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Spectral Studies of Some 4*f*-Metal Complexes with 4-Amino Benzene Sulfonamide

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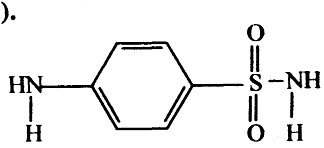
Complexes of La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+} and Dy^{3+} with 4-amino benzene sulfonamide have been prepared. These complexes have been characterized on the basis of elemental analysis, infrared spectra, electronic spectra, X-ray powdered diffraction, magnetic moment, molar conductance and thermal analysis.

Key Words: La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+} and Dy^{3+} Complexes, 4-Aminobenzene sulfonamide.

INTRODUCTION

There is growing interest in the studies of 4-amino benzene sulfonic acid which is a biologically important ligand. This ligand and its derivatives are more popularly known as sulfa drugs[1]; these are commonly used for the treatment of various infectious diseases, *i.e.*, meningitis, sepsis, pneumonia, etc. caused by gram +ve and gram −ve bacteria which are commonly occurring in the biological systems. The action of a drug also requires, apart from the reactant substrates, the presence of specific enzymes as catalysts most of which require one or other of the biological metal ions[2]. Due to complexity of the enzyme structures, it is difficult to elucidate the specific role played by metal ions in the enzymic processes. However, related studies with model systems have often yielded very useful results, although the metals binding properties of the functional groups in the model compounds throw some light upon the interactions of sulfa drugs. In the present work we report the synthesis of some 4*f*-metal complexes of 4-amino benzene sulphonamide (I).



(I) 4-aminobenzene sulphonamide

EXPERIMENTAL

The lanthanide chlorides were obtained from Indian Rare Earths Ltd., Kerala (India) and 4-amino benzene sulfonamide from S.D. Fine Chemicals. The solvents

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were purified using standard procedure. The respective metal chlorides and ligand were mixed in 1 : 3 ratio in hot ethanol. The reaction mixtures were heated for *ca.* 2 h on a water bath using water condenser. The complexes were formed after keeping the reaction mixture for 48 h at room temperature. These complexes were filtered, washed with alcohol and dried *in vacuo*.

The infrared spectra were recorded using KBr pellets on Perkin-Elmer Paragon-500 FTIR spectrophotometer; electronic spectra recorded on Cintra-500 UV-Vis spectrophotometer. Magnetic susceptibility measurements were carried out on Faraday electro balance using $Hg[Co(CNS)_4]$ as calibrant. The thermal data were recorded in the range 25–1000°C at 10°C/min using Mettler Toledo star system at C-MET Pune. Molar conductivity measurements were carried out on Equi-tronic digital conductivity bridge. X-ray powder data collected by Joel-8030 goniometry using CuKa (1.5418 Å) radiation using the indexing of X-ray powder line.[3] The metal contents of the complexes were determined by reported method. The chloride was estimated by Mohr's method[4].

RESULTS AND DISCUSSION

The analytical and physical data for the present complexes are summarized in Table-1, which correspond to general composition $[Ln(C_6H_8N_2SO_2)_3 \cdot 2H_2O]Cl_3$ (Ln = La, Pr, Nd, Sm, Gd, Tb or Dy). Complexes are insoluble in toluene, methanol, ethanol and acetonitrile, but soluble in dimethyl sulfoxide and dimethyl formamide. The molar conductivity values are commensurate with electrolytic behavior of the complexes[5]. It is decomposed in the range 180–195°C. Infrared spectra of Ln^{3+}-4-amino benzene sulfonamide complexes were compared with those of 4-amino benzene sulfonamide[7] and their substituted heterocyclic moieties[6, 7]. In ligand the ν(NH) bands due to anilino-NH_2 group are observed at 3470 and 3320 cm^{-1} and that due to ligand (SO_2NH_2) group is observed at 3256 cm^{-1}. In the present complexes, the ν(NH) band due to lower frequency in Ln^{3+}-4-amino benzene sulfonamide complexes indicating coordination of anilino-NH_2 to Ln^{3+} ions.

$[La(C_6H_8N_2SO_2)_3 \cdot 2H_2O]Cl_3$ is diamagnetic, while other paramagnetic at room temperature. Magnetic susceptibities of all other camplexes except those of Sm^{3+} show a little deviation from Van Vleck values[8] indicating slight participation of the 4*f* electron in bonding. The electronic spectra of the Pr^{3+} and Nd^{3+} complexes are recorded in dimethyl sulfoxide with those of metal chloride solution[9]. The spectral data and various parameters calculated are given in Table-2. The slight red shift clearly indicates that interaction of metal ion with the ligand, Jorgensen[10] attributed these shifts to the effect on crystal field upon the interelectronic repulsion among the 4*f* electron, *i.e.*, to lowering of the inter electronic repulsion parameter (β) in the complex. The bonding parameter ($b^{1/2}$) and Sinha's parameter (δ) have also been calculated using literature produced[11, 12]. These values indicate partial covalent bonding developing between the metal ions and the ligands[13].

TABLE-1
ANALYTICAL AND PHYSICAL DATA

S.N.	Complexes	Colour and yield (%)	m.p. (°C)	Analysis %, Found (Calcd.)						μ_{eff} (B.M.)	Ω (ohm^{-1} cm^2 mol^{-1})
				C	H	N	S	Cl	M		
1.	$[La(C_6H_8N_2SO_2)_3 \cdot 2H_2O]Cl_3$	Colourless 54.2	196–199	27.09 (26.86)	3.51 (3.18)	10.53 (10.24)	12.04 (11.82)	3.35 (3.12)	17.40 (17.02)	Diamag	158.7
2.	$[Pr(C_6H_8N_2SO_2)_3 \cdot 2H_2O]Cl_3$	Light green 51.1	188–191	27.04 (26.76)	3.50 (3.08)	10.51 (10.22)	12.02 (11.78)	3.33 (3.15)	17.63 (17.26)	3.47	159.9
3.	$[Nd(C_6H_8N_2SO_2)_3 \cdot 2H_2O]Cl_3$	Light pink 53.4	182–185	26.91 (26.45)	3.48 (3.98)	10.46 (10.26)	11.96 (11.77)	3.27 (3.19)	17.95 (17.65)	3.55	139.4
4.	$[Sm(C_6H_8N_2SO_2)_3 \cdot 2H_2O]Cl_3$	Light orange 52.8	180–183	26.71 (26.42)	3.46 (3.94)	10.38 (10.17)	11.87 (11.68)	3.17 (3.06)	18.57 (18.02)	1.88	150.4
5.	$[Gd(C_6H_8N_2SO_2)_3 \cdot 2H_2O]Cl_3$	Colourless 51.9	183–186	26.51 (26.21)	3.44 (3.03)	10.31 (10.08)	11.78 (11.52)	3.07 (2.91)	19.28 (18.76)	7.98	151.6
6.	$[Tb(C_6H_8N_2SO_2)_3 \cdot 2H_2O]Cl_3$	Light buff 51.7	191–194	26.42 (25.96)	3.43 (3.12)	10.27 (10.98)	11.74 (11.38)	3.03 (3.89)	19.42 (18.94)	9.76	148.5
7.	$[Dy(C_6H_8N_2SO_2)_3 \cdot 2H_2O]Cl_3$	Colourless 51.3	185–188	26.32 (25.72)	3.41 (3.16)	10.23 (10.97)	11.69 (11.49)	2.97 (2.74)	19.77 (19.27)	10.43	141.7

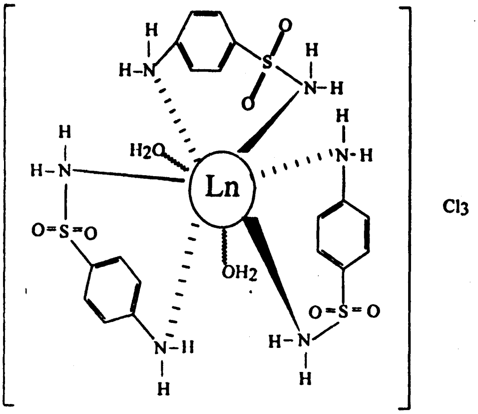
TABLE-2
ELECTRONIC SPECTRA AND THEIR ASSIGNMENTS

Complexes	β	δ	$b^{1/2}$
$[Pr(C_6H_8N_2SO_2)_3·2H_2O]Cl_3$	0.986	1.41	0.0830
$[Nd(C_6H_8N_2SO_2)_3·2H_2O]Cl_3$	0.987	1.31	0.0806

The complexes were examined for their powder diffraction data. The nature of spectra indicates low crystallinity of the complexes; the major refluxes were used to calculate crystal lattice parameters using Back-cal program on computer by Ito's method[14]. The observed values are reported in Table-3. The system was found orthorhombic with space group P_{222} or P_{mmm}[16, 17]. The Z = 10 factor values were calculated from density of the complexes using toluene solvent. The observed value of density of the $[Pr(C_6H_8N_2SO_2)_3·2H_2O]Cl_3$ complex is 1.7628 g/cm^3 and calculated 1.7815 g/cm^3. These values are in well agreement with each other reflecting accuracy in assigning the correct crystal system and indexing it. The standard deviations observed for these complexes are 0.0–0.3% respectively which are within permissible limits.

Thermogravimetric and differential thermal analysis of $[Pr(C_6H_8N_2SO_2)_3·2H_2O)Cl_3$ complexes showing some losses due to exo- and endothermic processes. The study of thermal analysis of Pr^{3+}(III) complex of 4-amino benzene sulfonamide shows a loss at 110–290°C, which corresponds to loss of two water molecules and some part of complex[18]. The complex indicates that two water molecules are present inside the coordination sphere. The complex losses at the range 300–350°C. The theoretical value is 35.06% and experimental value is 34.96%. The differential thermal analysis curve is exothermic at the temperature 380–810°C leading to the formation of praseodymium oxide[17].

In conclusion, the general structure of the present complexes is shown as:



Complex sructure of lanthanide(III) with 4-aminobenzene sulfonamide

TABLE-3

X-RAY POWDER DIFFRACTION DATA FOR $[Pr(C_6H_8N_2SO_2)_3{\cdot}2H_2O]Cl_3$ COMPLEX

a (Å) = 17.0141	D_{cal} (g/cm^3) = 1.7830
b (Å) = 10.2348	D_{obs} (g/cm^3) = 1.7728
c (Å) = 15.6251	Space group = P222 or P_{mmm}
α = 90°	Crystal system = Orthorhombic
β = 90°	V (Å)^3 = 7447.18
γ = 90°	Z= 10

S.No.	2θ	h	k	L	d_{obs}	d_{cal}	I/I_0
1.	10.15	1	0	1	8.7147	8.6969	26
2.	10.38	1	1	0	8.5221	8.5180	24
3.	10.68	0	1	1	8.2834	8.2848	29
4.	11.50	2	0	0	7.6945	7.6823	24
5.	14.44	2	1	0	6.1326	6.1440	29
6.	18.89	1	1	2	4.8956	4.8913	42
7.	20.81	0	0	3	4.6970	4.7034	59
8.	22.33	2	2	1	3.8278	3.8326	100
9.	24.94	0	2	3	3.4566	3.4629	68
10.	26.95	1	2	3	3.1677	3.1701	34
11.	28.34	0	3	2	3.0664	3.0713	27
12.	29.12	5	1	0	2.9460	2.9431	65
13.	31.63	3	1	3	2.7910	2.7892	28
14.	33.21	0	4	0	2.5566	2.5587	26
15.	37.27	2	2	3	2.4125	2.4123	24

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