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COORDINATION STUDIES OF SOME SALICYLIDENE HETEROCYCLIC SCHIFF BASES WITH La(III), Ce(III) AND Sm(III).

A.A. GABR

Chemistry Department, Faculty of Science, Aswan, Egypt.

Coordination compounds formed by the interaction of some salicylidene heterocyclic Schiff bases with La(III), Ce(III) and Sm(III) are prepared and characterized by elemental analysis, electronic and I.R. spectra as well as conductometric methods. The data of analyses indicate that coordination takes place through the azomethine nitrogen atoms and OH groups where the ligands are coordinated as bidentate molecules.

INTRODUCTION

The preparation of coordination compounds from hydroxy Schiff bases with metal ion has drawn much attention[1–4], due to their importance in biological, pharmacological and biochemical processes[5–8]. The salicylidene derivatives are expected to have a tendency to form complexes which should be related to that of other hydroxy derivatives. However, the hydroxy compounds salicylidene-3-amino-1,2,4-triazole (L_1), salicylidene-2-amino-1,3-pyrimidine (L_2) and salicylidene-2-amino-4-methyl-1,3-pyrimidine (L_3) have two coordinating sites. This paper represents a study on the chelate of these ligands with metal ions, viz., La(III), Ce(III) and Sm(III). The aim of the present work, therefore, is to prepare and characterize the complexes of some new heterocyclic Schiff bases.

EXPERIMENTAL

The chemicals used in the present work were A.R. products from BDH. The Schiff bases under investigation were prepared by the condensation of salicylaldehyde with the corresponding amine in the requisite amount in ethanolic medium as previously described[7]. The solid products obtained were then recrystallized from pure ethanol. The purities of the compounds were checked by elemental analysis.

A stock solution (10^{-2} mol. dm^{-3}) of the ligands, $La(NO_3).6H_2O$, $Ce(NO_3)_3.6H_2O$ and $Sm(NO_3)_3.5H_2O$ were prepared by dissolving the requisite amount in pure ethanol. Solutions for spectrophotometric measurements were obtained by accurate dilution of the stock.

The solid metal chelates were prepared by mixing hot saturated ethanolic solutions of each ligand and metal salt containing the appropriate quantities of the reactants. The reaction mixture was then refluxed for about an hr. The deposited complex was filtered, washed with ethanol and dried over silica gel. Microanalyses of the solid complexes for C, H, N were performed using the recommended procedures (Table 1).

TABLE 1
ANALYTICAL DATA, % CALCULATED (FOUND), COLOUR, DECOMPOSITION TEMPERATURE (°C) AND MOLAR CONDUCTIVITY Λ_M (ohm^{-1} mole^{-1}cm^2) OF THE SCHIFF BASES COMPLEXES (L_1–L_3)

Complex	C	H	N	Λ_M	Colour	Decomposition temperature
L_1-Complexes						
$[(C_9H_7N_4O)La(NO_3)_2(H_2O)_2]$	22.24 (22.00)	2.28 (2.19)	17.29 (17.38)	43.48	brownish orange	>320
$[(C_9H_7N_4O)_2LaNO_3(H_2O)_2]$	35.37 (35.60)	2.97 (2.91)	20.62 (20.91)	42.79	piege	>320
$[(C_9H_7N_4O)Ce(NO_3)_2(H_2O)_3]$	21.39 (21.10)	2.59 (2.70)	16.63 (16.93)	40.67	pale brown	310
$[(C_9H_7N_4O)_2Ce(H_2O)_2]NO_3$	35.30 (35.00)	2.96 (2.81)	20.58 (20.29)	65.97	pale brown	320
$[(C_9H_7N_4O)Sm(NO_3)_2(H_2O)_2]$	21.72 (21.60)	2.23 (2.40)	16.89 (16.99)	57.36	pale brown	>320
$[(C_9H_7N_4O)_2SmNO_3(H_2O)_2]$	34.72 (34.50)	2.91 (2.99)	20.24 (20.58)	39.48	piege	>320
L_2-Complexes						
$[(C_{11}H_8N_3O)La(NO_3)_2(H_2O)_2]$	26.58 (27.00)	2.43 (2.30)	14.09 (14.40)	53.10	piege	>320
$[(C_{11}H_8N_3O)_2La(H_2O)_4]NO_3$	39.48 (39.80)	3.61 (3.72)	14.65 (14.38)	79.50	deep yellow	>320
$[(C_{11}H_8N_3O)CeNO_3(H_2O)_3]NO_3$	25.59 (25.10)	2.73 (2.60)	13.56 (13.06)	71.60	brown	>320
$[(C_{11}H_8N_3O)_2Ce(H_2O)_2]NO_3$	41.64 (41.90)	3.18 (3.00)	15.45 (15.00)	94.38	brown	>320
$[(C_{11}H_8N_3O)SmNO_3(H_2O)_3]NO_3$	25.09 (25.00)	2.68 (2.72)	13.30 (13.50)	95.99	deep yellow	>320
$[(C_{11}H_8N_3O)_2Sm(H_2O)_4]NO_3$	38.81 (38.50)	3.55 (3.70)	14.40 (14.00)	87.99	deep yellow	>320
L_3-Complexes						
$[(C_{12}H_{10}N_3O)LaNO_3(H_2O)_3]NO_3$	27.24 (27.00)	3.05 (3.00)	13.24 (13.50)	84.31	piege	282
$[(C_{12}H_{10}N_3O)_2La(H_2O)_2]NO_3$	43.59 (43.09)	3.66 (3.60)	14.83 (14.99)	90.88	deep yellow	312
$[(C_{12}H_{10}N_3O)CeNO_3(H_2O)_3]NO_3$	27.18 (27.00)	3.04 (3.19)	13.21 (13.48)	91.39	brown	200
$[(C_{12}H_{10}N_3O)_2Ce(H_2O)_3]NO_3$	43.51 (43.90)	3.65 (3.70)	14.80 (14.62)	86.76	brown	180
$[(C_{12}H_{10}N_3O)SmNO_3(H_2O)_3]NO_3$	26.66 (26.09)	2.98 (3.08)	12.95 (13.18)	82.91	deep yellow	240
$[(C_{12}H_{10}N_3O)_2Sm(H_2O)_3]NO_3$	41.70 (42.01)	3.79 (3.82)	14.19 (13.99)	82.21	deep yellow	255

The absorption spectra of the metal chelates in solutions were determined on a Shimadzu-UV/vis. 240-recording spectrophotometer using 1 cm matched silica cells. The i.r. spectra were recorded on a Perkin-Elmer-599 B spectrophotometer as the KBr disks (4000–200 cm^{-1}). The conductance measurements were carried out on a WPA CM 25 conductivity meter at 25 ± 0.1°C

RESULTS AND DISCUSSION

The band located at longer wavelengths (340–365 nm) in the electronic spectra of the free ligands in ethanol medium exhibits a red shift on complexation with the metal ions La(III), Ce(III) (370–410 nm) and Sm(III) (370–415 nm). The low excitation energy observed for this band in the spectra of the complex solutions can be attributed to the expected easier intramolecular CT interaction in the complexed ligand ($M^{3+} \leftarrow N$), relative to that in the free ligand ($H^+ \leftarrow N$), as a result of the high positive charge of the coordinated metal ion.

The stoichiometry of the complexes formed in solution, from the reaction of each of the ligands under investigation (L_1 – L_3) with the metal ions used, was confirmed by the application of spectrophotometric continuous variation c.v.[9] and molar ratio m.r.[10] methods at each λ_{max} of the formed complexes. In all measured solutions, the blank was a solution of ligand of the same concentration as in the solution of the chelate. Representative results are shown in Figs. 1 and 2. The results reveal the possible formation of both 1 : 1 and 1 : 2 (M : L) in the case of all ligands studied.

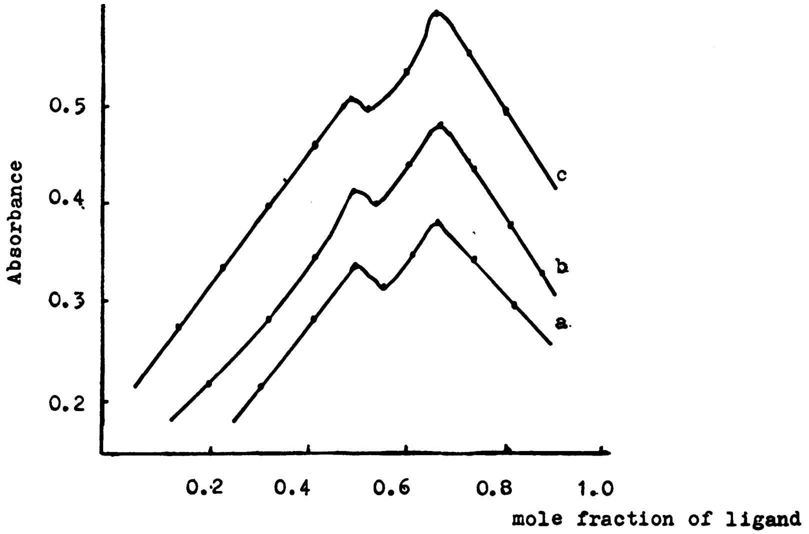

Fig. 1. Gobs continuous variation method for M-L_2 chelates:

(a) La(III), λ = 410 nm, total concentration = 1 × 10^{-3} mol dm^{-3}

(b) Ce(III), λ = 410 nm, total concentration = 1 × 10^{-3} mol dm^{-3}

(c) Sm(III), λ = 415 nm, total concentration = 1 × 10^{-3} mol dm^{-3}

The results of continuous variation and molar ratio methods have been utilized in calculating the stability constants (K_f) and energy of formation (– ΔG) of the metal chelates under investigation[11]. It is evident from the results shown in Table

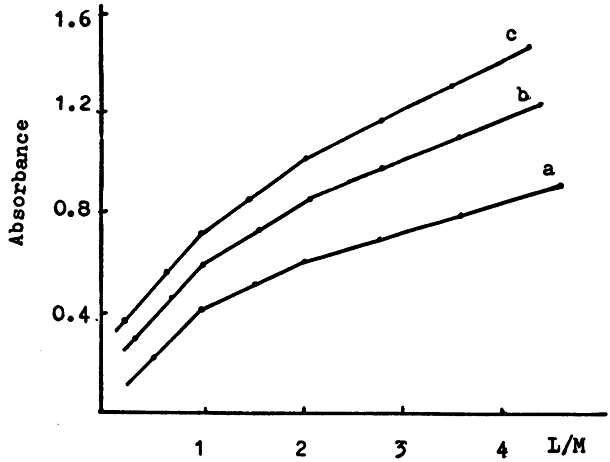

Fig. 2 Molar ratio method for M-L_2 chelates:
(a) La(III), λ = 410 nm, total concentration = 1 × 10^{-3} mol dm^{-3}
(b) Ce(III), λ = 410 nm, total concentration = 1 × 10^{-3} mol dm^{-3}
(c) Sm(III), λ = 415 nm, total concentration = 1 × 10^{-3} mol dm^{-3}

2, that the stability constant value of the complex depends on the nature of both the metal ion and the ligand. In general, for the same ligand stability values run as follows; La(III) > Ce(III) > Sm(III) which is the same order as the decreasing radii of the metal ion[12]. Moreover, the stability constant values of the metal chelates decrease in the following order: $L_1 > L_2 > L_3$. This is in agreement with decreasing the basicity of the central azomethine nitrogen in the same direction, where the tendency toward complex formation is expected to decrease.

TABLE 2
THE STABILITY CONSTANTS (K_f, L mol^{-1}) AND ENERGY OF FORMATION ($-\Delta G$, kcal. mol^{-1}) FOR La(III), Ce(III) AND Sm(III)-SCHIFF BASE COMPLEXES

Metal ion	Å	M : L	L_1		L_2		L_3	
			K_f	ΔG	K_f	ΔG	K_f	ΔG
La(III)	1.15	1 : 1	1.30×10^6	8.39	1.04×10^6	8.26	7.80×10^5	8.09
		1 : 2	7.02×10^{10}	14.89	5.09×10^{10}	14.69	3.37×10^9	13.08
Ce(III)	1.11	1 : 1	1.10×10^6	8.29	9.03×10^5	8.17	1.96×10^5	7.26
		1 : 2	5.17×10^{10}	14.70	3.52×10^{10}	14.47	2.73×10^9	12.95
Sm(III)	1.04	1 : 1	8.91×10^5	8.17	8.70×10^5	8.15	1.71×10^5	7.18
		1 : 2	3.55×10^{10}	14.48	3.01×10^{10}	14.38	2.17×10^9	12.81

The results of conductometric titration of the metal ions with ligands used are in accordance with those obtained from the spectrophotometric methods. Representative curves are shown in Fig.3. The increase in the conductance for the above ligands may be attributed to the liberation of HNO_3 in the medium as a result of interaction of the ligand with metal salt.

The molar conductance values (Table 1) of the solid complexes in DMF solution (1 × 10^{-3} mol dm^{-3}) indicate that the metal chelates of L_2 and L_3 behave

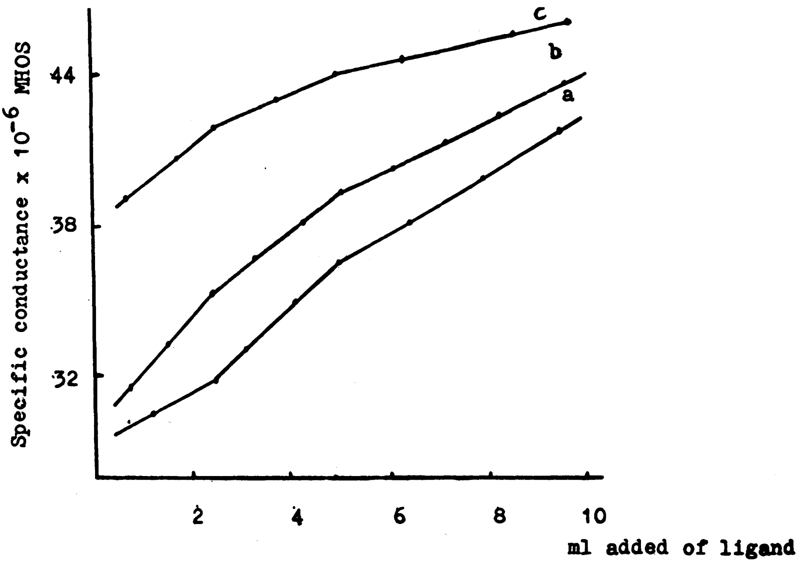

Fig. 3. Conductometric titration of 25 ml (1×10^{-3} mol dm^{-3}) of (a) La(III), (b) Ce(III) and (c) Sm(III) with 1×10^{-3} mol dm^{-3} L_2.

as 1 : 1 electrolytes except 1 : 1 La(III) of L_2 behaves as non-electrolyte. On the other hand, the metal chelates of L_1 behave as non-electrolytes, while the molar conductance value for 1 : 2 Ce(III) chelate of L_1 behaves as 1 : 1 electrolyte[13]

The infrared spectral data also provide some significant results which support the proposed formula of each complex isolated in the present study. Tentative assignments of some important bands belonging to the ligands and their complexes are recorded in Table 3. The examination of the results indicates that complex formations between ligands and each metal ion studied, probably occur through coordination of metal ion with the azomethine group and formation of $O-M^{++}$. This is based on the following:

(i) The appearance of a broad band at 3080–2812 cm^{-1} which is assigned to the intramolecular hydrogen bonded *o*–OH in the molecule[14]. This band disappears in the complexes formed, indicating that OH group participates in complexation. Moreover, a new broad band appearing in the region 3550–3420 cm^{-1} indicates that the water molecules in the complexes prepared exist as molecules of crystallization[15].

(ii) The phenolic ν_{C-O} at 1285–1240 cm^{-1} shows negligible red shift in all complexes. This is in agreement with previously discussed results, which have shown that the metal complexes of the ligands are formed where O–M bond is formed.

(iii) The i.r. spectra of the free ligands show two bands in the regions 1550–1610^{-1} and 1620–1670 cm^{-1}; one can assign the shorter frequency band to the stretching vibration of azomethine $\nu_{C=N}$ and the longer one to the stretching of $\nu_{C=N}$ within the hetero ring[4, 16]. These bands shift towards higher frequency on complexation, the observed shift value of the central $\nu_{C=N}$ bond is more than the $\nu_{C=N}$ ring. This indicates that the nitrogen atom of the azomethine group and not of the hetero ring is involved in the complex formation.

(iv) The appearance of two bands in the regions 1400–1430 cm^{-1} and 450–600 cm^{-1} in the i.r. of the solid chelates which did not appear in the free ligands. The first band can be assigned to $\nu_{NO_3^-}$[14] and the second band due to the metal-ON ligand stretching frequency. This assignment is consistent with those previously made[17, 18].

TABLE 3

PRINCIPAL I.R. BANDS (cm^{-1}) OF SCHIFF BASES AND THEIR 1 : 1 CHELATES

Compound	ν_{OH}	$\nu_{C=N}$	ν_{C-O}	ν_{M-L}	$\nu_{NO_3^-}$
L_1	3050 b	1670 1610 m	1285	—	—
L_1–La	3530 b	1700 sh 1660 sh	1250 s	600 sh	1430
L_1–Ce	3530 b	1700 1650	1260 s	540 w	1420
L_1–Sm	3520 b	1700 1630	1260 s	450 w	1420
L_2	3080 b	1630 s 1550 w	1240	—	—
L_2–La	3520 b	1650 1580	1260	450 b	1420
L_2–Ce	3540 b	1650 1580	1260 s	550 b	1400
L_2–Sm	3540 b	1650 1580	1260 s	450 w	1420
L_3	2812 b	1620 m 1550	1250	—	—
L_3–La	3520 b	1640 1570	1260 s	580	1420
L_3–Ce	3420 b	1620 1570	1260 s	520	1400
L_3–Sm	3520 b	1640 1570 b	1260 s	490	1420

b = broad; m = medium; sh = shoulder; w = weak; s = strong

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