Preparation of salicylidene-2-iminoacethydroxamic acid and some of its complexes

B. KOPECKÁ, V. ŠPRINGER, and J. MAJER

Department of Analytical Chemistry, Faculty of Pharmacy, Komenský University, 880 34 Bratislava

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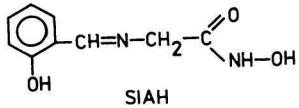
The preparation of salicylidene-2-iminoacethydroxamic acid and its complexes with Fe(III), Cu(II), and Ni(II) is described. The composition of the isolated complexes is $Na[Fe(L)_2]\cdot 3H_2O$ or $[M(HL)_2]\cdot xH_2O$. The dissociation constants of the reagent, $pK_{a1}=9.23$, $pK_{a2}=11.13$, were determined *via* spectrophotometry and the involvement of the donor atoms in the chelation was studied by means of the i.r. spectroscopy.

В работе описывается приготовление салицилиден-2-иминоацетгидроксамовой кислоты и ее комплексов с Fe(III), Cu(II) и Ni(II). Состав изолированных комплексов соответствует формулам $Na[Fe(L)_2]\cdot 3H_2O$ или $[M(HL)_2]\cdot xH_2O$. Константы диссоциации реагента, $pK_{a1}=9{,}23$, $pK_{a2}=11{,}13$ были определены спектрофотометрически и участие донорных атомов в хелатообразовании было изучено ИК спектрометрией.

Compounds with the azomethine functional group play an important role in the analytical chemistry but most of the reagents of this type have other complex-forming donor groups as well. *West* [1] described a number of such reagents, their stereochemistry, hydrogenation, mechanism of their complex formation, and the corresponding stability constants. Various types of their complexes with M(II) and M(III) metals were reported by *Sinn* and *Harris* [2]. Analytical applications of the azomethine reagents were compiled by *Jungreis* and *Thabet* [3]. They summarized the structure—colour relations of these reagents and their complexes as well as the stability factors. They thoroughly described analytical utilization of the reagents in qualitative and quantitative analysis (gravimetric methods, photometry, fluorometry, complexometric indicators, chromatographic methods, *etc.*). *Holzbecher* [4] also paid a great attention to the preparation and the study of the azomethine reagents, mainly with regard to the fluorescence properties of their metal chelates.

In this paper we describe the preparation, acid-base and complex formation properties of a Schiff base reagent which is characterized, besides of the azomethine group, also by the phenolic and hydroxamic functional groups. The studied reagent is salicylidene-2-iminoacethydroxamic acid (SIAH).



SIAH

After *Schwarzenbach* and coworkers [5—7] the hydroxamic group itself exhibits pronounced complex formation properties, some of its intensively coloured complexes are utilized in analytical praxis [8].

Experimental

Elemental analysis was performed with the C. Erba (Milan) analyzer, model 1102. The metal content in the prepared complexes was determined by chelatometry after their mineralization with $HClO_4$ and HNO_3. The content of water was determined by drying them *in vacuo* at 100°C. The i.r. spectra of the substances in KBr pellets were measured with a Perkin—Elmer 377 spectrophotometer and the electronic absorption spectra with a spectrophotometer Unicam SP 700. Radiometer PHM 25 was used for pH measurements with a combined GK 2301 C electrode.

Preparation of salicylidene-2-iminoacethydroxamic acid (SIAH)

Aminoacethydroxamic acid (9.0 g; 100 mmol) prepared after *Safir* and *Williams* [9] was suspended in methanol (50 cm^3). Freshly redistilled salicylaldehyde (12.2 g; 100 mmol) was added dropwise to the mixture with continuous stirring at 60°C and the mixture was allowed to react for 4 h. The light yellow crystalline product precipitated during the reaction was filtered off, washed with cool methanol and recrystallized twice from water—methanol (1 : 1) mixture. The obtained product was very poorly soluble in water, well soluble in methanol and dimethyl sulfoxide. Yield 8.3 g (92%), m.p. 156—157°C.

Spectrophotometric determination of the dissociation constants

Dissociation constants of SIAH were calculated from the measured pH dependences of the absorption curves of the SIAH solutions ($c_L = 2.20$—4.20×10^{-5} mol dm^{-3}) in 50% (w/w) methanol in the 238—450 nm spectral region. The solutions were placed in quartz cells with 100 cm^3 volume and 35 mm length so that absorption curves could be measured simultaneously with the pH measurements and acidity adjustments of the solutions in the cell with 0.2 M-NaOH. The electrode was calibrated by the acetate and phosphate buffer solutions in 50% (w/w) methanol with NaCl as a background electrolyte [10].

Preparation of the complex salts

$[Cu(HL)_2] \cdot 2H_2O$

The solution of $Cu(CH_3COO)_2 \cdot H_2O$ (0.5 g; 2.57 mmol) in ethanol (10 cm^3) was added to the suspension of SIAH (1.0 g; 5.14 mmol) in 50% ethanol (70 cm^3). The reaction mixture was adjusted to pH 6.5 by 0.5 M-NaOH and stirred for 2 h at room temperature. The powdered green complex was filtered off and washed with ethanol and ethyl ether.

$[Ni(HL)_2] \cdot H_2O$

The solution of $Ni(CH_3COO)_2 \cdot 4H_2O$ (0.65 g; 2.57 mmol) in ethanol (20 cm^3) was added to the solution of SIAH (1.0 g; 5.14 mmol) in 50% ethanol (70 cm^3). The reaction mixture was adjusted to pH 6.5 by 0.5 M-NaOH and stirred for 2 h upon mild heating. The light green complex was filtered off and washed with ethanol and ethyl ether.

$Na[Fe(L)_2] \cdot 3H_2O$

The aqueous 0.5 M-$Fe(ClO_4)_3$ (5.2 cm^3) was added to the suspension of SIAH (1.0 g; 5.14 mmol) in 50% ethanol (70 cm^3). The formed violet-red solution with pH *ca.* 2 was adjusted to pH 9.0 by 0.5 M-NaOH and stirred for 2 h upon mild heating. The precipitated brown-red complex was filtered off and washed with ethanol and ethyl ether.

Results and discussion

The reagent SIAH was prepared by condensation of aminoacethydroxamic acid with salicylaldehyde, analogously with the described preparation of *N*-salicylideneamino acids [11—12]. In contrast to the cited works, the condensation at mildly elevated temperature (40—60°C) proved here to be more advantageous. After twofold recrystallization (aqueous methanol) the prepared reagent was sufficiently pure as followed from the results of the potentiometric neutralization titration. The colour of the reagent is light yellow, it is very poorly soluble in water, well soluble in methanol, ethanol, and dimethyl sulfoxide. The reagent forms red-brown complexes with Fe(III) and less intensive coloured complexes also with Cu(II), Ni(II), and Co(II).

The complexes of the reagent with Cu(II), Ni(II), and Fe(III) were isolated. After the results of the elemental analysis and the determination of their water content by drying them *in vacuo* at 100°C, all the prepared complexes are stoichiometrically defined compounds (Table 1). In the complexes of the divalent cations the ligand is assumed to be in the HL^- form, thus the arising problem of the site of the dissociating proton is discussed below from the i.r. spectroscopy results. In the Fe(III) complexes, the ligand is apparently in a fully deprotonized form.

Table 1

Elemental analysis of the studied compounds

Compound	Formula	M	Calculated/found				
			% C	% H	% N	% Me	% H_2O
SIAH	$C_9H_{10}O_3N_2$	194.2	55.66 55.44	5.19 5.17	14.43 14.42	—	—
$[Cu(HL)_2]\cdot 2H_2O$	$C_{18}H_{22}O_8N_4Cu$	485.9	44.48 44.91	4.57 4.43	11.53 11.34	13.07 12.89	7.41 8.00
$[Ni(HL)_2]\cdot H_2O$	$C_{18}H_{20}O_7N_4Ni$	463.1	46.69 47.06	4.37 4.47	12.09 12.39	12.67 12.92	3.89 4.00
$Na[Fe(L)_2]\cdot 3H_2O$	$C_{18}H_{22}O_9N_4FeNa$	517.2	41.80 40.89	4.28 4.12	10.83 10.56	10.80 10.24	10.30 10.50

Dissociation constants of SIAH were determined spectrophotometrically with respect to the mutually different location of the absorption maxima and different absorption coefficients of the respective H_2L, HL^-, and L^{2-} forms of this reagent. The corresponding absorption curves are seen in Fig. 1, some spectrophotometric data are in Table 2. The region of the wavelength 382 nm was selected for the determination of the dissociation constants, since in this region the contribution of other dissolved species (NaOH, NaCl) to the measured absorbance of the reagent

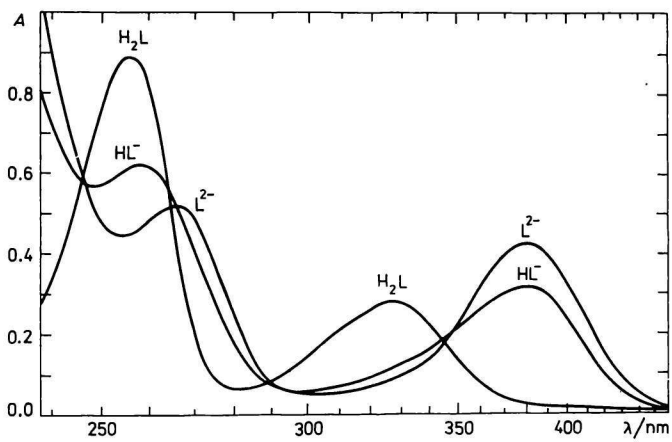


Fig. 1. Spectrophotometric absorption curves of SIAH.
$c = 2.20 \times 10^{-5}$ mol dm^{-3}, $l = 35$ mm, H_2L — pH 6.60, HL^- — pH 10.20, L^{2-} — pH 12.05.

Table 2

Spectrophotometric characteristics of SIAH

Species	λ_{max}/nm	ε/cm^2 mmol^{-1}
H_2L	256	11 500
	329	3 600
HL^-	260	7 980
	382	3 900
L^{2-}	268	6 650
	382	5 740

may be neglected. The absorption curves of the reagent in the pH interval 6.60—10.10 intersect in an isosbestic point at 343 nm while the curves measured at pH 10.50—12.05 intersect in another isosbestic point at 350 nm. It confirms that a simple reaction equilibrium occurs in the solution, thus the absorption curves in the region of the corresponding λ_{max} are suitable for the estimation of the dissociation constants. The $A = f(pH)$ dependence evaluated from the absorption curves at λ_{max} is seen in Fig. 2. Graphic analysis [13] of this dependence produced

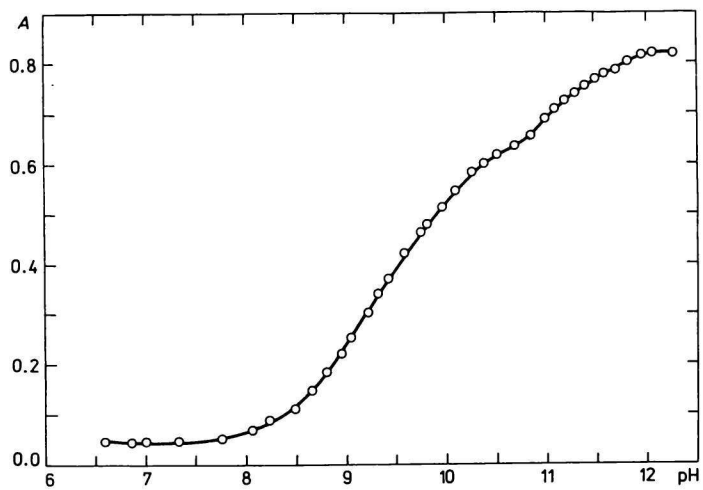


Fig. 2. The $A = f(pH)$ dependence of SIAH.
$c = 4.18 \times 10^{-5}$ mol dm^{-3}, $\lambda = 382$ nm, $l = 35$ mm, $I = 0.1$ mol dm^{-3} (NaCl).

the values of the respective molar absorption coefficients of the HL^- and L^{2-} forms of the reagent while the absorption coefficient of the H_2L form was evaluated directly from the absorption curves. The molar absorption coefficients were calculated from the relations

$$A = f(A - \varepsilon_{H_2L}\, c)\, [H]^n$$

or

$$A = f(A - \varepsilon_{HL}\, c)\, [H]^n \qquad (1)$$

which showed the linear course only for $n = 1$. The logarithmic analysis by eqns (2) and (3) also confirmed the dissociation of one proton in each of the two dissociation steps (Fig. 3)

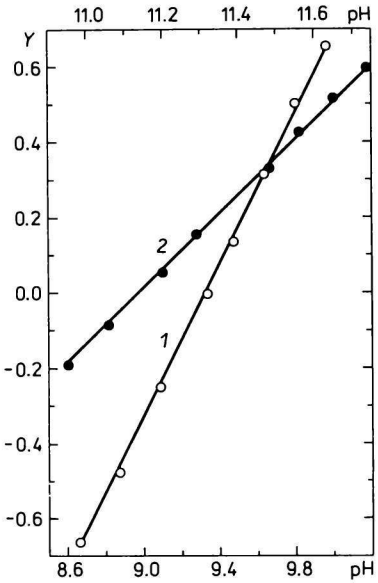


Fig. 3. Logarithmic analysis of the $A = f(pH)$ curve of SIAH.
$c = 4.18 \times 10^{-5}$ mol dm^{-3}, $\lambda = 382$ nm, $l = 10$ mm.
1. $Y = \log (A - \varepsilon_{H_2L}\, c)/(\varepsilon_{HL}\, c - A)$, lower pH scale;
2. $Y = \log (A - \varepsilon_{HL}\, c)/(\varepsilon_{L}\, c - A)$, upper pH scale.

$$\log (A - \varepsilon_{H_2L}\, c)/(\varepsilon_{HL}\, c - A) = f(pH) \qquad (2)$$

$$\log (A - \varepsilon_{HL}\, c)/(\varepsilon_{L}\, c - A) = f(pH) \qquad (3)$$

Dissociation constants were then calculated as pK_{a1} and pK_{a2} using eqns (4) and (5).

$$pK_{a1} = pH - \log (A - \varepsilon_{H_2L}\, c)/(\varepsilon_{HL}\, c - A) \qquad (4)$$

$$pK_{a2} = pH - \log (A - \varepsilon_{HL}\, c)/(\varepsilon_{L}\, c - A) \qquad (5)$$

Values of pK_{a1} and pK_{a2} given in Table 3 represent average results from three spectrophotometric determinations, about 20 points of the A—pH curve were measured in each of them. Our assumption is that pK_{a1} corresponds to the deprotonization of the hydroxamic group while pK_{a2} of the phenolic one. In an attempt to prove the suggested course of deprotonization, we employed ^{1}H-n.m.r. spectroscopy with the instrument Tesla BS 487 A (working frequence 80 MHz). The ^{1}H-n.m.r. spectra of both reagent (acid) and its potassium salt dissolved in dimethyl sulfoxide were measured and interpreted, the result corroborated the prior dissociation of the hydroxamic group. However, more compounds of similar type should be measured by this technique for the definitive elucidation of the structure and acid-base properties of the reagent and it is a subject of our further research.

Table 3

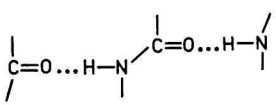
Dissociation constants of SIAH

$I = 0.1$ mol dm^{-3} (NaCl), 20°C

Equilibrium	Constant
[HL] [H]/[H_2L]	$pK_{a1} = 9.23 \pm 0.04$
[L] [H]/[HL]	$pK_{a2} = 11.13 \pm 0.07$

The i.r. spectra of the reagent and its isolated complexes are very complicated. The unequivocal assignment of the absorption bands to the vibrations of individual functional groups or bonds is difficult since several bands are always located in the same spectral region. Therefore, for the sake of comparison, the i.r. spectra of aminoacethydroxamic acid and salicylidene-2-iminoacetic acid were also measured.

The main attention was paid to the identification of the phenolic O—H group, C=O, N—H, and O—H fragments of the hydroxamic group, and to the C=N group which are important for the identification of the whole reagent and its complexes as well as for the recognition of the chelation sites. The phenolic group (bonded) of the reagent manifests itself as a shoulder (3480 cm^{-1}) on a relatively intensive band of the N—H stretching vibration (3260 cm^{-1}). Since both the reagent and all its studied complexes exhibit the mentioned N—H vibration at about 3260 cm^{-1}, it suggests an intramolecular interaction between the N—H and C=O groups in the *trans* configuration [14].



A diffusion band of the associated O—H bond is seen in the 2800—2400 cm^{-1} region of the i.r. spectrum of the reagent. This band is missing in the spectra of all the prepared complexes due to the chelation through the oxygen which is accompanied by the proton dissociation. An intensive band of the C=O stretching vibration is exhibited at 1670 cm^{-1} by the reagent as well as by its Cu(II) and Ni(II) complexes, thus we assume that the C=O oxygen of these complexes is not involved in the chelation. On the other hand, the intensive C=O band of the Fe(III) complex is shifted towards 1622 cm^{-1} obviously due to the chelation through the C=O oxygen.

The C=N stretching vibration is not seen in the spectrum of the reagent, however the band at 1670 cm^{-1} is supposedly a combined band of C=O and C=N groups. The position of the medium intensive band in the spectra of the Cu(II) and Ni(II) complexes (at 1640 and 1645 cm^{-1}, respectively) indicates that in these complexes the nitrogen atom of the azomethine group takes part in the chelation. However, a similar medium intensive band of the Fe(III) complex at 1670 cm^{-1} corroborates that in this case the azomethine group is not involved in the chelation.

It is even more difficult to decide unambiguously from the i.r. spectra if the phenolic group has any role in the chelation since in the spectra of the complexes an intensive H_2O band is located in the region of the stretching vibration of the phenolic O—H group. From the spectra of the dried complexes only that of the Fe(III) complex indicates certain involvement of the phenolic group in the chelation. Such a conclusion is also supported by a shift of the C—O stretching vibration from 1220 cm^{-1} in the spectrum of the reagent to 1200 cm^{-1} in the spectrum of the Fe(III) complex. No shift of this kind was recorded in the spectra of the Cu(II) and Ni(II) complexes.

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