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Mono- and Bi-Nuclear Metal Complexes of Arylidene-Anthranilic Acid *Schiff* Bases

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Arylidene-anthranilic acid *Schiff* base complexes with Th(IV), UO_2(II), La(III), Ce(III), and Zr(IV) have been isolated and studied by several techniques, e.g. elemental analysis, electronic and IR spectra and conductance measurements. It is concluded that the salicylideneanthranilic acid L_3 is coordinated to the metal ion as bivalent tridentate ONO ligand (L^{-2}) while the other ligands behave as monovalent bidentate ON ligands. Furthermore, the molecular structure effect of these compounds on their tendency towards complex formation was investigated and discussed. The possibility that the Cu(II) complex of L_3 can act as bidentate ligand, coordinating through its *cis*-oxygen atoms to form binuclear metal complexes was studied.

(Keywords: Schiff-base complexes)

Ein- und zweikernige Metall-Komplexe von Aryliden-Anthranilsäure-Schiff-Basen

Es wurden Aryliden-Anthranilsäure-*Schiff*-Basen mit Th(IV), UO_2(II), La(III), Ce(III) und Zr(IV) isoliert und mittels Elementaranalysen, Elektronen- und IR-Spektroskopie und Leitfähigkeitsmessungen untersucht. Es wird aus den Untersuchungen geschlossen, daß Salicylidenanthranilsäure (L_3) als bivalenter dreizähniger ONO-Ligand (L^{-2}) an das Metallion koordiniert, währenddessen die anderen Liganden als monovalente zweizähnige Liganden agieren. Außerdem wurden Struktureffekte dieser Verbindungen in bezug auf ihre Komplexbildungstendenz untersucht. Die Möglichkeit, daß der Cu(II)-Komplex von L_3 über die Koordination mit den *cis*-Sauerstoff-Atomen und unter Bildung eines zweikernigen Metallkomplexes als zweizähniger Ligand agieren kann, wurde untersucht.

Introduction

Generally, although metal complexes of *Schiff* bases derived from various amines and substituted benzaldehyde have been studied extensively, little attention has been given to systems in which the *Schiff* base is derived from anthranilic acid and aromatic aldehydes[1]. It is of considerable interest to study these metal chelate systems since salicylidene-anthranilic acid complex may serve as model for N-pyridoxylidene-amino acid systems which are believed to act as intermediates in the biologically important amination process[2—4]. In this paper we have undertaken an investigation of the reaction of *Schiff* bases derived from anthranilic acid and some aromatic aldehydes: *p*-dimethylaminobenzaldehyde (L_1), *p*-hydroxybenzaldehyde (L_2), salicylaldehyde (L_3), cinnamaldehyde (L_4) and *p*-nitrobenzaldehyde (L_5) with some metal ions: Th(IV), UO_2(II), La(III), Ce(III) and Zr(IV). The study involves synthesis of these complexes and characterization of their structures. In addition the work represented here involves an examination of the possibility that the Cu(II) complex of the *Schiff* base salicylidene-anthranilic acid (L_3) can act as a bidentate ligand through its *cis*-oxygen atoms to form binuclear complexes with the metal ions studied.

Experimental

All reagents used in this investigation were A. R. products (Merck or B.D.H.). Arylidene-anthranilic acids were prepared by the usual condensation reaction as described before[5]. The compounds were purified by recrystallisation from ethanol.

Synthesis of Mononuclear Metal Complexes

All the mononuclear metal complexes were prepared by mixing the required amount of the *Schiff* base dissolved in the least amount of ethanol with the appropriate amount of the metal salt $UO_2(NO_3)_2 \cdot 6\,H_2O$, $Th(NO_3)_4 \cdot 5\,H_2O$, $La(NO_3)_3 \cdot 5\,H_2O$, $Ce(NO_3)_3 \cdot 6\,H_2O$ and $Zr(NO_3)_4$ (B.D.H. or Merck Products) in molar ratios 1 : 1 and 2 : 1. In case of Zr(IV), due to the sparingly soluble character of $Zr(NO_3)_4$ in ethanol, a small quantity of doubly distilled water was added to the reaction mixture. The reaction mixture was refluxed for a period of time depending upon the molecular structure of the *Schiff* base (0.5–2, 4–6, 0.5–1), 0.5–1 ∼ 6, ∼ 8 hours in case of the ligands L_1, L_2, L_3, L_4 and L_5 respectively). Then the reaction mixture was evaporated to a small volume and left to cool whereby the solid complexes were separated as fine crystals. The deposited metal complexes were filtered, washed with small quantities of absolute ethanol and dried in a vacuum desiccator over dried silica gel. It is worth to note that Zr(IV) complexes with all ligands used were separated as resinous substances which were triturated successively with ether several times to give the solid products. The isolated solid complexes were then analyzed for their carbon and nitrogen contents. The results of analysis of the various metal complexes are given in Table 1.

Synthesis of Binuclear Metal Salicylidene-Anthranilic Acid Complexes

The proper metal nitrate salt dissolved in the least amount of absolute ethanol was added slowly and under stirring to the ethanolic concentrated solution of 1 : 1 Cu(II) salicylideneanthranilic acid complex "CuL_3". The reaction mixture was refluxed for ∼ 8 hours. On cooling the solid complexes were separated as fine

Table 1. *Analytical data of the different metal complexes of Schiff bases; arylidene-anthranilic acids* (L_1–L_5)

Formula	% Calcd.		% Found	
	C	N	C	N
Complexes of L_1				
$[(C_{16}O_2H_{15}N_2)(H_2O)_2Th](NO_3)_3$	26.64	9.71	26.10	9.30
$[(C_{16}O_2N_{15}N_2)_2(H_2O)_2Th](NO_3)_2$	41.47	9.07	41.73	8.65
$[(C_{16}O_2H_{15}N_2)_2(H_2O)_2UO_2]$	45.72	6.66	45.35	6.60
$[(C_{16}O_2H_{15}N_2)_2(H_2O)_2Ce](NO_3)$	49.74	9.06	49.16	8.67
$[(C_{16}O_2H_{15}N_2)_2(H_2O)_2La](NO_3)$	49.81	9.08	49.43	9.19
$[(C_{16}O_2H_{15}N_2)(H_2O)_2Zr](NO_3)_3$	33.10	12.06	33.70	11.60
$[(C_{16}O_2H_{15}N_2)_2(H_2O)_2Zr](NO_3)_2$	48.90	10.70	48.92	10.20
Complexes of L_2				
$[(C_{14}O_3H_{10}N)_2(H_2O)_2Th](NO_3)_2$	38.53	6.42	37.69	6.60
$[(C_{14}O_3H_{10}N)(H_2O)_2UO_2](NO_3)$	27.64	4.60	27.70	5.50
$[(C_{14}O_3H_{10}N)_2(H_2O)_2UO_2]$	42.75	3.56	42.20	3.80
$[(C_{14}O_3H_{10}N)(H_2O)_4Ce](NO_3)_2$	29.16	7.29	28.90	7.20
$[(C_{14}O_3H_{10}N)_2(H_2O)_2Ce](NO_3)$	46.80	5.85	45.98	5.32
$[(C_{14}O_3H_{10}N)(H_2O)_4La](NO_3)_2$	29.23	7.20	28.90	7.60
$[(C_{14}O_3H_{10}N)_2(H_2O)_2La](NO_3)$	46.88	5.86	46.61	5.95
$[(C_{14}O_3H_{10}N)(H_2O)_2Zr](NO_3)_3$	30.48	10.12	30.10	9.70
Complexes of L_3				
$[(C_{14}O_3H_9N)(H_2O)_3Th](NO_3)_2$	25.89	6.47	26.50	6.50
$[(C_{14}O_3H_9N)_2(H_2O)_2Th]$	45.04	3.75	44.34	3.88
$[(C_{14}O_3H_9N)UO_2(H_2O)]$	31.87	2.65	32.10	2.50
$[(C_{14}O_3H_9N)_2Ce(H_2O)_2]H$	51.30	4.27	50.90	4.40
$[(C_{14}O_3H_9N)(H_2U)_3La](NO_3)$	34.03	5.67	33.80	6.10
$[(C_{14}O_3H_9N)_2La(H_2O)_2]H$	51.39	3.28	51.13	4.50
$[(C_{14}O_3H_9N)Zr(H_2O)_3](NO_3)_2$	33.07	8.26	33.60	8.60
Complexes of L_4				
$[(C_{16}O_2H_{12}N)_2(H_2O)_2Th](NO_3)_2$	43.05	6.27	43.45	6.10
$[(C_{16}O_2H_{12}N)_2(H_2O)_2UO_2]$	47.64	3.47	4.79	3.62
$[(C_{16}O_2H_{12}N)(H_2O)_4Ce](NO_3)_2$	33.76	7.17	33.73	6.90
$[(C_{16}O_2H_{12}N)_2(H_2O)_2Ce](NO_3)$	52.03	5.69	50.30	5.20
$[(C_{16}O_2H_{12}N)(H_2O)_4La](NO_3)_2$	32.82	7.18	32.90	7.35
$[(C_{16}O_2H_{12}N)_2(H_2O)_2La](NO_3)$	52.11	5.70	51.90	5.30
$[(C_{16}O_2H_{12}N)(H_2O)_2Zr](NO_3)_3$	34.10	9.94	33.70	9.30
$[(C_{16}O_2H_{12}N)_2(H_2O)_2Zr](NO_3)_2$	51.13	7.45	50.70	7.10
Complexes of L_5				
$[(C_{14}O_4H_9N_2)(H_2O)_2Th](NO_3)_3$	23.25	9.68	22.90	9.70
$[(C_{14}O_4H_9N_2)_2(H_2O)_2Th](NO_3)_2$	36.14	9.03	36.86	8.71
$[(C_{14}O_4H_9N_2)_2UO_2(H_2O)_2]$	39.81	6.63	39.20	6.29
$[(C_{14}O_4H_9N_2)_2(H_2O)_2Ce](NO_3)$	42.30	9.02	42.80	8.58
$[(C_{14}O_4H_9N_2)_2(H_2O)_2La](NO_3)$	43.37	9.03	43.10	8.60

precipitates. The complexes formed were collected, washed with ethanol and dried in vacuo over silica gel. The solid complexes separated were analyzed for their carbon and nitrogen contents, and the results obtained are recorded in Table 2.

It is noteworthy that the Cu(II)-salicylideneanthranilic acid complex "CuL_3" was prepared following the method described above.

Solutions

10^{-2} *M* stock solutions of the *Schiff* bases and metal salts in absolute ethanol were prepared. Solutions of low molarity were obtained by accurate dilution.

Physical Measurements

The electronic absorption spectra measurements were carried out on a UNICAM SP 8000 Ultraviolet recording spectrophotometer using 1 cm matched silica cells. The IR spectra of the *Schiff* bases and their complexes were obtained on a Beckman IR-spectrophotometer using KBr discs. Conductance measurements were carried out using PYE conductance bridge at 25 °C using a dip type cell.

Results and Discussion

Mononuclear Complexes

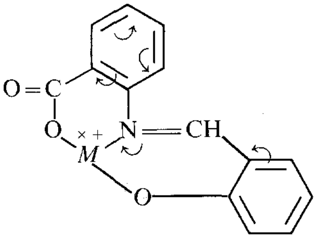
Schiff Base Molecular Structure Effect on Complex Formation

It was deduced that the *Schiff* base salicylidene-anthranilic acid L_3 has a greater tendency to complex formation relative to the other *Schiff* bases investigated. This was deduced from the fact that instantaneous complex formation occurred in the case of L_3 ($1 \cdot 10^{-4}$ *M*) with the metal ions Th(IV), UO_2(II), Ce(III) and La(III) while for the other *Schiff* bases instantaneous complex formation was observed only with Th(IV) and UO_2(II) when a higher concentration of the *Schiff* base was used ($\geqslant 5 \cdot 10^{-4}$ *M*). It was observed that the electronic absorption spectrum of the free *Schiff* base L_3 solution ($1 \cdot 10^{-4}$ *M*) did not resemble those of its complex solutions with Th(IV), UO_2(II), La(III) and Ce(III) in 2 : 1 molar ratio, using ethanol as blank. Furthermore a new absorption band was observed in the spectra recorded for the Th(IV) and UO_2(II) complex solutions with the *Schiff* bases L_1, L_2, L_4 and L_5, the blank being a solution of the *Schiff* base of the same concentration as in the complex solution. In the metal complex solutions the longer wavelength band of L_3 showed a red shift in its λ_{max} (5–8 nm) and a higher molar extinction coefficient compared with the free ligand. Moreover, in the case of the L_3-Th(IV) complex solution, a new band was observed at longer wavelength (440 nm). This behaviour can be interpreted on the basis that the longer wavelength band observed in the spectrum of free L_3 can be ascribed to an intramolecular charge transfer transition which takes place within the *Schiff* base molecule[5]. Thus the low excitation energy observed for this band in the spectra of the different metal ion complex solutions of this *Schiff* base can be attributed to the expected easier intramolecular charge

Table 2. *Analytical data and molar conductance values (ohm^{-1} mol^{-1} cm^{2}) of the binuclear metal complexes of Schiff base salicylideneanthranilic acid (L_3).*

Formula	Molar conductance	% Calculated		% Found	
		C	N	C	N
$[(C_{14}O_3H_9N)CuTh(H_2O)_3(NO_3)_2](NO_3)_2$	100	20.08	8.36	19.60	8.10
$[(C_{14}O_3H_9N)CuUO_2(H_2O)_2](NO_3)_2$	132	22.94	5.73	22.90	6.00
$[(C_{14}O_3H_9N)CuLa(H_2O)_4(NO_3)](NO_3)_2$	145	24.02	8.00	23.60	8.10
$[(C_{14}O_3H_9N)CuCe(H_2O)_4(NO_3)](NO_3)_2$	120	23.97	7.99	22.50	7.70

transfer in the complexed ligand relative to that in the free ligand. This results from the high positive charge of the coordinated metal ion. In the light of our conclusions drawn from this study the intramolecular CT takes place within the complexed L_3 moiety, which can be represented schematically as follows:



Accordingly, the new band observed at longer wavelength in the spectrum of the Th(IV)-L_3 complex solution can be presumably ascribed to an intramolecular CT transition within the chelated Th(IV) ring.

It is noteworthy that, due to the low solubility of $Zr(NO_3)_4$ in ethanol, no spectral data for the Zr(IV)-L_3 complex solution can be reported.

The observed difference in the tendency of the *Schiff* bases in complex formation can be attributed mainly to the difference in the strength of the intramolecular hydrogen bond established between the hydrogen carboxyl and the azomethine nitrogen under the electronic effect of the polar substituent attached to the aldehyde moiety. Thus, in L_3 the interaction between the *o*-OH and *o*-COOH groups belonging to the aldehyde and the amine moieties, respectively, through hydrogen bonding will weaken the strength of the hydrogen bond existing between the hydrogen carboxyl and the central azomethine nitrogen relative to that existing in the other *Schiff* bases molecules[5]. This behaviour is reflected in a relatively high basicity of the azomethine nitrogen of *Schiff* base L_3 relative to that of the other *Schiff* bases. Moreover, L_3 contains an additional donor OH group at the *ortho* position of the aldehyde moiety which is expected also to promote complex formation. Thus one should expect that L_3 is characterised by high tendency in complex formation relative to the other *Schiff* bases, where two stable six member chelated rings can be formed as represented schematically above.

Structure of the Complexes

The stoichiometry of the complexes formed in solution from the reaction of the *Schiff* base L_3 with metal ions, as well as of these formed from the reaction of each of the *Schiff* bases L_1, L_2, L_4 and L_5 with Th(IV) and UO_2(II) was ascertained by applying the conventional spectrophotometric molar ratio and continuous variation methods[6,7]. The blank being however, in all cases a solution of the *Schiff* base of the same concentration as in the solution of the complexes. The results clearly indicate the possible formation of 1 : 1 complexes with all metal ions used. Representative results are shown in Figs. 1 and 2. Moreover, the stoichiometry of these complexes is also confirmed by conductometric titration of each of the absolute ethanolic solution of the metal ions studied with high concentration of the ligand (Fig. 3).

The results of the continuous variations method were applied to the determination of the apparent stability of the different metal complexes formed in solution[8]. The K_f values obtained are listed in Table 3. The results recorded in this table shows that the La(III) and Ce(III)-L_3 complexes are less stable than the corresponding Th(IV) and UO_2(II) complexes. This is understandable if one recalls the fact that the lanthanide metal ions are characterized by weak tendency towards complex formation relative to the actinide ions[9]. Furthermore, it is evident that the stability of L_3 complexes is higher than those of the other *Schiff* bases. Moreover, careful examination of the apparent formation constant values given in Table 3 reveals that the stability of the same metal complex

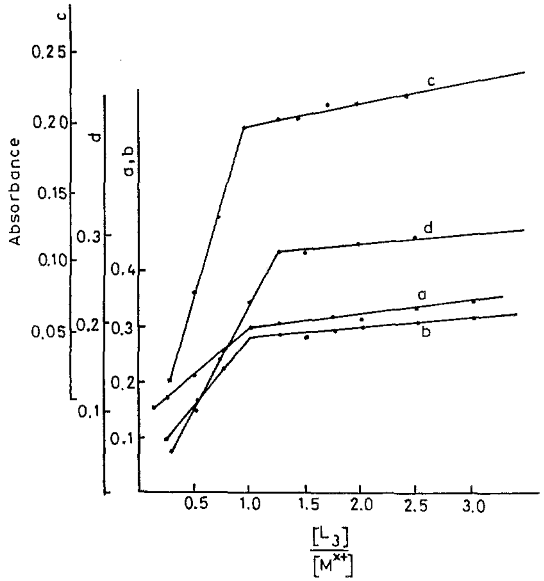


Fig. 1. Molar ratio method for *Schiff* base L_3-metal complexes: a) Th(IV), $[\mathrm{Th(IV)}] = 5 \cdot 10^{-4} M$, $\lambda = 360\,\mathrm{nm}$; *b* UO_2(II), $[\mathrm{UO_2(II)}] = 1 \cdot 10^{-4} M$, $\lambda = 350\,\mathrm{nm}$; *c* La(III), $[\mathrm{La(III)}] = 4 \cdot 10^{-4} M$, $\lambda = 356\,\mathrm{nm}$; *d* Ce(III), $[\mathrm{Ce(III)}] = 2 \cdot 10^{-4} M$, $\lambda = 344\,\mathrm{nm}$

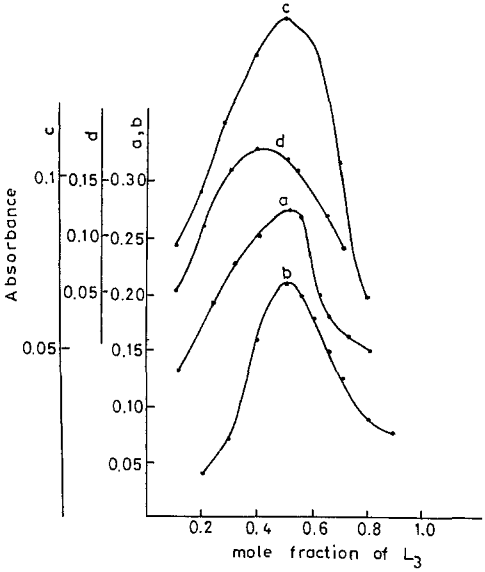


Fig. 2. Continuous variation method for *Schiff* base L_3-metal complexes: *a* Th(IV), Total molar concentration $= 1 \cdot 10^{-3} M$, $\lambda = 364$ nm; *b* UO_2(II), Tot. m. conc. $= 2 \cdot 10^{-4} M$, $\lambda = 345$ nm; *c* La(III), Tot. m. conc. $= 2 \cdot 10^{-3} M$, $\lambda = 346$ nm; *d* Ce(III), Tot. m. conc. $= 1 \cdot 10^{-3} M$, $\lambda = 346$ nm

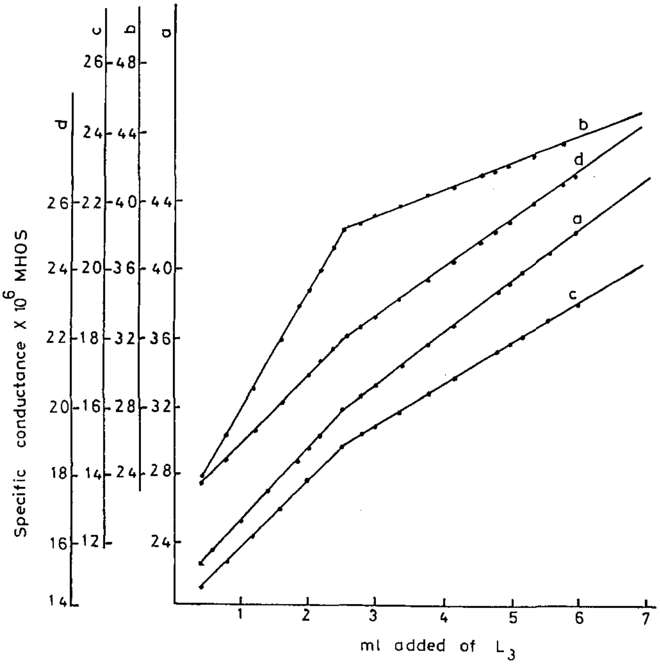


Fig. 3. Conductometric titration of 25 ml $1 \cdot 10^{-3} M$ metal ion solution with $1 \cdot 10^{-2} M$ of *Schiff* base L_3: *a* Th(IV); *b* UO_2(II); *c* La(III); *d* Ce(III)

Table 3. *Apparent formation constant values* (K_f) *for the different 1 : 1 complexes formed in solution*

Ligand	Th(IV)						UO_2(II)						La(III)						Ce(III)					
	λ_{nm}	K_f x 10^5	λ_{nm}	K_f x 10^5	λ_{nm}	K_f x 10^5	λ_{nm}	K_f x 10^5	λ_{nm}	K_f x 10^5	λ_{nm}	K_f x 10^5	λ_{nm}	K_f x 10^5	λ_{nm}	K_f x 10^5	λ_{nm}	K_f x 10^5	λ_{nm}	K_f x 10^5	λ_{nm}	K_f x 10^5	λ_{nm}	K_f x 10^5
L_1	360	2.9	368	2.5	377	2.2	357	6.84	366	7.20	375	8.2	-	-	-	-	-	-	-	-	-	-	-	-
L_2	355	1.4	364	1.7	373	1.1	360	4.80	360	5.80	380	5.6	-	-	-	-	-	-	-	-	-	-	-	-
L_3	358	6.8	364	7.1	371	7.8	335	10.2	345	9.20	350	10.8	335	4.2	346	4.8	355	4.3	336	8.2	346	8.4	355	7.6
L_4	-	-	-	-	-	-	350	3.10	360	2.60	370	3.5	-	-	-	-	-	-	-	-	-	-	-	-
L_5	345	0.72	354	0.65	363	8.4	350	0,54	360	0.41	370	0.61	-	-	-	-	-	-	-	-	-	-	-	-

with the different *Schiff* bases studied decreases according to the following sequence:

$$I > II > IV > V$$

This order is in line with lowering of the basicity of the central azomethine nitrogen in the same direction under the electronic effect of the polar substituent attached to the aldehyde moiety. Thus the *Schiff* base tendency in complex formation is expected to decrease in the same direction. The results of chemical analysis of the different solid complexes prepared reveal that the divalent L_3 and the monovalent L_1, L_2, L_4 and L_5 molecules are coordinated to the metal ion.

The significant IR absorption bands of the free ligands under investigation and their metal complexes are shown in Table 4 along with their assignments to group vibration where possible. No absorption band is observed due to the stretching vibration of the OH group of the carboxyl one in the case of all free ligands or for the OH group in case of L_3. Instead, the spectra of all free ligands show a broad weak band having a fine structure in the region 2 600–3 000 cm^{-1} and this is attributed to the stretching vibration of the intramolecular hydrogen bonded OH with the azomethine nitrogen atom. This assignment agrees well with that given by *Baker* and *Shulgin*[10], *Freedman*[11], *Ueno* and *Martell*[12] in the case of salicylideneaniline. This band totally disappeared on complexation suggesting that the carboxyl group or the *o*-OH group (L_3) has taken part in complex formation. However, the band found at 3 040 cm^{-1} in the IR spectrum of L_2 is due to the stretching vibration of the *p*-OH group of the aldehyde moiety. The strong band found at 1 288 and 1 285 cm^{-1} in the IR spectra of the free L_2 and L_3 respectively is ascribed to the phenolic C—O stretching[13, 14]. The absence of this band in the IR spectra of the other free ligands confirms this assignment. This band exhibits a blue shift in the IR spectra of the resultant complexes, which can be ascribed to the perturbing effect of the electric field of the coordinating metal ion on such type of vibration. The IR spectra of all free ligands show a strong band in the region 1 678–1 690 cm^{-1} which may be assigned to the stretching vibration of the carboxyl group belonging to the carbonyl one[15]. On complexation, this band completely disappears and in some cases two bands appear instead in the regions 1 570 to 1 608 cm^{-1} and 1 385 to 1 440 cm^{-1}. These two bands can be assigned to the antisymmetric and symmetric stretching of the COO$^-$ group[15]. This behaviour can be considered as a convincing evidence for the above mentioned fact that the anions and not the molecules of the ligands under investigation are coordinated to the metal ion. It is worth mentioning that the difficulty in ascertaining the antisymmetric and symmetric stretching vibration bands of the COO$^-$ group in the IR spectra of some complexes is presumably due to their overlaping with the high intensity bands of the C = C stretching vibrations (1 400–1 580 cm^{-1})^{16}.

The strong band observed in the region 1 600–1 612 cm^{-1} in the IR spectra of all free ligands can be assigned to —C = N-stretching vibration. This band acquired a marked shift in its frequency on complexation, suggesting that the subject ligands L_1–L_5 are coordinated to the metal ions studied through the azomethine nitrogen atom.

The IR spectra of all complexes prepared show a broad band in the region 3 200–3 460 cm^{-1}. This indicates that water molecules exist in the complexes prepared, a fact which is confirmed by the results of the analysis of the complexes prepared (c.f. Table 1). The most important conclusions drawn from this study are:

(i) L_3 is coordinated to the metal ion as divalent tridentate ligand (L_3^{-2}). The three bonding sites are the oxygens of the carboxyl and hydroxyl groups and the azomethine nitrogen atom where two six member chelated rings are formed.

(ii) L_1, L_2, L_4, L_5 are coordinated to the metal ion as monovalent bidentate ligand (L^{-1}). The two bonding sites are the oxygen carboxyl and the azomethine nitrogen where a six member chelated ring is formed.

Table 4. *Some infrared frequencies (in cm^{-1}) of ligands L_1–L_5 and their metal complexes*

Cu(II)-L_3 complex	Mixed Metal complexes with				Assignment
	Th(IV)	UO_2(II)	La(II)	Ce(III)	
-	3460	3400	3460	3500	OH—stretching
1570	1600	1610	1600	1620	C=H stretching
1230	1310	1290	1350	1350	C-O phenyl stretching
--	-	925	-	-	UO_2 asym.stretching

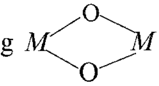
Binuclear Metal Complexes of L_3

The analytical data of the binuclear metal complexes synthesized by the reaction of the "complexes ligand" "CuL_3" with the nitrate salts of Th(IV), UO_2(II), La(III) and Ce(III) reported in Table 2 indicate that these complexes are of the type $[CuL_3Th(H_2O)_3(NO_3)_2](NO_3)_2$, $[CuL_3UO_2(H_2O)_2](NO_3)_2$, $[CuL_3La(H_2O)_4](NO_3)_2$ and $[CuL_3Ce(H_2O)_4(NO_3)](NO_3)_2$. The measured molar conductance values of these complexes in *DMF* at the concentration 10^{-3} *M* fall in the range

Table 5. *Some infrared frequencies (in* cm^{-1}*) of the* $Cu(II)$*-*L_3 *complex and its mixed metal complexes*

	Complexes						Complexes					
L_1	Th(IV)	UO_2(II)	La(III)	Ce(III)	Zr(IV)	L_2	Th(IV)	UO_2(II)	La(III)	Ce(III)	Zr(IV)	Assignment
---	3460^{w}	3400^{w}	3400^{w}	3400^{w}	3400	3400	3200^{b}	3000	3400^{b}	3380^{b}	3380^{b}	OH-Stretching
2800^{b}	--	--	--	--	--	2600^{b}	--	--	--	--	--	H-Bonded OH stretching
1678	--	--	--	--	--	1690	--	--	--	--	--	C=O Stretching
1600^{sh}	1630	1635	1640	1635	1590	1612	1642	1640	1647	1640	1693	C=N Stretching
--	1600	1600	1605	1608	--	--	1575	1572	1570	1570	--	$C{\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O}}$ Antisym-stretching
--	--	--	--	--	--	--	1402	1402	1398	1390^{sh}	1400^{w}	$C{\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O}}$ Sym.stretching
--	--	--	--	--	--	1288	1295	1290	1300	1302	1296	Phenolic C-O stretching
L_3						L_4						
--	3420^{w}	3400^{w}	3420^{w}	3400^{b}	3380^{b}	--	3400	3380	3400	3400	3400	OH-Stretching
3000^{b}	--	--	--	--	--	2600^{b}	--	--	--	--	--	H-Bonded OH stretching
1685	--	--	--	--	--	1692	--	--	--	--	--	C=O Stretching
1610	1590	1585	1605	1602	1608	1605	1608	1605	1598	1598	1600	C=N Stretching
--	--	--	--	--	1570	--	--	--	--	--	--	$C{\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O}}$ Antisym-stretching
--	1400^{sh}	1445	1440	1430	1400	--	1385	1420	1390	1380	1395	$C{\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O}}$ Sym.stretching
1285	1290	1295	1290	1290	1296	--	--	--	--	--	--	Phenolic C-O stretching
L_5												
3300	3400^{w}	3400^{w}	3300	3200								OH-Stretching
2900^{b}	--	--	--	--								H-Bonded OH stretching
1700	--	--	--	--								C=O Stretching
1602	1600	1610	1608	--								C=N Stretching
--	--	--	--	--								$C{\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O}}$ Antisym-stretching
---	1385	1385	1400	1410								$C{\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O}}$ Sym.stretching
--	--	--	--	--								Phenolic C-O stretching

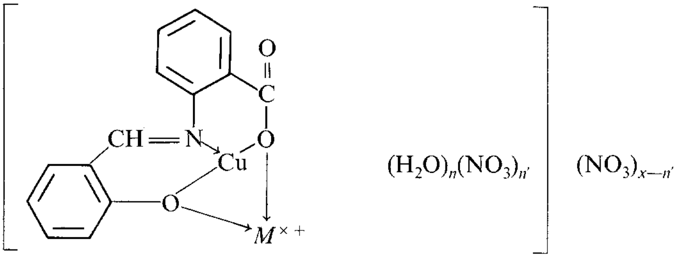
100–145 ohms^{-1} cm^2 mol^{-1} suggesting that these complexes are of the type 1 : 2 electrolytes[17].

Significant changes in the IR spectrum of the "complexes ligand" "CuL_3" were observed on coordinating to metal ion to form binuclear complexes (Table 5). It is evident that the bands at 1 670 and 1 280 cm^{-1} attributed to the conjugated C=N and phenolic C—O stretching vibration respectively in the "complexed ligand" "CuL_3" acquire a shift to high frequencies on complexation. This is compatible with the increasing constraint introduced by the oxygen bridging 

(Ref.[18]). Since UO$_2$(II) is characterized by three vibrational frequencies, the symmetric (ν_1), asymmetric (ν_3) and the binding (ν_2) frequency[19, 20], one can assign the band appearing in the IR spectrum of the binuclear UO$_2$(II) complex at 925 cm^{-1} to the ν_3 vibration of the UO$_2$(II). However, the bands due to ν_1 and ν_2 vibration could not be noted.

The appearance of a broad band centred around 3 400–3 460 cm^{-1} in the IR spectra of the resultant binuclear complexes indicates the presence of water molecules in these complexes. This was confirmed by the results of analysis of such complexes (c.f. Table 2).

Based on the above discussion the structure of the synthesized binuclear complexes can be suggested as follows:



M^{x+} = Th(IV), $n = 3$, $n' = 2$
M^{x+} = UO$_2$(II), $n = 2$, $n' = 0$
M^{x+} = La(III), $n = 4$, $n' = 1$
M^{x+} = Ce(III), $n = 4$, $n' = 1$

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