WEIGHT AND MAGNETIC MOMENTS OF THE COMPLEXES

S. No.	Formula of the complex	Calcd %					Found %					Color	Mp °C	μ_{eff} (B.M.)
		mol wt	C	H	N	Metal	mol wt	C	H	N	Metal			
1	$La(C_{15}H_{10}N_3O)_3$	884	61.16	3.41	14.27	15.72	900.0	61.00	3.80	13.90	16.48	Dark red	133	Dia
2	$Pr(C_{15}H_{10}N_3O)_3 \cdot H_2O$	903	59.81	3.57	13.95	15.59	923.4	59.94	3.80	13.84	15.41	Dark red	220	3.85
3	$Nd(C_{15}H_{10}N_3O)_3 \cdot H_2O$	907	59.60	3.56	13.90	15.90	920.0	59.69	3.77	14.17	15.67	Dark red	296	3.87
4	$Sm(C_{15}H_{10}N_3O)_3 \cdot H_2O$	913	59.17	3.53	13.80	16.46	917.0	58.60	3.78	13.75	16.96	Dark red	297	1.60
5	$Eu(C_{15}H_{10}N_3O)_3$	897	60.29	3.38	14.06	16.95	912.6	60.22	3.31	14.21	16.39	Dark red	302	3.30
6	$Gd(C_{15}H_{10}N_3O)_3$	902	59.92	3.35	13.98	17.42	880.0	59.30	3.36	13.85	17.13	Dark red	305	7.30
7	$Tb(C_{15}H_{10}N_3O)_3$	904	59.81	3.35	13.95	17.59	931.3	60.00	3.50	14.10	17.74	Dark red	299	9.06
8	$Dy(C_{15}H_{10}N_3O)_3$	907	59.58	3.33	13.90	17.91	890.2	60.10	3.60	13.80	17.35	Dark red	302	10.48
9	$Ho(C_{15}H_{10}N_3O)_3$	909	59.41	3.32	13.87	18.12	926.4	59.26	3.77	14.32	18.30	Dark red	294	10.54
10	$Er(C_{15}H_{10}N_3O)_3$	912	59.27	3.32	13.82	18.34	928.1	59.64	3.88	13.35	18.34	Dark red	249	9.69
11	$Yb(C_{15}H_{10}N_3O)_3$	918	58.88	3.29	13.73	18.85	940.4	59.24	3.30	14.00	19.02	Dark red	231	4.70
12	Ligand $C_{15}H_{11}N_3O$	—	72.00	4.40	16.80	—	—	72.20	3.80	16.50	—	Orange	—	—

TABLE 2. MOLAR CONDUCTANCE OF COMPLEXES IN DMF SOLUTION TEMPERATURE 28 °C

S. No.	Metal complex	Concentration mol $l^{-1} \times 10^3$	λ ohm s^{-1} cm^2
1	$La(C_{15}H_{10}N_3O)_3$	1.621	41.21
2	$Pr(C_{15}H_{10}N_3O)_3 \cdot H_2O$	0.850	6.58
3	$Nd(C_{15}H_{10}N_3O)_3 \cdot H_2O$	0.904	3.95
4	$Sm(C_{15}H_{10}N_3O)_3 \cdot H_2O$	1.109	1.99
5	$Eu(C_{15}H_{10}N_3O)_3$	1.307	1.81
6	$Gd(C_{15}H_{10}N_3O)_3$	0.878	1.01
7	$Tb(C_{15}H_{10}N_3O)_3$	1.093	0.58
8	$Dy(C_{15}H_{10}N_3O)_3$	1.009	0.51
9	$Ho(C_{15}H_{10}N_3O)_3$	0.959	0.24
10	$Er(C_{15}H_{10}N_3O)_3$	1.338	1.18
11	$Yb(C_{15}H_{10}N_3O)_3$	0.527	0.44

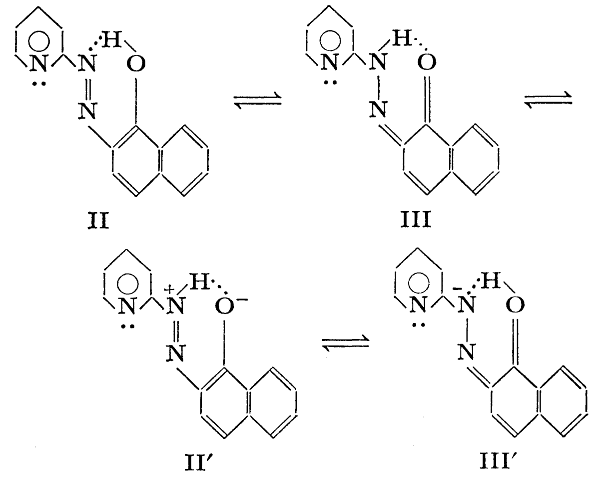
Infrared Spectra. Although the spectra of PAN and its chelates are complicated owing to the extensive overlap of a number of bands arising due to ν(N=N), ν(C=N), ν(C=C), ν(C–H) and other bending modes in the region below 1700 cm^{-1}, the systematic shifts in the positions of a few ligand bands in the spectra of the complexes suggest the probable modes of bonding in the complexes. Some of these major shifts along with the conclusions drawn from them are given below.

a) The absorption bands observed at 3020 and 3080 cm^{-1} in the spectrum of PAN are due to ν(C–H). These bands are stable in position as well as in intensity when one goes from the ligand to the metal chelates indicating that these are purely due to ν(C–H). It is interesting to note that instead of a well defined band, only a very broad and weak band appeared in the spectrum of the ligand around 3300 cm^{-1} due to ν(O–H). This suggests a strong intramolecular hydrogen bonding in the ligand which was confirmed earlier by NMR studies.[5] In the spectra of all the metal chelates except those of Pr^{3+}, Nd^{3+}, and Sm^{3+}, the intensity of the very broad band further decreased; but in the spectra of Pr^{3+}, Nd^{3+}, and Sm^{3+} chelates, the weak and broad band was evident indicating the presence of water molecule in these chelates.

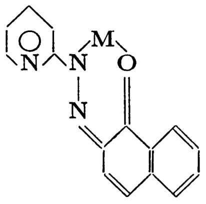
TABLE 3. POSITIONS AND ASSIGNMENTS OF THE IR SPECTRAL BANDS OF THE LIGAND AND COMPLEXES

Ligand (PAN) cm^{-1}	Complexes cm^{-1}	Assignment
3080	3080	ν(C–H)
3020	3020	ν(C–H)
1620	1550—1555	ν(C=O)
1570	1510—1515	ν(N=N)
1450	1390—1375	ν(N=N)
1230	—	δ(C-O-H)
1615, 1600, 1525, 1415, 1325, 1310, 1270, 1150, 1040, 995, 880, 850, 800, 780, 765	Same position as in the spectrum of PAN (±5 cm^{-1})	Bands due to pyridyl and naphthyl rings
—	450—555	Two bands due to ν(M–N) + ν(M–O)

b) The ligand molecule can exist in equilibrium both in azo and hydrazone forms as shown in II and III. An intense band observed at 1620 cm^{-1} in the spectrum of the ligand may be due to ν(C=O) of the hydrogen bonded ring systems of the hydrazone form. Although the carbonyl band normally should appear around 1700 cm^{-1}, such a bathochromic shift



is observed in hydrogen bonded ring systems.[19–20] The band at 1620 cm^{-1} in the ligand is shifted to lower frequencies (1550—1555 cm^{-1}) in the metal chelate spectra as a result of the involvement of the C=O··· linkage in metal chelate ring as shown in IV.



IV

c) The absorption bands due to azo linkage are generally observed at 1410 and 1570 cm^{-1}.[21] The main difficulty in the assignment of a frequency to azo linkage is that the band due to ν(N=N) would overlap with other absorption bands such as those of pyridine and/or naphthol rings. However, the positions of the two bands at 1570 and 1450 cm^{-1} present in the ligand spectrum are shifted to 1510 and 1375 cm^{-1}, respectively. These shifts suggest the linkage of the metal ion with the azo group of the ligand. Since the positions of the other pyridine bands are not changed in the spectra of the chelates, it further suggests that the pyridine moiety of the ligand is possibly not involved in bonding.

d) A band at 1230 cm^{-1} present in the spectrum of the ligand was missing from the spectra of all the chelates. Hadzi[22] has assigned a band at 1272 cm^{-1} in the spectra of similar azo compounds to the in-plane bending mode of C–O–H group. It is possible that the band at 1230 cm^{-1} may arise due to the in-plane bending mode of C–O–H and the fact that the corresponding band is missing in the spectra of metal chelates suggests the deprotonation of the C–O–H group for the bond formation. This is essential in order to keep a charge balance between the metal ion and the ligand molecules.

e) Two new bands appeared in the spectra of all the chelates between 450 and 550 cm^{-1}. They may be coupled bands having contributions from both ν(M–O) and ν(M–N).

The IR spectral study, thus, suggests the bonding of the metal ions with the oxygen atom of the carbonyl and the nitrogen of the azo groups of the ligand.

Electronic Spectra. The positions of absorption bands in the spectrum of PAN in the aqueous and non-aqueous media corresponded with those given in the literature.[7] It presented three well defined broad maxima in the visible region (555, 480, and 415 nm) besides other bands due to pyridine and 2-naphthol moiety in the UV region. The 480 nm band has two shoulders one at 465 nm and the other at 510 nm. The peaks at 555 and 510 nm may be attributed to the hydrazone form (III and III′) whereas the short wave maxima (480, 465, and 415 nm) due to azo (II and II′) chromophore.[22–25] In the spectra of all the chelates the bands at 555 nm and the shoulder band at 510 nm are intensified to a very large extent. Further, the shoulder band at 465 nm and the one at 415 nm showed a bathochromic shift (≈10 nm). There was also a lowering in the intensity of the band at 460 nm. The positions of all the bands in the UV region remained practically constant. It, therefore, appears that in the chelate formation, the nitrogen atom of the azo group and the oxygen atom of the C–O–H group after deprotonation are taking part. It is interesting to note that the relative increase in the intensity of 555 and 510 nm bands and also the relative decrease in the intensity of 465 nm band compared to that of 485 nm band decreases with the increase in the atomic number of the metal ion. Similar effect is observed in the bathochromic shift of the 465 and 415 nm bands (the higher the atomic number, the lower the shift). This correlation may be due to the fact that the interaction of the metal ion decreases with the increase in atomic number.

The bands due to f-f transitions corresponding to the metal ions could not be located in the spectra of the chelates. This is what one should expect because the bands due to metal ions will be very weak ($\varepsilon \approx$ 1—10) and they will be masked by the intense bands of the ligand molecule.

Magnetic Moments. The values of the magnetic moments of the complexes are summarized in Table 1. These values compare very well with those measured for other simple compounds[26] and those calculated for the uncomplexed ions.[27,28] The relatively small differences from the calculated values of Van Vleck suggest either minor or no involvement of the 4 f orbitals in the bonding.

The differential thermal analysis curves indicated in general the decomposition of the complexes around 250—300 °C. In case of Pr^{3+}, Nd^{3+}, and Sm^{3+} complexes a dehydration step beginning at about 80 °C is observed indicating the presence of water molecule in these complexes as water of hydration.

Thus, on the basis of the above studies, the octahedral structure of the complexes having metal ion bonded through nitrogen of azo and oxygen of carbonyl group of the ligand has been proposed.

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