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Preparation and Characterization of Cu(II)-*N*-Salicylideneanthranilic Acids, Their Reduction Products and Hydrolysis of the Schiff Base

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Abstract. Copper (II) complexes of *N*-salicylideneanthranilic acid (**I**) and its derivatives (**II, III**) as well as their $NaBH_4$ reduction products, namely *N*-(2-hydroxybenzyl) anthranilic acids (**IV–VI**) have been prepared and their structures have been determined analytically. Tetracoordinated planar structures of the Cu(II) complexes of the Schiff bases and distorted tetrahedral structures of the Cu(II) complexes of compounds **V–VI** have been elucidated by ESR and other spectral methods. During the preparation of the complex the hydrolysis of the Schiff base often takes place in the presence of water giving anthranilates and salicylaldehydates of metals to some extent along with the complexes of the Schiff base. The kinetic data for the hydrolysis of *N*-salicylideneanthranilic acid (**I**) in methanol–water solution also are reported.

Key words: *N*-Salicylideneanthranilic acids, reduction, hydrolysis, stability, Cu(II) complexes.

1. Introduction

N-Salicylideneanthranilic acid (**I**) behaves as a tridentate, doubly negatively charged ligand in metal complex formations in which the metal to ligand ratios range from 1 : 1 to 1 : 3 [1, 2]. However, our findings showed that, during complex preparation hydrolysis often takes place giving anthranilates and salicylaldehydates of metals to some extent along with the complexes of the Schiff bases.

The present paper reports new copper (II) complexes of **I** and its derivatives (**II, III**) and the rates of hydrolysis of *N*-salicylideneanthranilic acid **I** in water–methanol solution.

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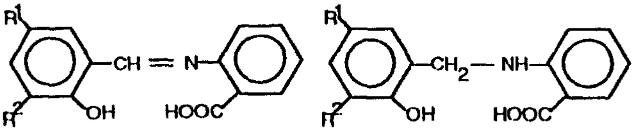


	I, IV	II, V	III, VI
R	H	Br	Br
R'	H	H	Br

In addition, the N-salicylideneanthranilic acids (**I-III**) are selectively reduced by sodium borohydride to give N-(2-hydroxybenzyl) anthranilic acids (**IV-VI**), which possess an analogous ability for the formation of complexes but are more stable against hydrolysis.

2. Experimental

All the chemicals were of analytical grade from Fluka and Merck. All spectra were obtained in purified solvents. Infrared spectra were recorded in KBr discs on Unicam Mattson 1000 FTIR and Specord M 80 (Carl Zeiss Jena) spectrometers. Visible and UV spectra were obtained on a Shimadzu UV 1208 spectrophotometer. Magnetic susceptibilities were measured on a Faraday type balance using $HgCo(SCN)_4$ as the calibrant. ESR spectra were obtained on JES-PE–3X (JEOL) and Radiopan spectrometers.

2.1. KINETIC MEASUREMENTS

For the kinetic measurements the initial solutions were prepared by dissolving N-salicylideneanthranilic acid (**I**) in methanol, adding the required amount of water followed by make up in graduated flasks. The concentration of compound **I** was followed by absorbance measurements at 270 nm ($\varepsilon = 7200$).

The dependence of the rates of hydrolysis on the temperature was measured in a methanol solution of **I** with a water concentration of 0.22 mol L^{-1}.

2.2. PREPARATION OF COMPOUNDS

2.2.1. *N-Salicylideneanthranilic Acid* (**I**)

N-Salicylideneanthranilic acid (**I**) was obtained as reported [2] from a mixture of salicylaldehyde and anthranilic acid in absolute ethanol or methanol m.p.: 199 °C ^{1}H-NMR($CDCl_3$) δ (ppm): 4.31 (br, Ar-OH), 6.90–7.65 (m, Ar-H), 8.10 (s, CH), 8.54 (s, COOH).

Other Schiff bases (**II** and **III**) were prepared in the same manner.

2.2.2. *N-(2-hydroxybenzyl)anthranilic Acid* (**IV**)

Finely ground N-salicylideneanthranilic acid 2.41 g (0.01 mol) was added to 50 mL of methanol. A slurry was obtained. To this slurry was added by stirring 0.5 g of powdered sodium borohydride in small portions, within 30 min. At the end of the reaction the solution became colourless. The reaction mixture was diluted with water to a volume of 200 mL and 10% HCl was added to the solution to adjust the pH of the reaction mixture to 3. A white fine precipitate crystallized out. The separated crystals were filtered off by a vacuum filter. The product was purified by crystallization from a mixture of methanol–water 1 : 5. m.p.: 127 °C. ^{1}H-NMR(DMSO-d_6) δ (ppm): 3.25 (s, NH), 4.34 (s, CH_2), 6.53–7.80 (arom. CH), 9.51 (s, OH).

The compounds **V** and **VI** were prepared in the same manner as **IV**.

2.2.3. *Bis-(N-salicylideneanthranilato)Cu(II)* (**VII**)

To a suspension of cupric hydroxide in 20 mL methanol, obtained from 0.249 g (0.001 mol) of $CuSO_4 \cdot 5H_2O$ and 0.4 g NaOH and washed with absolute methanol, was added with stirring and gentle heating (40 ± 1 °C) 0.241 g *N*-salicylideneanthranilic acid dissolved in 40 mL of methanol. The hot reaction mixture was filtered, a dark green precipitate of compound **VII** crystallized out. m.p. >250 °C.

Compounds **VIII** and **IX** were prepared in the same manner.

The analytical data of the compounds are given in Tables I and II.

2.2.4. *Bis-[N-(2-hydroxybenzyl)anthranilato] Cu(II)* (**X**)

To a solution of $Cu(CH_3COO)_2.H_2O$ (0.199 g, 0.001 mol) in a mixture of 20 mL methanol and 1 mL water was added with stirring and gentle heating *N*-(2-hydroxybenzyl)anthranilic acid (0.241 g, 0.001 mol) in 10 mL of methanol. A green crystalline powder was obtained. The yield was 98%. m.p.: >250 °C.

The compounds **XI** and **XII** were prepared in the same manner as **X**.

The analytical data of the compounds are given in Tables I and II.

3. Discussion

3.1. COPPER (II) COMPLEXES

When the metal complexes of *N*-salicylideneanthranilic acid (**I**) were synthesized in the organic solvents containing small amounts of water, the pure reaction products could not be easily obtained. This observation is in agreement with the results on the hydrolysis of the Schiff's base given in the next part.When the complexes of Cu(II) and also of Ni(II) were obtained in methanolic solutions containing small amounts of water (~1–2%;w/v) the basic products were bisanthranilates and salicylaldehydates of metals which were identified by comparison of the spectral and analytical data of the reaction products with those of the authentic samples. Thus, it was concluded that the synthesis of metal complexes starting with Schiff bases of anthranilic acid should be carried out in the absence of water and the best results were obtained by the use of metal hydroxide washed with absolute methanol.

In accordance with the data of the elemental analyses, the Cu(II) complexes **VII–IX** have a metal : ligand ratio of 1 : 1 (Table I). The broad band at ~3400 cm^{-1} arising from the hydroxyl stretching vibration of water is observed in the IR spectrum. The carbonyl stretching band of the carboxylic groups in the ligands appeared around 1680–1705 cm^{-1} and disappeared on complexation. Strong bands appeared around 1580 and 1380 cm^{-1} due to the bonded carboxylic group. A marked shift to lower wavenumbers is observed for the azomethine band of the ligands **I–III** at 1624–1636 cm^{-1}. New absorption bands arising from complexation induced electronic transitions appeared at the longer wavelengths of the UV-visible spectra of Schiff base copper(**II**) complexes.

The magnetic moments of the complexes correspond to the electronic configuration of the Cu^{2+} ion ($3d^9$). With one unpaired electron in the 3d shell, its compounds were expected to have magnetic moments close to the spin-only value of 1.73 B.M. In fact, the observed magnetic moment values of 1.9–2.2 B.M. and 1.72–1.82 B.M. are observed for ionic or rather weak covalent bonds and for strong covalent bonds, respectively. The copper (II) complexes of the Schiff bases (**VII–VIII**) have magnetic moments in the 1.87–1.90 B.M. range. However, the dibromosubstituted salicylideneanthranilic acid complex (**IX**) has a lower magnetic moment (1.65 B.M.), indicating a substituent effect on the bond strengths. ESR spectra indicate the axial symmetry of the complexes. Thus, complex **IX** has g_{II} = 2.25 and $g_{\perp}$ = 2.037 and the constant of isotropic superfine structure with the nucleus of $^{63.65}Cu$ A_{iso} Cu = $66\tau_c$. The complexes of **VII** and **VIII** have nearly the same parameter values.The results obtained suggest a tetracoordinated planar structure for the complexes **VII–IX**.

The formation of tricoordinated Cu(II) complexes of 5-bromosalicylideneanthranilic acid **II** prepared in aqueous alcoholic solution from Cu(II) acetate and the Schiff base has been reported [3]. We, however, obtained a tetracoordinated Cu(II) complex in which H_2O is also involved in coordination. Complex **VIII** has a magnetic moment of 1.87 B.M. which is in agreement with Kishita's value [4].

N-(2-Hydroxybenzyl) anthranilic acid **IV**, and related acids **V** and **VI**, also form complexes with cupric ions in a metal : ligand ratio of 1 : 1. The IR spectral data (Table II) indicate the participation of carboxylic, hydroxylic and amino groups in the coordination with cupric ion. In fact the bands around 2600 and 1660 cm^{-1} arising from the carboxylic acid group disappear and the latter shifts to lower wavenumbers indicating coordination. The band from the secondary amino group at 3357–3392 cm^{-1} is broadened and shifted to longer wavelength and the bonded phenolic hydroxyl band at 3400 cm^{-1} disappears.

Comparison of UV spectral data of *N*-(2-hydroxybenzyl)anthranilic acids (**IV–VI**) and their complexes also indicated coordination through HN—, O^- and COO^- both by the disappearance of the absorption bands around 350 nm and by the appearance of the new bands at higher wavelengths.

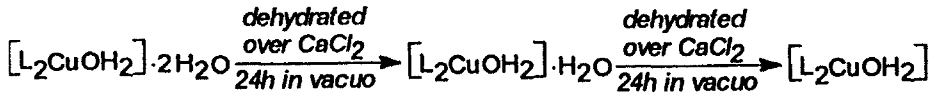
Table I. Analytical and other physicochemical data of compounds (I–VI)

Compounds **No**	**Melting Point (°C)**	**Elemental Analysis (Calcd) (Found)** **C**	 **H**	 **N**	**IR Spectral Data (cm^{-1})**	**UV-VIS Spectral Data λ_{max}, nm (MeOH)**
I $C_{14}H_{11}NO_3$	199	69.00 69.62	4.59 4.51	5.80 5.69	3430 b, 3072 m, 2936 mb 1706 m, 1684 mb, 1628 s, 1575 s, 1460 w, 1395 m, 1364 s, 1250 s, 1000 bs, 808 m, 760 s, 704 m, 680s	213 270 334 450
II $C_{14}H_{10}NO_3Br$	196	52.52 52.40	3.14 3.03	4.37 4.25	3440 b, 3056 w, 2930 mb 1705 m,1680 mb, 1636 s, 1610 m,1480 w, 1340 s, 1240 s, 832 m, 760 s	225 273 347 465
III $C_{14}H_9NO_3Br_2$	164	42.01 42.13	2.13 2.27	3.39 3.51	3440 mb, 3057 w, 1695 w 1624 s, 1600 m, 1578 w, 1488 s, 1320 m, 1268 m, 1332 m, 1132 m, 1080 w 1032 w,832 w,756m,696m	220 338 327 420
IV $C_{14}H_{13}NO_3$	127	69.13 69.02	5.35 5.47	5.76 5.65	3464 sb, 3357 s, 3060 w, 2930w, 2860 w, –2600 wb 1668 s, 1583 s, 1524 s, 1498 s, 1280 s, 1255 s 1229s,1156 s,1093m,838m	261 275 (sh) 281 (sh) 353
V $C_{14}H_{12}NO_3Br$	138	52.19 52.03	3.75 3.62	4.34 4.21	3470 w, 3384 w, 3168 sb –2600 b, 1660 s, 1576 s, 1516 s, 1440 s, 1320 m, 1264 s, 1250 w, 1216 s, 1168 s,1120 m,1100w, 1048 m,888 m,816 s,752s	221 254 284 290 351
VI $C_{14}H_{11}NO_3Br_2$	189	41.92 41.80	2.76 2.61	3.46 3.38	3430 s, 3392 s, 2940 w, 2600 w, 1664 s, 1576 s, 1520 s,1464 s, 1408 m, 1324 m, 1264 s, 1248 s, 1216 s, 1144 s , 864 s, 744 s	221 254 290 345

s-strong sb-strong broad b-broad m-medium w-weak sh-shoulder

Although complexes **XI** and **XII** have magnetic moments in the range expected for relatively weak coordinative bonds, complex **X** has a subnormal magnetic moment (1.17 B.M.) possibly indicating Cu—Cu interactions between complex molecules. During the preparation, the monoaqua complex **X** is separated as dihydrate **Xa** first, and then by drying over $CaCl_2$ at room temperature under vacuum as monohydrate **Xb**. The subnormal magnetic moments of the hydrates can also indicate Cu—Cu interactions arising from the reduction in the Cu—Cu distance.

ESR spectra of compounds **XI–XII** in the solid state give an almost symmetrical singlet with $2.12 < g < 2.15$, which can indicate a distorted tetrahedral structure of these compounds.



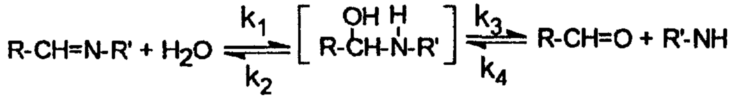
$$[L_2CuOH_2]\cdot 2H_2O \xrightarrow[\text{24h in vacuo}]{\text{dehydrated over } CaCl_2} [L_2CuOH_2]\cdot H_2O \xrightarrow[\text{24h in vacuo}]{\text{dehydrated over } CaCl_2} [L_2CuOH_2]$$

Xa	**Xb**	**X**
Green	Light Green	Dark Green
(L = Dianion of the ligand)		
Analysis for $C_{14}H_{17}NO_6Cu$	$C_{14}H_{15}NO_5Cu$	$C_{14}H_{14}NO_4Cu$
(Calcd) C, 46.86; H, 4.74; N, 3.90	C, 49.33; H, 4.40; N, 4.11	C, 52.09; H, 4.06; N, 4.34
(Found) C, 46.34; H, 3.60; N, 3.68	C, 50.07; H, 3.54; N, 4.02	C, 53.02; H, 3.26; N, 4.23
Magnetic Moment 1.35 B.M.	1.49 B.M.	1.17 B.M.

3.2. THE HYDROLYSIS OF *N*-SALICYLIDENEANTHRANILIC ACID

N-Salicylideneanthranilic acid and its derivatives are stable in the crystalline state and in waterfree solvents; however, they hydrolyze in the presence of water into salicylaldehydes and anthranilic acid.

The hydrolysis was followed by the decreasing absorbance at 270 nm. The hydrolysis reaction proceeds practically to completion in concentrations of **I** lower than 10^{-2} mol L^{-1} (Figure 1). The hydrolysis rate has been found to be first order with respect to the concentrations of both **I** and water. Thus, the hydration of Schiff base is the rate determining step. Two steps of Schiff base hydrolysis are the addition of water to the azomethine bond yielding a carbinolamine intermediate followed by deamination.



$$R\text{-}CH{=}N\text{-}R' + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \left[R\text{-}\overset{OH}{C}H\text{-}\overset{H}{N}\text{-}R' \right] \underset{k_4}{\overset{k_3}{\rightleftharpoons}} R\text{-}CH{=}O + R'\text{-}NH$$

Since the intermediate carbinolamine could not be observed it may indicate that the decomposition of carbinolamine into the reaction products proceeds at a high rate, that is $k_3 \gg k_1$. The dehydration rates of carbinolamine into Schiff bases of amino acid derivatives [5] and of some aliphatic amines [6] should be considerably higher than its formation rates. Thus, it is acceptable to assume that $k_2 \gg k_4$. The kinetic scheme can be simplified as follows:

$$\text{SAA} + H_2O \underset{k_f}{\overset{k_h}{\rightleftharpoons}} \text{Sal} + \text{AA}.$$

Then, the rate equation of hydrolysis has the form,

$$-d[\text{SAA}]/dt = k_h[\text{SAA}][H_2O] - k_f[\text{Sal}][\text{AA}]$$

The data obtained showed that the formation rate of the Schiff base, and thus k_f [Sal] [AA], can be neglected under the working conditions used. The kinetic

Table II. Analyses and other physicochemical data of complexes

Complexes	Melting Point t°C (Decomp)	Elemontal Analyals (Calcd) (Found) C	H	N	Cu	IR Spectral Data (cm^{-1})	UV-VIS Spectral Data λ_{max},nm (MeOH)	μ_{eff} B.M (298K)
VII $C_{14}H_{11}NO_4Cu$	>250	52.42 52.38	3.45 3.31	4.36 4.28	19.81 19.94	3440 sb, 1600 s,1580s 1536 s, 1444 s, 1400m 1370 m,1322m,1240w 1188 s, 1152 s, 1020w 980 m, 878 s, 798 s, 760 s , 705 m	201 216 242 288 405	1.90
VIII $C_{14}H_{10}NO_4BrCu$	>250	42.07 41.89	2.52 2.41	3.50 3.39	15.90 16.05	3400 sb, 1630w,1596s 1575m,1550m,1520m 1448 s, 1410 m, 1384s 1320 w, 1168 m	247 292 427 690	1.87
IX $C_{14}H_9NO_4Br_2Cu$	>250	35.13 35.27	1.89 1.74	2.92 2.83	13.27 13.39	3400 s, 1640 w,1592s 1568 m,1575m,1520w 1436 s, 1380 s, 1360 s 1160 s, 770 m, 720 s	247 307 426 704	1.65
X $C_{14}H_{13}NO_4Cu$	>250	52.09 53.02	4.06 3.26	4.34 4.23	19.68 20.10	3400 s,3230 m,3080w 2930 w, 2850 w,1600s 1564 s, 1480 s,1456w, 1410 w,1360 s, 1272 s 1208 w,1128w,1048w 880 w, 864 m, 824 m, 784 w, 752 s, 704 m	206 230 (s h) 276 410	1.17
XI $C_{14}H_{12}NO_4BrCu$	>250	41.36 41.68	3.01 2.83	3.49 3.38	15.82 15.81	3400 s, 3192m,3080w 2930 w,2850w,1600s 1564 s, 1480 s, 1456w 1410 w, 1360 s,1272s, 1208 w,1128w,1048w 880 w, 864 m, 824 m, 784 w, 725 s, 704 m	292 (sh) 247 427 690	1.93
XII $C_{14}H_9NO_4Br_2Cu$	>250	34.99 34.81	2.31 2.16	2.91 2.81	13.22 13.18	3400 s,3200m,2920w, 2860 w, 1596 s, 1564s 1457 m, 1440 s, 1384s 1368 m,1296m,1264w 1248 w, 1164 w, 864s 760 m, 704 m	244 270 (sh) 303 (sh) 413 694	2.0
Complexes obtained through the hydrolysis of Schiff base I								
$C_{14}H_{10}O_4Cu$ Bis(Salicylaldehydo) copper (II)	240	54.99 55.37	3.27 3.37		20.78 20.20	3438 w, 1614 s, 1595s 1534s,1443 m, 1147m 910 m, 774 m, 551 m, 358 m, 316 m, 307 m, 299 s , 290 m, 276 m	204 215 242 285(sh) 403	1.87 (300K)
$C_{14}H_{12}N_2O_4Cu$ Bis(Anthranilato) copper (II)	288	50.07 49.90	3.57 3.48	8.34 7.28	20.65 21.00	3285 m, 3131m,1616s 1584 m, 1557 s, 1387s 763 s, 347 s, 322 m, 316 s, 304 s, 296 s, 290s, 282 s	202 216 241 290 400	1.66 (300K)

s- strong sb-strong broad b-broad m-medium w-weak sh-shoulder

measurements were carried out at a concentration ratio of $[H_2O] : [SAA] > 10^2$, so that the pseudo-first order rate constant k_{obs} could be calculated (Figure 2a).

$$-d[SAA]/dt = k_{obs}.[SAA]; \text{ where } k_{obs} = k_h.[H_2O]$$

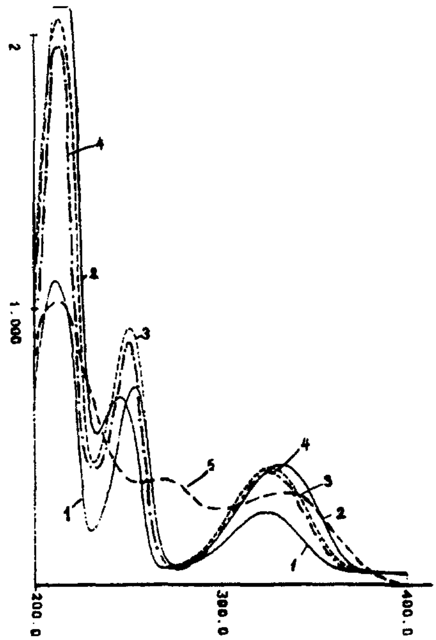


Figure 1. UV spectra in methanol; (1) Salicylaldehyde $c = 9.10^{-5}$ mol L^{-1}, (2) Anthranilic acid $c = 10^{-4}$ mol L^{-1}, (3) Equimolar mixture of 1 and 2, (4) Hydrolysis products of SAA, (5) Spectrum of SAA.

Table III. The pseudo-first order constants k_{obs} and the hydrolysis constants k_h for various water concentrations in methanol

$[H_2O]$ in Methanol (mol L^{-1})	$k_{obs}.10^4$ (s^{-1})	$k_h.10^3$ (L mol^{-1} s^{-1})
0.22	2.25	1.02
0.44	3.76	0.85
0.66	6.15	0.93
1.33	1.67	1.25
2.22	2.08	0.94

The rate constant of hydrolysis k_h (Table III) did not change appreciably when the concentration of water in methanol was varied and had an average magnitude of 0.96×10^{-3} $Lmol^{-1}$ s^{-1} reflecting the saturate value.

The activation energy and pre-exponential factor have been calculated from the temperature dependence of the rate constants as $E_a = 36.1$ kJ mol^{-1} and $k_0 = 4.6 \times 10^3$ L mol^{-1} s^{-1}, respectively. The enthalpy and entropy of activation are 33.6 kJ mol^{-1} and -46.7 e.u., respectively.

The rate constant of hydrolysis of SAA **I** obtained in water at pH 7 was 1.07×10^{-4} L mol^{-1} s^{-1}, which is lower than k_h obtained for a methanolic–water

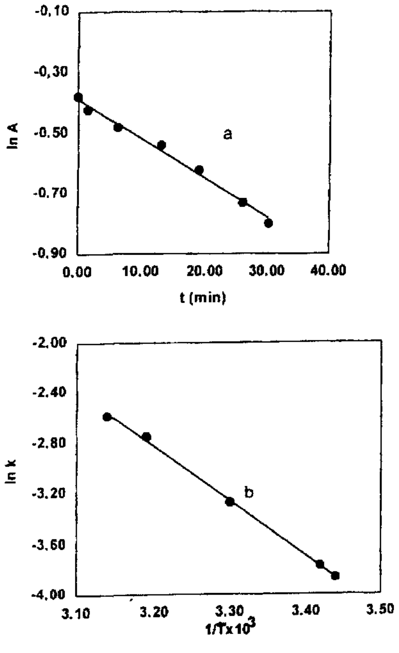


Figure 2. (a) First order plot for hydrolysis of SAA, $[H_2O]$: 0.22 mol L^{-1}. (b) Plot of ln k vs $10^3/T$.

Table IV. Rate data at different temperatures

t, °C	$\frac{I}{T}.10^3$	k, min^{-1}	ln k	Half-life (min)
18	3.44	0.021	−3.86	33.00
19	3.42	0.023	−3.17	30.13
30	3.30	0.038	−3.27	18.24
40	3.19	0.064	−2.75	10.83
45	3.14	0.076	−2.58	9.12

solution, which may indicate that in hydrolysis a considerable catalytic contribution of the carboxylic acid proton could exist. IR data of **I** reveal a shift of the carboxyl stretching band around 1700 cm^{-1} to lower wavenumbers (1680 cm^{-1}) as a broad line from which it can be concluded that the protonated azomethinic group $>C{=}NH^+$— could take part in the hydrolysis process by promoting the addition of water molecule on the imine. The possible intramolecular hydrogen bonding can facilitate the protonation and thus can make the $>C{=}NH^+$— group more susceptible to nucleophilic attack of OH^- of the added water.

Under similar conditions, the copper(**II**) complex of SAA **I** was resistant to hydrolysis indicating the increased stability of the imine group by complexation. Once the copper(**II**) complex is formed the Schiff base is no longer susceptible to hydrolysis, and since the hydrolysis rate of the first Schiff base is sufficiently large, the copper complexes of the Schiff base components are also formed.

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