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Characterization and Toxicity of Lanthanide Complexes with Nitrogen- and Sulphur-containing Schiff Bases

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Abstract

La(III), Ce(III), Pr(III), Nd(III), Gd(III), Dy(III), Ho(III) and Er(III) complexes of Schiff bases derived from sulphamethoxazole and salicylaldehyde (**I**), and thiophene-2-aldehyde (**II**) have been characterized on the basis of IR, NMR, UV–Vis spectroscopy, elemental analysis, conductance measurements and molecular weight determinations. The Schiff bases act as monobasic bidentate ligands, rendering the metal eight-coordinated. The equilibrium constants have been studied in solution at 25, 30 and 35 °C. The nephelauxetic effect $(1-\beta)$, bonding parameter (β), $b^{1/2}$ and Sinha covalency parameter (δ) have been calculated. The positive values indicate the covalent nature of the metal–ligand bond. The covalent nature of the complexes is also supported by molar conductance measurements. The toxicities of the Schiff bases and their complexes were evaluated against insects. The LD_{50} value for cockroaches and percent growth inhibition of the fungi show greater efficacy for the complexes than the Schiff bases.

Introduction

Substantial work has been carried out on Schiff bases derived from amides or amines and aromatic aldehydes [1–4]. Besides their extensive application in analytical, pharmacological and polarographic studies, they are also important biocides [5–10].

In continuation of our earlier work [11], we report in this communication the synthesis of Schiff bases derived from sulphamethoxazole and salicylaldehyde (**I**) and thiophene-2-aldehyde (**II**). Their complexes with La(III), Ce(III), Pr(III), Nd(III), Gd(III), Dy(III), Ho(III) and Er(III) have been characterized by elemental analysis, IR, NMR, UV–Vis spectroscopy, conductance measurements and molecular weight determinations. Their pH-metric measurements have also been carried out at three different temperatures to examine the effect of temperature on the equilibrium constants. The toxicities of the Schiff bases and their complexes have also been evaluated against insects and fungi.

Experimental

Materials and Methods

Rare earth chlorides (reagent grade or May and Baker), NaOH and $NaClO_4$ (Riedel); salicylaldehyde, thiophene-2-aldehyde and $HClO_4$ (E. Merck); sulphamethoxazole (Roche) were used as obtained. The IR spectra (600–4000 cm^{-1}) were run on a Beckman IR20. The NMR spectra were recorded on a Varian A-60D instrument in deuterated DMSO. The conductivity measurements were made on an Elico conductivity bridge, type CM-82T. The molecular weights were determined by the viscosity measurement method in DMF using an Ostwald viscometer. The pH-metric titrations were performed on an Elico pH-meter, model LI-10T. All the calculations were made on a model VAX/11-780 computer. The estimation of sulphur was carried out by the usual gravimetric method, while the metals were estimated by EDTA titration using bromopyrogallol red and Eriochrome Black T as indicators.

Synthesis of the Schiff Bases

Sulphamethoxazole (10 mmol, 2.22 g) dissolved in ethanol was mixed with salicylaldehyde (**I**) (10 mmol, 1.22 g) and thiophene-2-aldehyde (**II**) (10 mmol, 1.12 g). The resulting mixture was refluxed on a water bath for 3 to 4 h to yield coloured crystals or amorphous powders. These were filtered, washed with ethanol and dried *in vacuo*.

Synthesis of the Complexes

Ethanolic solutions (30 mmol 1.17 g, 1.14 g) of the Schiff bases **I** and **II** were mixed with 10 mmol of metal chloride in the same solvent and stirred for 24 h until an amorphous solid was obtained. This was kept overnight and filtered. The complexes were washed with ethanol and dried *in vacuo*.

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TABLE I. Analytical Data, Melting Points and Molecular Weights of the Schiff Bases I and II and their Complexes

	Melting point (°C)	Found (Calculated) (%)				Metal	Molecular weight (Found (Calculated))
		C	H	N	S		
$(C_{16}H_{14}S_2O_4N_4)$	215	49.20	3.56	14.28	16.36		386.20
(Schiff base I)		(49.27)	(3.61)	(14.36)	(16.43)		(390.03)
$(C_{16}H_{13}S_2O_4N_4)_3La\cdot 2H_2O$	240	42.85	3.78	12.47	14.27	10.30	1340.59
		(42.92)	(3.82)	(12.51)	(14.32)	(10.34)	(1343.08)
$(C_{16}H_{13}S_2O_4N_4)_3Ce\cdot 2H_2O$	250	42.80	3.77	12.42	14.25	10.43	1340.58
		(42.88)	(3.82)	(12.49)	(14.30)	(10.47)	(1344.29)
$(C_{16}H_{13}S_2O_4N_4)_3Pr\cdot 2H_2O$	244	42.80	3.76	12.45	14.27	10.43	1341.99
		(42.86)	(3.82)	(12.49)	(14.30)	(10.47)	(1345.07)
$(C_{16}H_{13}S_2O_4N_4)_3Nd\cdot 2H_2O$	258	42.68	3.75	12.40	14.20	10.63	1342.50
		(42.72)	(3.80)	(12.45)	(14.25)	(10.66)	(1349.41)
$(C_{16}H_{13}S_2O_4N_4)_3Gd\cdot 2H_2O$	256	42.30	3.71	12.30	14.10	11.52	1356.00
		(42.34)	(3.77)	(12.34)	(14.13)	(11.55)	(1361.42)
$(C_{16}H_{13}S_2O_4N_4)_3Dy\cdot 2H_2O$	260	42.13	3.72	12.23	14.03	11.85	1357.58
		(42.18)	(3.76)	(12.27)	(14.07)	(11.89)	(1366.69)
$(C_{16}H_{13}S_2O_4N_4)_3Ho\cdot 2H_2O$	258	42.04	3.72	12.25	14.00	12.00	1362.00
		(42.09)	(3.75)	(12.27)	(14.04)	(12.04)	(1369.70)
$(C_{16}H_{13}S_2O_4N_4)_3Er\cdot 2H_2O$	258	42.00	3.70	12.20	13.98	12.03	1365.25
		(42.03)	(3.74)	(12.25)	(14.02)	(12.19)	(1371.43)
$(C_{14}H_{12}N_4S_3O_3)$	190	44.24	3.14	14.70	25.30		375.90
(Schiff base II)		(44.31)	(3.18)	(14.76)	(25.35)		(379.42)
$(C_{14}H_{11}N_4S_3O_3)_3La\cdot 2H_2O$	220	38.37	3.41	12.75	21.92	10.50	1308.51
		(38.41)	(3.45)	(12.79)	(21.97)	(10.57)	(1313.20)
$(C_{14}H_{11}N_4S_3O_3)_3Ce\cdot 2H_2O$	230	38.33	3.92	12.72	21.91	10.62	1305.99
		(38.38)	(3.45)	(12.78)	(21.95)	(10.66)	(1314.31)
$(C_{14}H_{11}N_4S_3O_3)_3Pr\cdot 2H_2O$	235	38.32	3.41	12.74	21.90	10.65	1309.54
		(38.35)	(3.44)	(12.77)	(21.94)	(10.71)	(1315.19)
$(C_{14}H_{11}N_4S_3O_3)_3Nd\cdot 2H_2O$	240	38.21	3.42	12.70	21.85	10.90	1312.23
		(38.25)	(3.44)	(12.74)	(21.88)	(10.93)	(1318.53)
$(C_{14}H_{11}N_4S_3O_3)_3Gd\cdot 2H_2O$	235	37.83	3.37	12.59	21.62	11.78	1327.60
		(37.88)	(3.40)	(12.62)	(21.67)	(11.80)	(1331.54)
$(C_{14}H_{11}N_4S_3O_3)_3Dy\cdot 2H_2O$	244	37.70	3.36	12.53	21.53	12.12	1330.75
		(37.73)	(3.39)	(12.57)	(21.58)	(12.15)	(1336.81)
$(C_{14}H_{11}N_4S_3O_3)_3Ho\cdot 2H_2O$	245	37.62	3.35	12.50	21.50	12.26	1333.45
		(37.66)	(3.38)	(12.54)	(21.54)	(12.31)	(1339.25)
$(C_{14}H_{11}N_4S_3O_3)_3Er\cdot 2H_2O$	243	37.55	3.33	12.48	21.47	12.40	1338.72
		(37.60)	(3.38)	(12.52)	(21.51)	(12.46)	(1341.55)

For the determination of equilibrium constants a modified Bjerrum–Calvin pH-metric titration technique was adopted [12].

All the solutions were prepared in carbon dioxide-free distilled water. The Schiff bases were dissolved in the minimum amount of ethanol and the volume was made up with water. Metal halide solutions were prepared in perchloric acid to prevent hydrolysis.

Toxic Effects

Experiments were carried out on cockroaches (*Periplaneta americana*). The concentrations of the Schiff bases and their complexes were kept within the 6–10 ppm range. Five insects were taken in each set and were kept under constant observation. A control set was also run simultaneously. The percent mortality after 96 h was noted. The LD_{50} value was calculated in terms of probit.

Fungitoxicity was also evaluated against *Aspergillus niger, Aspergillus flavus* and *Alternaria pori*. Aqueous solutions of 2–4% of the Schiff bases and their complexes were sprayed on a measured area of fungus colony. The results were compared against a control set under the same experimental conditions. The percent inhibition in growth was calculated.

Results and Discussion

The complexes were formed according to the reaction

$$3(C_{16}H_{14}S_2O_4N_4) + MCl_3 \longrightarrow (C_{16}H_{13}S_2O_4N_4)_3M + 3HCl$$

$$3(C_{14}H_{12}N_4S_3O_3) + MCl_3 \longrightarrow (C_{14}H_{11}N_4S_3O_3)_3M + 3HCl$$

The analytical data of the complexes (Table I) showed the formation of $MLH_3 \cdot 2H_2O$ complexes where M = lanthanide ion and LH = Schiff base. The molecular weights determined by viscosity measurements in DMF are close to the theoretical values. The molar conductance of millimolar solutions of the complexes in DMF lie in the range for non-electrolytes and suggest they are covalent (45–55 ohm^{-1} cm^2 mol^{-1}).

NMR Spectra

The NMR spectra of **I** and **II** were recorded in deuterated DMSO. Singlets observed at δ 2.5, δ 3.33 and δ 10.50 with the Schiff bases are due to the NH, OCH_3 and OH protons, respectively. The proton signal of the OH group in **I** and the NH proton signal in the case of **II** disappear in the complexes, showing the replacement of a proton by the metal. The fine splitting of the ring proton persists at δ 6.16–7.96 with both the Schiff bases and their complexes.

IR Spectra of Schiff Base I and its Complexes

The IR spectrum of the Schiff base shows a broad band at 2750 cm^{-1} due to an intramolecularly hydrogen bonded OH group which disappears on complexation. In such cases the ν(C–O) mode appearing at 1280 cm^{-1} is insensitive to coordination. Our observations are consistent with those of Kulkarni *et al.* [13].

A strong band in the range 1625–1635 cm^{-1}, assigned to the azomethine group (H–C=N), has been observed to be positively shifted after complexation (Table II). The ν(NH) mode at 3150 cm^{-1} does not appear to be involved in coordination as its position remains unaltered. The sulphur atom has been found to be inactive as the characteristic band remains unchanged. The ν(C–C), ν(C–N) and ring vibrations at 1095, 1170 and 1560 cm^{-1}, respectively, also appear in the same region of the spectrum for the Schiff base and the complexes. Some new bands of medium intensity at 3400 (ν(OH)) and 1600 cm^{-1} (ν(H–OH)), together with a very wide band at 1140 cm^{-1}, 880 cm^{-1} and 600–620 cm^{-1} in the spectra of the complexes of the Schiff bases have been reported to be due to coordinated water. These observations are in agreement with those reported earlier [14].

TABLE II. IR Spectra of Complexes of Schiff Bases I and II and their Assignments

	ν(N–H)	ν(O–H)	ν(H–C=N)
$(C_{16}H_{14}S_2O_4N_4)$ (Schiff base I)	3080(s)	2750(m)	1625(s)
$(C_{16}H_{13}S_2O_4N_4)_3La$	3085(s)		1640(m)
$(C_{16}H_{13}S_2O_4N_4)_3Ce$	3080(s)		1645(m)
$(C_{16}H_{13}S_2O_4N_4)_3Pr$	3080(s)		1640(m)
$(C_{16}H_{13}S_2O_4N_4)_3Nd$	3080(s)		1640(m)
$(C_{16}H_{13}S_2O_4N_4)_3Gd$	3080(s)		1640(m)
$(C_{16}H_{13}S_2O_4N_4)_3Dy$	3085(s)		1645(m)
$(C_{16}H_{13}S_2O_4N_4)_3Ho$	3080(s)		1640(m)
$(C_{16}H_{13}S_2O_4N_4)_3Er$	3080(s)		1645(m)
$(C_{14}H_{12}N_4S_3O_3)$ (Schiff base II)	3080(s)		1625(s)
$(C_{14}H_{11}N_4S_3O_3)_3La$			1625, 1645(s)
$(C_{14}H_{11}N_4S_3O_3)_3Ce$			1625, 1640(s)
$(C_{14}H_{11}N_4S_3O_3)_3Pr$			1625, 1640(s)
$(C_{14}H_{11}N_4S_3O_3)_3Nd$			1625, 1640(s)
$(C_{14}H_{11}N_4S_3O_3)_3Gd$			1625, 1640(s)
$(C_{14}H_{11}N_4S_3O_3)_3Dy$			1625, 1645(s)
$(C_{14}H_{11}N_3S_3O_3)_3Ho$			1625, 1640(s)
$(C_{14}H_{11}N_4S_3O_3)_3Er$			1625, 1645(s)

It is ascertained that the Schiff base coordinates through the azomethine nitrogen and the phenolic oxygen; the presence of two molecules of water renders the metal to be eight-coordinated.

IR Spectra of Schiff Base II and its Complexes

A strong band at 3150 cm^{-1} in the spectrum of the Schiff base is assigned to ν(N–H) which disappears in the complexes, inferring the replacement of an amino hydrogen by a metal atom. The complexes show one more band in addition to a single azomethine absorption band in the Schiff base at 1625 cm^{-1}. The other frequencies are insignificant and occupy the same positions in the free and chelated ligand.

On the basis of IR studies it is found that the coordination occurs through the azomethine nitrogen and the amino nitrogen atom together with two molecules of water, rendering the metal eight-coordinated.

Electronic Spectra

The electronic spectra were recorded in DMF. The sharp lines due to an f–f transition originating within the 4f^n configuration of the lanthanide(III) ions are affected by the ligands on complexation. The shift of the absorption band to a lower wave

TABLE III. Electronic Spectral Data for Pr^{3+}, Nd^{3+}, Ho^{3+} and Er^{3+} Complexes of Schiff Bases **I** and **II**

Complexes	$1-\beta$	$\bar{\beta}$	$b^{1/2}$	δ %	Energy (Kaisers)	*J* Level
Schiff base **I** complexes						
$(C_{16}H_{13}S_2O_4N_4)_3Pr$	0.0129	0.9870	0.0800	1.3000	16.75	$^1D_2 \leftarrow {}^3H_4$
$(C_{16}H_{13}S_2O_4N_4)_3Nd$	0.0007	0.9993	0.0187	0.0700	13.51	$^4F_{7/2} \leftarrow {}^4I_{9/2}$
$(C_{16}H_{13}S_2O_4N_4)_3Ho$	0.0296	0.9707	0.1217	3.0000	15.51	$^4F_5 \leftarrow {}^5I_8$
Schiff base **II** complexes						
$(C_{14}H_{11}N_4S_3O_3)_3Pr$	0.0200	0.9800	0.1000	2.0400	16.94	$^1D_2 \leftarrow {}^3H_4$
$(C_{14}H_{11}N_4S_3O_3)_3Nd$	0.0040	0.9900	0.0440	0.4040	17.24	$^4G_{5/2} \leftarrow {}^4I_{9/2}$
$(C_{14}H_{11}N_4S_3O_3)_3Er$	0.0170	0.9820	0.0920	1.7300	17.54	$^4S_{3/2} \leftarrow {}^4I_{15/2}$

TABLE IV. Metal–Ligand Stability Constants at 25, 30 and 35 °C

Complexes	Log *K*			$-\Delta G$		
	25 °C	30 °C	35 °C	25 °C	30 °C	35 °C
$(C_{16}H_{13}S_2O_4N_4)La$	3.82 ± 0.11	3.31 ± 0.20	3.20 ± 0.40	5.19	4.57	4.49
$(C_{16}H_{13}S_2O_4N_4)Ce$	4.08 ± 0.20	3.93 ± 0.22	3.43 ± 0.35	5.54	5.42	4.83
$(C_{16}H_{13}S_2O_4N_4)Pr$	4.22 ± 0.10	4.07 ± 0.28	3.63 ± 0.44	5.73	5.62	5.10
$(C_{16}H_{13}S_2O_4N_4)Nd$	4.50 ± 0.17	4.27 ± 0.19	4.02 ± 0.17	6.06	5.89	5.49
$(C_{16}H_{13}S_2O_4N_4)Gd$	4.46 ± 0.34	4.18 ± 0.29	3.91 ± 0.55	6.11	5.77	5.10
$(C_{16}H_{13}S_2O_4N_4)Dy$	4.58 ± 0.15	4.29 ± 0.14	4.10 ± 0.21	6.22	5.92	5.65
$(C_{16}H_{13}S_2O_4N_4)Ho$	4.67 ± 0.31	4.45 ± 0.15	4.13 ± 0.29	6.34	6.14	5.80
$(C_{16}H_{13}S_2O_4N_4)Er$	4.65 ± 0.14	4.32 ± 0.30	4.13 ± 0.19	6.31	5.96	5.80
$(C_{14}H_{11}N_4S_3O_3)La$	4.60 ± 0.26	3.94 ± 0.20	3.39 ± 0.10	6.25	5.45	4.60
$(C_{14}H_{11}N_4S_3O_3)Ce$	4.94 ± 0.20	4.00 ± 0.15	3.82 ± 0.20	6.71	5.53	5.20
$(C_{14}H_{11}N_4S_3O_3)Pr$	5.16 ± 0.26	4.10 ± 0.15	4.07 ± 0.26	7.02	5.67	5.72
$(C_{14}H_{11}N_4S_3O_3)Nd$	5.16 ± 0.20	4.36 ± 0.26	4.13 ± 0.16	7.02	5.93	5.80
$(C_{14}H_{11}N_4S_3O_3)Gd$	4.90 ± 0.16	4.25 ± 0.16	3.96 ± 0.26	6.66	5.87	5.57
$(C_{14}H_{11}N_4S_3O_3)Dy$	5.21 ± 0.20	4.42 ± 0.15	4.16 ± 0.26	7.09	6.00	5.85
$(C_{14}H_{11}N_4S_3O_3)Ho$	5.21 ± 0.16	4.60 ± 0.15	4.20 ± 0.16	7.09	6.35	5.91
$(C_{14}H_{11}N_4S_3O_3)Er$	5.21 ± 0.08	4.67 ± 0.15	4.40 ± 0.16	7.09	6.45	6.18

number (nephelauxetic effect), denoted by $(1-\beta)$, is usually of the order of a few percent. A general red shift of the f–f transition would be observed for these complexes with respect to the corresponding aqua ions [15]. The β values below one reflect the covalent nature of the bond between the metal and the ligand (Table III). The β value of the Nd(III) complexes is higher than that for the Pr(III) complexes, indicating the nephelauxetic effect is more pronounced at the beginning of the 4f group than with later numbers. The positive values of the bonding parameter, $b^{1/2}$ and Sinha's covalency parameter also support the covalent bonding.

The bands of the electronic spectra along with their assignments are given in Table III. These absorption spectra of rare earth metal complexes arise from electronic transitions within the 4f levels [16, 17]. The absorption bands of Pr(III), Nd(III), Ho(III) and Er(III) in the visible region appear due to transitions from the ground levels $^3H_4$, $^4I_{9/2}$, $^5I_8$ and $^4I_{15/2}$ respectively to the excited *J* level of the 4f configuration.

Proton–Ligand Stability Constant

The proton–ligand formation numbers $\bar{n}_A$ for the Schiff bases **I** and **II** were calculated using the Irving and Rossotti equation [12]. The proton–ligand stability constants (pK^H) were obtained by the pointwise calculation method. The acid ligand curves in all cases deviated from the pure acid curve at pH = 2.5. The highest $\bar{n}_A$ values obtained were 0.91 and 0.94 for **I** and **II**, respectively, showing the presence of only one dissociable proton, although the Schiff base **I** contains two protons.

Metal–Ligand Stability Constants

In order to prevent polymerization, very dilute solutions were used. The metal–ligand titration curves deviate from the pure ligand curve at pH = 2.5–3.5. The maximum $\bar{n}$ values in most of the curves are below unity and hence only log K_1 was obtained (Table IV) using the equation

$$\log K_1 = pL + \log \frac{\bar{n}}{1-\bar{n}}$$

TABLE V. Percent Inhibition Data of (a) *Aspergillus flavus,* (b) *A. niger* and (c) *Alternaria pori,* and (d) Percent Mortality and LD_{50} Values for Cockroaches with Corresponding Concentrations of the Schiff Bases and their Complexes

Ligand/Complex	Concentration (%)	Percent inhibition	Log concentration (ppm × 100)	Percent mortality	Probit values	LD_{50}
(a) ($C_{16}H_{14}S_2N_4O_4$)/complex	2	70/75				
	3	75/80				
	4	80/85				
($C_{14}H_{12}N_4S_3O_3$)/complex	2	75/80				
	3	80/85				
	4	85/90				
(b) ($C_{16}H_{14}S_2N_4O_4$)/complex	2	69/74				
	3	75/80				
	4	80/85				
($C_{14}H_{12}N_4S_3O_3$)/complex	2	74/80				
	3	80/85				
	4	85/90				
(c) ($C_{16}H_{14}S_2N_4O_4$)/complex	2	70/75				
	3	75/80				
	4	80/85				
($C_{14}H_{12}N_4S_3O_3$)/complex	2	75/80				
	3	80/85				
	4	85/90				
(d) ($C_{16}H_{14}S_2N_4O_4$)/complex			2.77	20/33.3	4.1584/4.5684	
			2.84	33.3/50	4.5684/5.0000	
			2.90	50/70	5.0000/5.5244	7.94/6.91
			2.95	70/80	5.5244/5.8416	
			3.00	80/100	5.8416/–	
($C_{14}H_{12}N_4S_3O_3$)/complex			2.77	33.3/40	4.5684/4.7467	
			2.84	40/60	4.7467/5.2533	
			2.90	60/70	5.2533/5.5244	7.41/6.31
			2.95	70/80	5.5244/5.8416	
			3.00	80/100	5.8416/–	

This infers the formation of a 1:1 complex. The free ligand exponent pL values were calculated at various $\bar{n}$ values and the metal–ligand formation curves were constructed by plotting $\bar{n}$ against pL values, yielding the values of the formation constant log K (Table IV). It has been observed that log K is inversely proportional to temperature. The values for free energy ($-\Delta G$) were also calculated using the equation (Table IV)

$$-\Delta G = RT \ln K$$

A plot of log K *versus* e^2/r shows a roughly linear relationship, suggesting an ionic character for the metal–ligand bond while the solid complexes appear to be covalent.

Toxic Effects

The ability of the Schiff bases **I** and **II** to exhibit insecticidal activity is shown in Table V and a comparative study is made with their complexes. It is evident from Table V that the toxicity of the Schiff bases is significantly enhanced when complexed.

The antifungal activities of the Schiff bases and their complexes were evaluated against *A. flavus, A. niger* and *Alternaria pori* in the 2–4% concentration range. It is demonstrated from percent inhibition data that the Schiff base complexes of **II** are more toxic than those of **I** (Table V)

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