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Reactions of polyhomofunctional organic compounds: 2—Kinetics of hydrolysis of four azomethine sites in a trinuclear cobalt(II) complex

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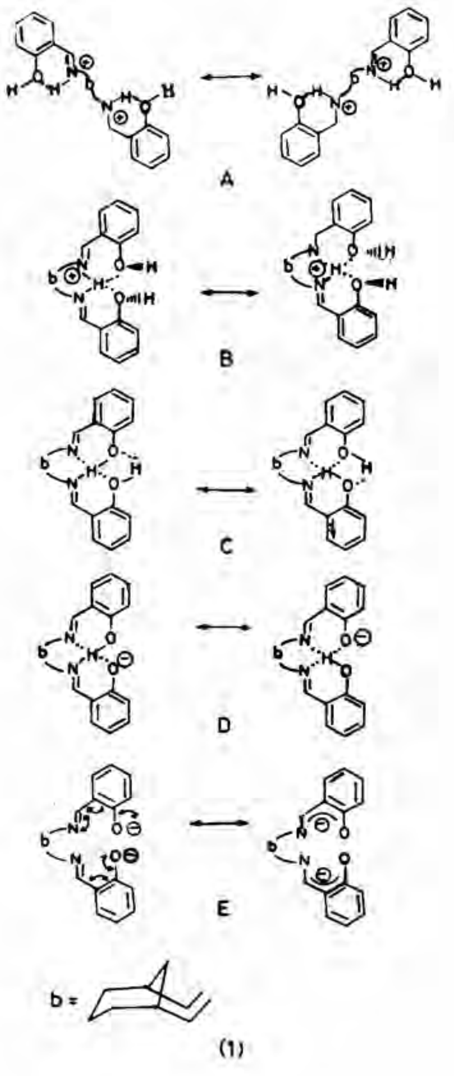
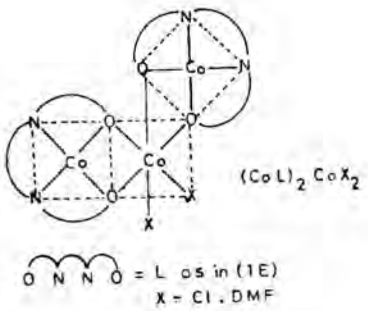
Kinetic studies on the hydrolysis of a novel trinuclear cobalt(II) complex, $(CoBAMC\text{-}Sal)_2\,Co(DMF)_2^{+2}$ (**2**) in buffered 90 : 10 aqueous /DMF (v/v) mixtures are reported. Repetitive spectral scans of the reaction mixture exhibit isosbestic points at all *p*H's. The hydrolysis follows pseudo - first order kinetics with respect to the complex. The rate constants are compared to those reported earlier for the ligand, BAMC - Sal (**1**) under similar conditions. The difference between the rates of hydrolysis of complex and those of the pure ligand is found to be due to steric factors and stability of the complex. The studies indicate different modes of cleavage of the trinuclear complex at different *p*H's before the ligand moieties undergo hydrolysis at their azomethine sites. Activation energy, E_a, and thermodynamic parameters such as $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$ are evaluated by Arrhenius and Eyring methods.

Schiff bases, with NO chelating donor sites are a class of well- studied ligands[1]. Organic molecules possessing homo- polyfunctional sites seldom exhibit characteristics quite different from those expected of a monofunctional equivalent. One of the best examples is the case of isochemical dicarboxylic acids, HOOC - R - COOH whose pK_{a1} and pK_{a2} differ considerably depending upon the nature of the bridging moiety, R. Only when R becomes sufficiently long, that the pK_{a1} and pK_{a2} tend to converage to the value of the pK_a of the mono functional equivalent H-R-COOH[2]. The value of the ΔpK_a which is the difference between the pK_{a1} and pK_{a2} is governed by intramolecular interactions between the two functional groups of the dicarboxylic acids; more the interaction, the higher is the value of ΔpK_a. Similar features are observed in the case of several binuclear coordination compounds, where some of their properties like magnetic moment, stability constant, electron transfer characteristics etc. differ from those expected of the mononuclear analogues[3]. We have recently reported the kinetics of hydrolysis of two isochemical azomethine sites of a novel organic compound, 1,3- bis(salicylidiniminomethyl)cyclohexane, referred to hereafter as either BAMC-Sal or LH_2, (IC)[4]. In the *p*H range where $LH_4^{\ 2+}$ is the predominant species, the protonated azomethine sites undergo near simultaneous hydrolysis. In $LH_4^{\ 2+}$, the two salicylidinimine group are suggested to be spread apart from each other due to coulombic repulsion



(1)



(2)

between the protonated azomethine sites and due to steric factors. Molecular energy minimisation by PCMODEL (Version 4.0) of Serina Software performed on the LH_4^{2+} has suggested the highest stability for LH_4^{2+} in structural conformation, **1A**. At all other *p*H's, where one or several of LH_3^+, LH_2 and LH^- are the predominant species, the two azomethine sites are brought closer by intramolecular hydrogen bonding between the salicylidine groups (IC), and undergo successive hydrolysis with varying speeds. On resonance considerations it was suggested that the two azomethine sites in any of LH_4^{2+}, LH_3^+,LH_2, LH^- and L^{2-} are chemically indistinguishable.

The synthesis and coordination chemistry of a novel trinuclear Co(II) complex, $(CoL)_2CoX_2$(2), where L is the same 1,3- bis(salicylidiniminomethyl)cyclohexane, was also recently reported from this laboratory[5]. The structure of the compound is shown in **2**. Here, we report the first results of the kinetics of hydrolysis of the four azomethine sites of this trinuclear cobalt(II) Schiff base complex (**2**) in various buffered aqueous- DMF mixtures.

Materials and Methods

All the chemicals used were of AnalaR grade. The procedures for the preparation of BAMC-Sal, (LH_2), and it's trinuclear Co(II) complex, $(CoL)_2CoX_2$, where X is a halide, are reported recently[4,5]. Freshly prepared DMF stock solution of $(CoL)_2CoX_2$($5 \times 10^{-4} M$) was used for the kinetic studies. In DMF, the complex, $(CoL)_2CoX_2$ becomes $(CoL)_2Co(DMF)_2^{2+}$ on ligand exchange of the halide by the solvent molecule[5]. Buffers of different *p*H's (ionic strength = $0.1M$) were prepared according to literature procedures[2,6].

A Shimadzu Model UV - 160A Ratio Recording Spectrophotometer was used for recording the spectra and for other photometric measurements with its double walled cuvett holders thermostatted by an Insref model cryostatic circulating liquid bath with a temperature stability of ±0.1°C. Each kinetic run at a given temperature and ionic strength was taken by mixing, as quickly as possible, 9 ml of a thermostatted aqueous buffer and 1ml of the DMF stock solution of the trinuclear cobalt complex ($5 \times 10^{-4} M$), followed by recording the spectrum or absorbance, as the case may be, after a constant lapse of 20 seconds from the instant of mixing and then onwards at regular intervals of 1 minute. More than 70% of the complex was hydrolysed in about 20 minutes of time. Appropriate reagent blanks were used as reference solutions. The ionic strength was adjusted and varied by mixing measured volumes of stock KCl solution ($1M$) into the stock buffers.

Results and Discussion

The repetitive spectra of $(CoL)_2Co(DMF)_2^{2+}$ in media of different *p*H's and $\mu = 0.1M$ are shown in Fig.1. Isosbestic points are observed in these and in as many as 16 other buffers, studied. Hence, it may be suggested that there are only two absorbing species throughout the course of the reaction and that the mechanism might be uniform.

Stoichiometry and the presence of isosbestic points

There are two BAMC - Sal (IC) components in the complex, $(CoBAMC\text{-} Sal)_2\ Co(DMF)_2^{2+}$, (2). The spectrum recorded after standing overnight (the infinite time spectrum) of $5.0 \times 10^{-5} M$ of (2) resembles the spectrum of the mixture of $2.0 \times 10^{-4} M$ solution of salicylaldehyde and $1.5 \times 10^{-4} M$ $CoCl_2$ under identical experimental conditions. It is also observed that neither a $1.0 \times 10^{-4} M$ solution of pure 1,3-bis(aminomethyl)cyclohexane, (BAMC), nor a $1.5 \times 10^{-4} M$ solution of pure $CoCl_2$ in DMF absorbs in the wavelength range of Fig.1. These observations indicate that throughout the course of the reaction, either $(CoBAMC\text{-}Sal)_2\ Co(DMF)^{2+}$ or an intermediate generated from $(CoBAMC\text{-}Sal)_2\ Co(DMF)_2^{2+}$ and sal or its cobalt complex are the only absorbing species available in the reaction mixture. In otherwords, the studies are suggestive of a near simultaneous hydrolysis of all the four azomethine sites of (**2**). Hence, the reaction may tentatively be written as in Eq.(1).

Table 1— Kinetic data of the hydrolysis of BAMC-SaL and $(CoBAMC\text{-}Sal)_2Co(DMF)_2{}^{2+}$ at 30°C

*p*H	Pseudo-first order rate constant $k \times 10^2$ (s^{-1})	
	BAMC-Sal	$(CoBAMC\text{-}Sal)_2$ $Co(DMF)_2{}^{2+}$
1.26	1.92	3.03
2.65	14.45	16.73
3.67	20.55	17.33
4.71	17.63	13.88
5.20	7.58	6.47
6.88	3.30	2.80,
8.42	3.42	2.11
9.97	7.27	2.20
10.68	17.29	2.70

$$(CoBAMC\text{-}Sal)_2Co(DMF)_2{}^{2+}\ (\mathbf{2}) + 4H_2O \xrightarrow{k_o} 2BAMC + [3Co^{+2} + 4\ sal^- + 2DMF] \quad .... (1)$$

Some of the products are parenthesised to allow the possibility of these members to be engaged in complexation. At extremely low and high *p*H's the complex $(CoL)_2Co(DMF)_2{}^{2+}$ decomposes to offer free Co^{2+} ion and gelatinous $Co(OH)_2$ respectively. According to Eq.(1) isosbestic points are expected at all those wavelengths, λ, where $\varepsilon^{\lambda}_{complex} = q^{\lambda}_{product}$. Here q is an appropriate numerical constant for stoichiometric balance between the reacting complex and the products at the given experimental conditions. Since the aqueous solution is buffered and the concentrations of the reacting solutes are far lower than that of water, the rate equation applicable to reaction (1) under pseudo- order conditions can be expressed as

$$d[\mathbf{2}]/dt = k[\mathbf{2}]_t{}^x \quad ..... (2)$$

where the pseudo- order rate constant, *k*, is given by

$$k = k_o[H_2O]^y{}_t[H^+]^z{}_t\ [Co^{2+}]^{\phi}{}_t\ = k'[Co]^{\phi}{}_t . \quad ...(3a)$$

Provision to $[H^+]$ and $[Co^{2+}]$ in Eq. (3a) is accorded to account for the effect of the *p*H and catalysis, if any, by Co^{2+} on the reaction rate. It was found through our studies that added cobalt(II) ion had hardly any effect on the reaction rate. Hence, it can be concluded that ϕ is zero and that *k* and *k'* are identical. This implies that free cobalt ion does not participate in the reaction mechanism at the rate determining step. With this, Eq.(3a) is restated as

$$k = k_o[H_2O]_t{}^y[H^+]_t{}^z . \quad ... (3b)$$

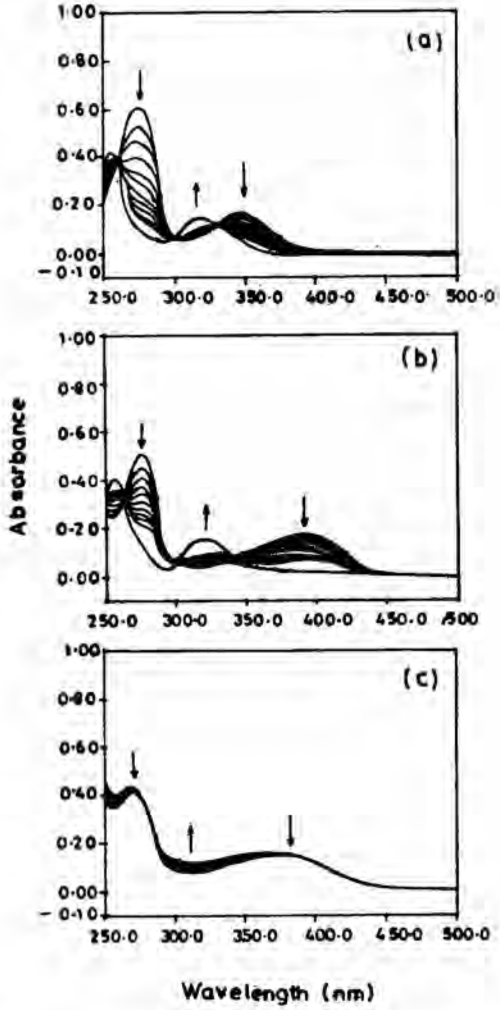


Fig.1 — Repetitive spectral scans of $(CoBAMC\text{-}Sal)_2Co(DMF)_2{}^{2+}$ in buffers of *p*H (a) 2.65, (b) 5.20 (c) 8.42 at 25°C

One then gets from Eq.(2), for pseudo-first order conditions i.e., x = 1, an integrated rate equation, as in Eq.(4)

$$2.303 \log [(A_t - A_\infty)/(A_o - A_\infty)] = kt. \quad ..(4)$$

where A_o is the initial absorbance and A_t that at time *t* of the reaction mixture whereas A_∞ is the absorbance of the reaction mixture keeping it standing overnight.

Kinetic results

Plots of log $[(A_t - A_\infty)/(A_o - A_\infty)]$ vs. time were linear for all the buffers suggesting that the hydrolysis of $(CoBAMC\text{-}Sal)_2Co(DMF)_2{}^{2+}$ follows first order kinetics. This fact is further proved by the invariance of the slopes of these plots at different concentrations of $(CoBAMC\text{-}Sal)_2Co(DMF)_2{}^{2+}$ under otherwise identical experimental reaction condi-

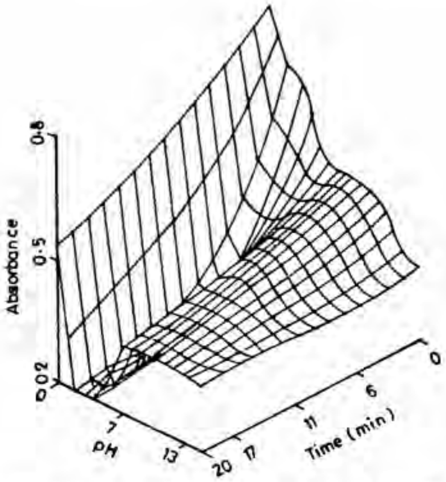


Fig.2 — Effect of pH on the hydrolysis of $(CoBAMC\text{-}Sal)_2Co(DMF)_2{}^{2+}$ at 25°C.

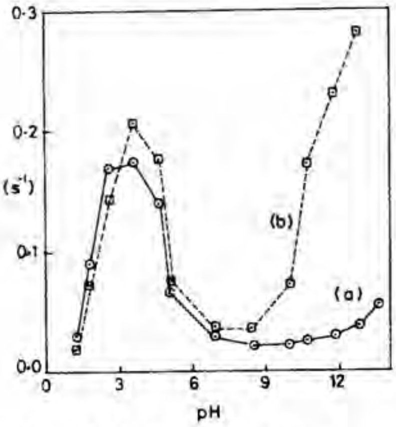


Fig.3— Effect of pH on the pseudo - first order rate constants (a) $(CoBAMC\text{-}Sal)_2Co(DMF)_2{}^{2+}$, (b) BAMC-Sal

tions. The pseudo-first order rate constants of the hydrolysis of $(CoBAMC\text{-}Sal)_2Co(DMF)_2{}^{2+}$ in several buffers are collected in Table 1. The corresponding values for the hydrolysis of the pure ligand, BAMC-Sal, are also placed in Table 1 for comparison.

*Effect of p*H

The effect of pH on the hydrolytic decay of $(CoBAMC\text{-} Sal)_2Co(DMF)_2{}^{2+}$ is shown in a 3-D perspective in Fig.2 while that on the rate of constant in Fig.3. The data in Table 1 and Fig.3 reveal that the general pH-dependence of the hydrolysis of BAMC-Sal and its cobalt(II) complex, $(CoBAMC\text{-}Sal)_2Co(DMF)_2{}^{2+}$, is on similar lines. At highly acidic pH's (pH) the log k is very low and pH-independent. It then increases with pH till pH = 4 and remains pH-independent upto pH=6 followed by a decline over the pH range 6-8. Effect of pH beyond 8 and upto 11 is negligible. Despite similarities in trends in log k versus pH profiles, the relative rates of hydrolysis of BAMC-Sal and $(CoBAMC\text{-}Sal)_2 Co (DMF)_2{}^{2+}$ vary with pH as can be seen from the crossing over of the profiles of BAMC-Sal and $(CoBAMC\text{-}Sal)_2Co(DMF)_2{}^{2+}$ in Fig.3.

In extremely high acidic conditions, the complex is unstable and is likely to break into its constituents. The broken ligand species are immediately protonated resulting in the establishment of carbonium ion character at the azomethine sites which eventually get attacked by water molecules in the usual mechanism as discussed earlier[4]. Since each mole of the complex has 2 moles of hydrolysable ligand (BAMC-Sal) substrates, the fall in absorbance in each reaction step is expected to be about two-fold that of BAMC-Sal alone. The first order rate constant which is independent of the concentration of the substrate, however, should be similar to that of the pure ligand in similar experimental conditions. Our observations, which are in agreement with these expectations, hence, suggest that the complex in DMF solution undergoes an early cleavage at lower pH's as

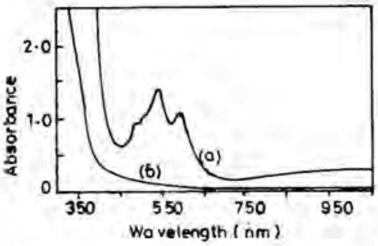


Fig.4 — Electronic spectrum of $(CoBAMC\text{-}Sal)_2 Co(DMF)_2{}^{2+}$ in (a) pure DMF (b) aqueous buffer of pH 2.65 (immediately after mixing) at 25°C.

$$(CoL)_2Co(DMF)_2{}^{2+} + 4H^+ \rightarrow LH_4{}^{2+} + [3Co^{2+}+2DMF] \quad \ldots (5)$$

That the complex undergoes immediate cleavage as in Eq. (5) is proved further by a loss of *d-d* transition of $(BAMC\text{-} Sal)_2Co(DMF)_2{}^{2+}$ in the very first kinetic spectrum (recorded within 20 second after mixing), as shown in Fig.4. The rate constants (Table 1) reveal a higher rate of hydrolysis for the complex. We propose that the substrate species, $LH_4{}^{2+}$, in free ligand kinetics and in the present kinetics differs in its conformational isomerism. Molecular energy minimisation calculations by PCMODEL (Serena Software Version 4.0) reveals that $LH_4{}^{2+}$ in *anti* conformation is stable than in *syn*. These conformations are shown in 3 and 4 respectively. In the pure free $LH_4{}^{2+}$ case, the functional groups are in the stable *anti* (**3**) conformation. In the case of the present complex, $(CoL)_2Co(DMF)_2{}^{2+}$, (**2**), the conformation of the ligand moiety has the two salicylidine functional groups in *syn* conformation and hence the $LH_4{}^{2+}$, just generated from the reaction in Eq.(5), has higher enthalpy and lower entropy. Hence, hydrolytic cleavage of this conformation is easier than the stabler conformer of the free ligand. In other words, the complex would exhibit slightly faster hydrolysis than the ligand and our observations reveal the same results.

At *p*H's greater than 3.60 the complex is not disintegrated readily and should undergo hydrolysis in the form of complex itself. The nitrogen atoms are engaged in ligation to the Co (II) ion and cannot be protonated. This avoids the generation of carbonium ion character. The only possibility of offering some carbonium character to the azomethine carbon is by labilisation of +ve charge of the metal via the nitrogen. Hence, the nucleophilic attack by water is less efficient on the complex. This trend continues upto a *p*H of 7.00. In solutions of *p*H 7, pure BAMC-Sal was suggested to undergo hydrolysis by the initial attack of OH^- ion on the azomethine carbon which possesses partial positive charge due to +I effect instead of development of carbonium ion character[4,7]. In the case of $(CoBAMC\text{-}Sal)_2Co(DMF)_2{}^{2+}$, the partial +ve charge on the azomethine carbon developed out of sheer +I effect and labilisation is not much affected. However, the attack of the azomethine carbon by the OH^- ion is directionally restricted due to complexation of the ligand. Hence, the pseudo-first order rate constants for the hydrolysis of the complex is expected to be slightly lower than those observed for the pure BAMC-Sal. The data shown in Table 1 are in agreement with this proposal. When the *p*H is considerably enhanced to *p*H 8, one would expect the cleavage of the complex molecule in favour of the formation of $Co(OH)_2$ as a precipitate because the solubility product of $Co(OH)_2$ is $\sim 2 \times 10^{-15}$ in aqueous media. If the $(CoBAMC\text{-}Sal)_2CoDMF_2{}^{2+}$ complex which is at 2.5×10^{-5} *M* in the present case, is dissociated, the expected concentration of free Co(II) ions is 7.5×10^{-5}*M*. The permissible concentration of free Co(II) ions, is then, given by the expression

$$\log [Co^{2+}] = 13.3010 - 2\,pH \qquad ...(6)$$

A theoretical plot of *p*H versus $[Co^2+]$ for pure Co^{2+} in aqueous media suggests that more than 90% of cobalt ion should be precipitated as $Co(OH)_2$ in the *p*H 8.50. However, our studies on the complex did not reveal immediate formation of any gelatinous blue precipitate even upto a *p*H of approximately 12.00 indicating that the complex is considerably stable upto a *p*H range ~ 12.00. The kinetics studies were hence continued upto this *p*H and the rate constants are collected in Table 1. Comparison of these values with the rate constants of the BAMC-Sal in similar environment reveals that the hydrolysis of the complex is very slow in the basic *p*H range whereas it is very fast for the free ligand. In fact, the rate constants of the hydrolysis of the complex are less by more than 2 orders of magnitude. In our previous report it was argued that resonance reorganisation of the negative charge on the deprotonated phenol was playing an important role in the kinetics of the hydrolysis of BAMC-Sal. In the present complex, which is stable as shown above, the phenol is engaged in coordination and hence no resonance delocalisation is possible. This means a drastic reduction in the rate of attack of azomethine site by the OH^- ion. It is also reasonable to consider that the enhanced concentration of OH^- ions might force each of the terminal cobalt centres of $(CoL)_2Co(DMF)_2$ to accept two OH^- ligands converting the complex into $[CoL(OH)_2]_2Co(DMF)_2{}^{2-}$. Thus the presence of negative charge on the complex reduces further attack of azomethine sites by the OH^- ions. It is only in media of *p*H. >12.00 that the formation of $Co(OH)_2$ precipitate was observed. As the solution turned turbidous due to the formation of $Co(OH)_2$, no further investigations of the kinetics of hydrolysis of the substrate in media of *p*H >12.00 were possible.

Primary salt effect

To ascertain the nature of the participating species in the hydrolysis reaction, the effect of ionic strength on the reaction rate was investigated. Log *k* versus $\sqrt{\mu}$ plots were linear with different slopes at different *p*H's. In solution of *p*H < 3.5, the slope is ~+4. If the absorbing reactant were $LH_4{}^{2+}$ as suggested by Eq. (5), the slope of log *k* versus $\sqrt{\mu}$ plots would be ~ 1 as reported earlier[4]. The higher value (~ 4) in the present case suggests higher +ve charge on the substrate. It is possible that the complex (CoBAMC-Sal)$_2$Co(DMF)$_2$ $^{2+}$ undergoes hydrolysis by initial expulsion of Co^{2+} ions from the azomethine coordination sphere (N_2O_2 sphere) and protonation of azomethine nitrogens followed by attack of water molecules. Hence, the composition of the apparent substrate appears to be(Co^{2+}) ...(LH_2 $^{2+}$ $2H_2O$)--Co(DMF)$_2$ $^{2-}$-- (LH_2 $^{2+}$$2H_2O$) ... Co^{2+} Then the participating species can be grouped as LH_2 $^{2+}$--Co(DMF)$_2$ $^{2-}$--LH_2 $^{2+}$, Co^{2+} and H_2O. In such cases, the slope of the plots of primary salt effect is given by[8].

$$\log k = \log ko' + 2B\,(Z_aZ_b+Z_bZ_c+Z_aZ_c)\sqrt{\mu} \qquad ...(7)$$

where B is a solvent constant (~ 0.51 at 25°C for water) and Z_a, Z_b and Z_c are the charges on [Co(DMF)$_2$ $^{2-}$ (LH_2 $^{2+}$)$_2$]$^{2+}$, Co^{2+} and H_2O respectively. The slope of log *k* versus $1/\overline{\mu}$ in this case works out to be 4.08 which is very close to the observed value of 4.2. When the *p*H is enhanced to ~ 4, considerable concentration of the conjugate base of LH_2 $^{2+}$ ....Co(DMF)$_2$ $^{2-}$...LH_2 $^{2+}$, i.e. either LH^+---Co(DMF)$_2$ $^{2-}$---LH_2 $^{2+}$ or LH_2 $^{2+}$--- Co(DMF)$_2$ $^{2-}$--LH^+ is expected. This species has an overall charge of +1. For this case Eq. (7) gives a theoretical slope of 1.02. The observed slope in the *p*H region 3.5 - 4.50 is ~ 1.07. At still higher *p*H's the attack of H^+ on the complex is less efficient and the demineralisation is likely to be limited to one azomethine site resulting in the substrate species LH_2 $^{2+}$---Co(DMF)$_2$---LCo or its chemically indistinguishable twin, LCo---Co(DMF)$_2$---LH_2 $^{2+}$. In either case the charge is +2 and the theoretical slope for this case is 2.04 which is very close to the observed value of 1.83. In the basic *p*H range the complex is stable and no demineralisation is expected. Hence the participating species are only the complex, i.e. (CoBAMC-Sal)$_2$ Co(DMF)$_2$ $^{2+}$ and the OH^- ion. Primary salt effect here gave a slope of 2.4. This suggests a development of negative charge on the complex substrate. This would be possible by the coordination of OH^- ion on the terminal Co^{2+} sites which are in square planar geometry[5]. This converts the complex into CoL$(OH)_2$ $^{2+}$--Co(DMF)$_2$ $^{2+}$--- $Co^{2-}(OH)_2$ possessing an overall charge of - 2. Hence, the primary salt effect assumes a slope of +2.02 which is very close to the observed value of 2.4. Taking these aspects into consideration, the mechanism of hydrolysis of the complex under various *p*H conditions is proposed as in Scheme 1.

In acidic media

$$[MLM(DMF)_2ML]^{+2} \xrightarrow[mH^+]{fast} A^* \xrightarrow[4H_2O]{slow} \text{Intermediate} \xrightarrow[-mH^+]{fast} 4B + \text{Other Products}$$

In neutral media

$$[MLM(DMF)_2ML]^{+2} \xrightarrow[4H_2O]{fast} \underset{[A]}{[M(H_2O)_2LM(DMF)_2M(H_2O)L]^{+2}} \xrightarrow{slow} 2\,BAMC + 4B + 2M(H_2O)^{+2} + M(DMF)_2^{+2}$$

In basic media

$$[MLM(DMF)_2ML]^{+2} \xrightarrow[4OH^-]{fast} \underset{[A]}{M(HO...L...OH)_2M(DMF)_2M(HO...L...OH)_2} \xrightarrow[H_2O]{slow} 2M^{+2} + M(DMF)^{+2} + 2BAMC + 4B$$

A and B constitute the pair for isosbesticity in the spectra
A*, as described in the text
B, salicylaldehyde

Scheme - 1

Table 2 — Thermodynamic data^{A} of the hydrolysis of $(CoBAMC\text{-}Sal)_2Co(DMF)_2{}^{2+}$ at 30°C

*p*H	E_A	ΔH	$-\Delta S^{\#}$	$\Delta G^{\#}$
2.65	13.82	11.30	0.19	67.51
4.71	14.47	11.95	0.22	78.74
6.88	15.52	13.00	0.23	82.63
8.42	17.18	14.66	0.22	84.90
A	kJ. (mol)$^{-1}$			
B	kJ (mol)$^{-1}$ K^{-1}			

Effect of temperature

The effect of temperature on the rates of hydrolyses of the complex has also been investigated. The activation energy values E_a, of the complex were calculated from the Arrhenius linear plots of log k versus 1/T. By making use of the Eyring Equation, the other thermodynamic parameters of the hydrolysis of $(Co\ BAMC\text{-}Sal)_2Co(DMF)_2{}^{2+}$ complex were also evaluated[8]. These data are provided in Table 2. The negative entropy changes of activation suggests that the activated complex is more orderly than the participating reactant species. These values are more scattered with the pH unlike in the case of pure ligand. This fact suggests variance of the skeletal structure of the reaction intermediate as shown in Scheme 1.

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