Physical Sciences Section

METAL COMPLEXES OF (SALICYLALDEHYDE) (2-HYDROXY-ACETOPHENONE) ETHYLENEDIIMINE

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The 1:1 (metal:ligand) solid complexes of Mn^{2+}, Fe^{3+}, La^{3+}, Ce^{3+}, and UO_2^{2+} and 1:2 complexes of Mn^{2+} and Fe^{3+}, with the non-symmetrical tetradentate Schiff base (salicylaldehyde) (2-hydroxy acetophenone) ethylenediimine (SAE) have been synthesized and characterized on the basis of elemental analysis, infrared and electronic spectral data. Stoichiometry and stability of the complexes have been tested in solution using electronic spectra and conductometric measurements. It is concluded that the Schiff base acts as a bivalent ONNO tetradentate ligand. The proton dissociation constants of the ligand have been determined potentiometrically at an ionic strength of 0.1M $NaClO_4$.

Key words: Complex, Schiff bases, Diiminoderivatives.

Introduction

Metal complexes of Schiff bases have contributed widely to the inorganic chemistry of chelate systems. Particular attention has been paid to the complexes of tetradentate diimino bases such as bis(acetylacetone) ethylenediimine and bis(salicylaldehyde) ethylenediimine[1-3]. Generally, it is reported [4-7] that the known non-symmetrical diimines have been obtained by a template synthesis and have not been isolated in the free uncoordinated state. However, the non-symmetrical diimines involving ethylenediamine, acetylacetone, salicylaldhyde and 2-hydroxy acetophenone and their Ni(II) and CO(III) complexes were prepared [8] to demonstrate the tetradentate behaviour of such ligands.

Experimental

The Schiff base (salicylaldehyde) (2-hydroxy-acetophenone) ethylenediimine (SAE) has been obtained in a two step process. In the first, one mole of hot ethanolic ethylenediamine is added to one mole of salicylaldehyde in ethanol to afford a 1:1 condensation product. In the second step, one mole of 2-hydroxy-acetophenone dissolved in a few drops of ethanol is added. The mixture was refluxed over a water-bath for about 30 mins with constant stirring and then allowed to cool at room temperature. The product was filtered off and crystallised several times from pure ethanol as shining yellow plates.

The metal complexes were prepared by reacting one mole of hot ethanolic solution of metal salt ($MnCl_2 4H_2O$, $UO_2(CH_3COO)_2 2H_2O$, $FeCl_3 6H_2O$, $Ce(NO_3)_3 6H_2O$, and $La(NO_3)_3 6H_2$)) to one or two moles of ethanolic solution of the Schiff base (SAE). The mixture was refluxed for 3 hrs on a water-bath and then concentrated to a small volume and allowed to cool when a precipitate separated. The solid was filtered off, washed several times with cold ethanol and finally with acetone. It was dried in vacuo at room temperature and then kept over dry silica gel. The purity of the ligand and its complexes was checked by thin layer chromatogrphy (TLC) silica gel plates using ethanol as developer where only single spots were detected in all the cases. The structures of the ligand and its complexes were confirmed by elemental analysis and infrared spectra (Tables 1,2). The structural formula of the ligand is:

For spectral and conductometric titration measurements,
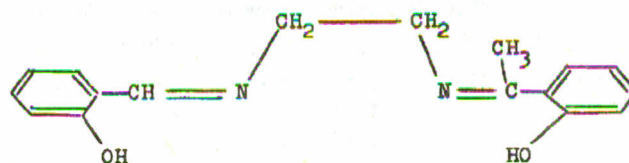
1×10^{-3} mol. dm^{-3} solution of the Schiff base as well as of the metal salts were prepared by dissolving the accurately weighed amount of each in absolute ethanol. More dilute solutions of the reagents were obtained as required by accurate dilution.

The electronic spectra were recorded on Cecil CE 599 spectrophotometer using 1cm matched silica cells. The infrared spectra of the ligand and its complexes were recorded on a Perkin-Elmer 599 spectrophotometer as KBr discs. Conductometric titrations were performed with a WPA, Saffron Walden, CM-25 conductivity meter. The solvents used were of spectro-grade. Other materials were of G.R. grade.

The proton dissociation constants of the Schiff base (SAE) have been evaluated potentiometrically by Calvin-Bjerrum [9,10] pH titration technique as adopted by Irving and Rossotti [11]. Sargent-Welch pH meter model LS with glass-calomel electrode assembly was used for pH measurements. Perchloric acid (BDH) and sodium hydroxide solutions were standardized potentiometrically. The following mixtures were prepared, (i) 25mM $HClO_4$ + 0.1M $NaClO_4$, (ii) 25mM $HClO_4$ + 0.1M $NaClO_4$ + 0.5mM Schiff base. The total volume was kept 25 ml. Each mixture was separately titrated against standard 0.104M NaOH. The average number of the protons

TABLE 1. ANALYTICAL DATA, COLOUR AND DECOMPOSITION TEMPERATURE OF THE LIGAND (SAE) AND ITS COMPLEXES.

	Colour	Decomp. temp. °C	Found (Calc.) %		
			C	N	H
$C_{17}H_{18}N_2O_2L$	Yellow	150	71.40 (72.32)	9.10 (9.92)	5.80 (6.42)
$[(L-2H)UO_2](H_2O)_6$	Orange	>330	30.90 (31.01)	3.10 (4.20)	4.10 (4.28)
$[(L-2H)CeNO_3(H_2O)_3](H_2O)_3$	Dark brown	300	35.20 (34.58)	7.30 (7.12)	4.00 (4.77)
$[(L-2H)LaNO_3(H_2O)_3](H_2O)_3$	Yellow	210	34.20 (34.65)	7.80 (7.13)	3.90 (4.79)
$[(L-2H)Mn(H_2O)_2](H_2O)_4$	Brown	280	46.20 (46.06)	7.20 (6.32)	5.70 (6.36)
$[(L-2H)FeClH_2O](H_2O)_3$	Dark brown	290	45.40 (46.02)	5.30 (6.31)	4.60 (5.45)
$[L(L-2H)Mn](H_2O)_4$	Brown	278	59.90 (59.22)	8.50 (8.12)	5.30 (6.13)
$[L(L-2H)FeCl H_2O](H_2O)_3$	Dark brown	250	56.20 (56.25)	7.20 (7.72)	4.80 (5.83)

TABLE 2. SOME INFRARED FREQUENCIES (cm^{-1}) OF THE LIGAND (SAE) AND ITS COMPLEXES.

Compound	Frequency				
	νfree OH and H_2O	νC=N	νphenyl C—O	νC=C aromatic	νM—N
Free ligand, L	3050*	1640 1610	1285	1570 1445	—
L-UO_2^{2+}	3300b	1630 1600	1295	1540 1465	685
L-Ce^{3+}	3490b	1630 1605	1310	1550 1475	—
L-La^{3+}	3450vb	1635 1605	1320	1525 1455	625
L-Mn^{2+}	3400b	1630 1605	1310	1540 1470	635
L-Fe^{3+}	3460b	1630 1600	1315	1550 1470	625
$(L)_2$-Mn^{2+}	3400b	1630 1600	1305	1545 1470	635
$(L)_2$-Fe^{3+}	3400b	1625 1600	1310	1545 1470	620

* H-bonded OH, b=broad and vb=very broad.

associated with the Schiff base molecule, $\bar{n}_H$ was determined at different pH values. The proton stability constants were calculated at half $\bar{n}_H$ values from the plot $\bar{n}_H$ vs. pH.

Results and Discussion

The proton-Schiff base formation curve shows only one pK^H value 9.25 at $\bar{n}_H = 1.5$ where the curve extended between 0.8 and 2 on $\bar{n}_H$ scale. This indicates that the deprotonation of the ligand takes place in one step. On the other hand, the microanalytical data given in Table 1 for the different complexes

reveal that the dianions of the ligand are coordinated to the metal ion. Accordingly, the general formula of the 1:1 chelates has been suggested to be $[(L-2H) M(H_2O)_n] (H_2O)_n$ where $M = Mn^{2+}$ and UO_2^{2+} and $[(L-2H) MX(H_2O)_n] (H_2O)_n$ where $M = Fe^{3+}$, La^{3+}, Ce^{3+} and $X=Cl^-$ or NO_3^- and for the 1:2 chelates the formula is suggested to be $[L(L-2H) M] (H_2O)_n$ where $M=Mn^{2+}$ and $[L(L-2H) MX (H_2O)_n] (H_2O)_n$ where $M=Fe^{3+}$ and $X=Cl^-$, n and $\bar{n}$ depend on the nature of the coordinating metal ion.

Assignment of the important infrared bands which aids in under standing of the mode of bonding of the ligand with the various metal ions used is presented in Table 2. In the spectra of free ligand, the band observed at 3050cm^{-1} is assigned to the stretching vibration of H-bonded OH group. This is in consistency with the expected involvement of this group with the azomethine nitrogen through intramolecular hydrogen bonding [12]. Bullock et al. [13] found that the N$^+$—H...O arrangement gives rise to a band located at 3000cm^{-1}. This band disappears in the IR spectra of the complexes. Therefore, it can be concluded that the OH groups of the Schiff base have taken part in complex formation. The phenolic C—O band of free ligand is observed [14] at 1285cm^{-1}. Upon complexation this is shifted to higher energy confirming the coordination of hydroxy group of the ligand. The shift to higher energy can presumably be attributed to the expected high mesomeric interaction within the chelated rings. The two bands observed at 1640 and 1610cm^{-1} in the spectrum of the free ligand are assigned to (C=N) [15] stretching vibrations. The lowering of the νC=N frequency in the complexes may tentatively be attributed to a lowering of the C=N bond order as a result of the

M—N bond formation. The bands that appeared at 1570–1500 cm^{-1} and at 1500–1445cm^{-1} in the spectra of the free ligand and its complexes are assigned to C=C stretching vibrations of the aromatic system. The band observed in the region 620-685 cm^{-1} in the spectra of the complexes could be attributed to stretching vibration of the formed M—N bond. The new bands appearing near 300cm^{-1} region (L-Fe; 330, (L)$_2$-Fe; 340cm^{-1}) are assigned to metal-chloride vibration [16]. The broad band that appeared in the region 3200-3600cm^{-1} in the spectra of all complexes indicates the presence of water molecules in such complexes. This is supported by the results of microanalyses given in Table 1. The similarity of the IR spectra of the complexes suggests that the mode of coordination of the ligand is the same in all the complexes irrespective of the metal ions used as given below:
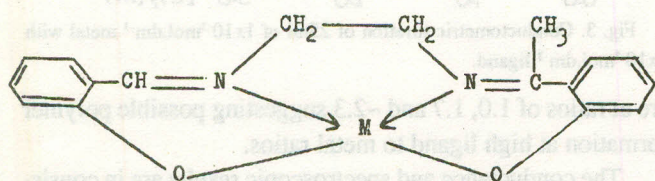
The UV-visible electronic spectra of the ethanolic solutions of the free ligand and some of its complexes have been given in Fig. 1. λ_{max} and ϵ_{max}. Values of the different absorption bands observed are given in Table 3. According to the work of Jaffe and Coworders[17], the band observed in the range 257-340nm can be assigned to a transition between π-orbitals included in the structure of the ligand. The band that
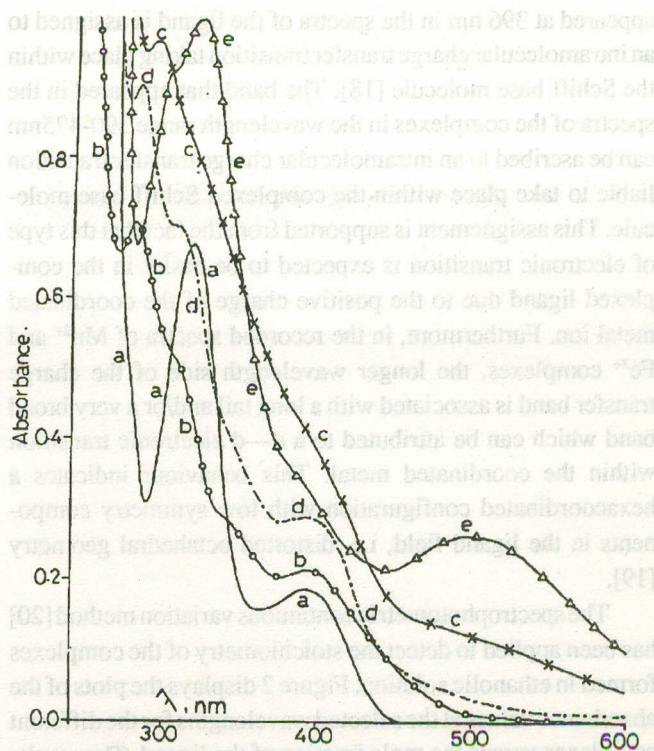

Fig. 1. UV-visible absorption spectra of ethanolic solutions of 1×10^{-4}mol.dm^{-3}of the free ligand and some of its complexes.
a-Freeligand, L,b-Mn^{2+}:L(1:1), c-Fe^{3+}:L(1:1), d-Mn^{2+}:L(1:2), e-Fe^{3+}:L(1:2).

appeared at 396 nm in the spectra of the ligand is assigned to an intramolecular charge transfer transition that takes place within the Schiff base molecule [18]. The band that appears in the spectra of the complexes in the was-clearly at 445-475nm can be ascribed to an intramolecular charge transfer transition liable to take place within the complexes. Schiff base molecule. This assignment is supported by the evidence that this type of electronic transition is expected to appear in the complexed ligand due to the positive charge of the coordinated metal ion. Furthermore, in the recorded spectra of Mn^{2+} and Fe^{3+} complexes, the longer wavelength of the charge transfer band is associated with a low intensity d—d very broad band which can be attributed to a d—d electronic transition within the coordinated metal ion. This observation indicates a hexacoordinated configuration of a low symmetry compound in the ligand field, i.e. a distorted octahedral geometry [19].

The spectrophotometric continuous variation method [20] has been applied to determine the stoichiometry of the complexes formed in ethanolic solution. Figure 2 displays the plots of the absorbance values against the molar ratio. The most obtained suggest that the mole fraction of the ligand at the obtained suggest that the molar ratio of the complexes formed between the ligand and the metal ions UO$_2^{2+}$, La^{3+}, Ce^{3+} and Fe^{3+}. The stability of the formed complexes in solution was inspected by determining their apparent formation constant values utilizing the results of the continuous variation method. The values obtained are given in Table 4. The results indicate that the complexes exhibit moderate stability and can be arranged according to their stability in the following order: UO$_2^{2+}$<Mn^{2+}<La^{3+}< for 1:1 and La^{3+}<Mn^{2+}<Fe^{3+} for 1:2.

Moreover, the stoichiometry of the complexes formed in solution was confirmed by conductometric titration of a 1×10^{-4} mol. dm^{-3} of each metal ion mixed with a 1×10^{-3} mol. dm^{-3} of the ligand (SAB) in ethanolic medium. As shown in Fig. 3, the conductance-volume curves are characterized by a distinct break at a 1:1 ligand to metal ratio with the five systems studied. In addition to the 1:1 ratio the Mn^{2+} shows a break at a ratio of 2:1. The breaks in the titration curve of Fe^{3+}

TABLE 3. ELECTRONIC SPECTRAL DATA OF 1×10^{-4}mol.dm^{-3} OF FREE LIGAND AND ITS COMPLEX ETHANOLIC SOLUTIONS.

| | $\lambda_{max,nm}(\epsilon_{max}\times10^{-3})$ | | |
	π—π*	C.T.	d—d
Free ligand, L	315(6.79)	396b(1.88)	—
L-UO$_2^{2+}$	257sh(12.72)	448sh(1.46)	—
	338(5.34)		
L-Ce^{3+}	258(5.88)	475sh(1.21)	—
	321b(3.21)		
L-La^{3+}	258(8.79)	390sh(0.36)	—
	281sh(3.76)		
	323b(2.42)		
L-Mn^{2+}	275(14.24)	403b(4.36)	484sh(0.94)
	296sh(10.42)		
	340sh(5.64)		
L-Fe^{3+}	292(10.42)	386sh(4.67)	528sh(1.83)
(L)$_2$-Mn^{2+}	280(18.12)	397b(5.76)	490sh(1.42)
	307sh(14.12)		
	340sh(8.00)		
(L)$_2$-Fe^{3+}	305sh(9.24)	386sh(3.59)	528vb(2.65)
	323(10.00)		

b=broad, vb=very broad and sh=shoulder.

Fig. 2. Job's continuous variation plots of the metal complexes of ligand (SAE) and a-Fe^{3+}, λ=500nm, b-Mn^{2+}, λ=354nm, c-Ce^{3+}, λ=360nm, d-UO$_2^{2+}$, λ=350nm, e-La^{3+}, λ=360nm.

appeared at 396 nm in the spectra of the ligand is assigned to an intramolecular charge transfer transition taking place within the Schiff base molecule [18]. The band that appeared in the spectra of the complexes in the wavelength range 390-475nm can be ascribed to an intramolecular charge transfer transition liable to take place within the complexed Schiff base molecule. This assignement is supported from the fact that this type of electronic transition is expected to be easier in the complexed ligand due to the positive charge of the coordinated metal ion. Furthermore, in the recorded spectra of Mn^{2+} and Fe^{3+} complexes, the longer wavelength side of the charge transfer band is associated with a long tail and/or a very broad band which can be attributed to a d—d electronic transition within the coordinated metal. This behaviour indicates a hexacoordinated configuration with low symmetry components in the ligand field, i.e. distorted octahedral geometry [19].

The spectrophotometric continuous variation method [20] has been applied to detect the stoichiometry of the complexes formed in ethanolic solution. Figure 2 displays the plots of the absorbance values at the selected wavelengths for the different complexes versus the mole fraction of the ligand. The results obtained suggest the formation of 1:1 complexes in the case of UO_2^{2+}, Ce^{3+}, La^{3+}, and 1:1, 1:2 complexes in the case of Mn^{2+} and Fe^{3+}. The stability of the formed complexes in solution was inspected by determining their apparent formation constant values utilizing the results of the continuous variation method. The values obtained are given in Table 4. The results indicate that the complexes exhibit moderate stability and can be arranged according to their stability in the following order: $UO_2^{2+} > Mn^{2+} > La^{3+} > Ce^{3+}$ for 1:1 complexes and $Mn^{2+} > Fe^{3+}$ for 1:2.

Moreover, the stoichiometry of the complexes formed in solution was confirmed by conductometric titration of 1×10^{-3} mol. dm^{-3} of each metal ions used with 5×10^{-3} mol. dm^{-3} of the ligand (SAE) in ethanolic medium. As shown in Fig. 3, the conductance-molar ratio curves are characterized by a distinct break at a 1:1 ligand to metal ion ratio with the five systems studied. In addition to the 1:1 ratio, the Mn^{2+} shows a clear break at a ratio of 2:1. The breaks in the titration curve of Fe^{3+}
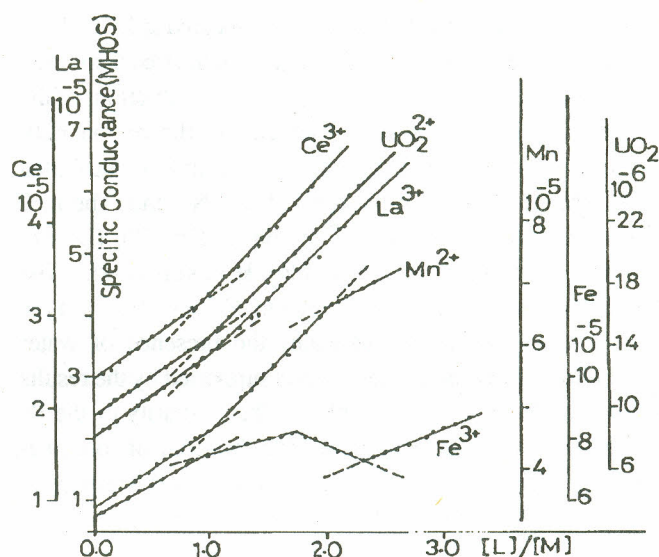

Fig. 3. Conductometric titration of 25ml of 1×10^{-3} mol.dm^{-3} metal with 5×10^{-3} mol.dm^{-3} ligand.

are at ratios of 1.0, 1.7 and ~2.3 suggesting possible polymer formation at high ligand to metal ratios.

The conductance and spectroscopic results are in consistence for the systems Mn^{2+}, UO_2^{2+}, Ce^{3+} and La^{3+} but not for Fe^{3+} at high ligand to metal ratios. The detection of the possible polymer formation by conductance and not by spectroscopic methods may be due to the high concentration used relative to that used in the continuous variation method, and also to the analytical wavelength chossen (c.f. Fig. 2, Fe^{3+}, λ=500nm).

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TABLE 4. APPATENT FORMATION CONSTANT VALUES (K_f) OF THE DIFFERENT (SALICYLALDEHYDE) (2-HYDROXY-ACETOPHENONE) ETHYLENEDIIMINE COMPLEXES.

1:1 complexes	K_f	1:2 complexes	K_f
UO_2^{2+}–L	1.72×10^7	Mn^{2+}–2L	1.55×10^{11}
Mn^{2+}–L	6.67×10^6	Fe^{3+}–2L	4.42×10^9
La^{3+}–L	5.95×10^6		
Ce^{3+}–L	2.13×10^6		

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