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گۆڤاری زانکۆی سلێمانی/ دیسمبر۲۰۰۱، بەرگ ٤ ژمارە (١) بەشی A

Stability Constants of the Complexes of N-Salicylidene -p-x-Aniline (Where x = H, CH_3 , OCH_3 , NO_2) with Co(II).

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ABSTRACT

Stability constants of the complexes formed by Co(II) whith N-Salicylidene-p-x-aniline (Where x = H, CH_3 , OCH_3, NO_2) have been determined by two spectrophotometric methods, in 50% (v / v) ethanol at 22 + 0.5° , pH = 9 , and 0.019 M (KNO_3) ionic strength. The values of the stability constants have also been discussed.

Introduction

Schiff bases and their metal-ion complexes find interest in organic chemistry, biochemistry and inorganic chemistry [1,2]. Complexes of Co(II) and various schiff bases have been extensively studied, mostly by pH- potentiometric method [3,5]. Also, complexes of Co(II) and various bidentate ligands, containing N and O donor atoms, have been investigated potentiometrically [6,7]. In the present study stability constants of the complexes of Co(II) with N-Salicylidene-p-x-aniline (Where x = H, CH_3 , OCH_3, NO_2) have been determined spectrophotometrically in 50% (v / v) ethanolic media at 22 ± 0.5°C , pH= 9 and 0.019 M ionic strength. Also values of the stability constants have been discussed.

Experimental

Reagents:

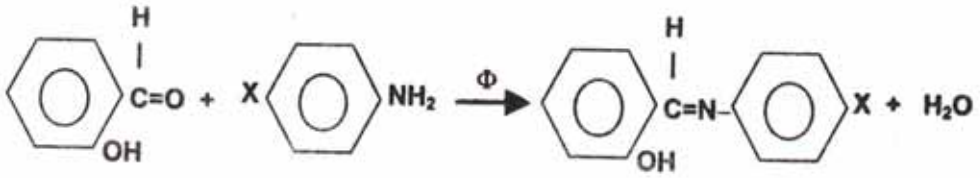
All chemicals used were of Analar grade. Cobalt, II (nitrate was obtained from Hopkin and Williams. P-Toluidene, P-Nitro aniline and Salicyladehyde were obtained from (Fluka AG), P-Anisidine, aniline and potasium nitrate were obtained from BDH. Also disodium tetraborate (Riedel De Haen AG) was used.

Apparatus:

A spectrophotometer model Phillips Pu 8620 uv/vis/nir was used to measure the absorbance. pH of the solutions was measured by a pH-meter model 7020 Kent.A thermostat model HAAKE was used for controlling the temperatures of the solutions. Varian A-60 instrument was used to obtain ^{1}H-n.m.r. spectra of the schiff bases.

Preparation of the schiff bases:

The schiff bases were prepared by refluxing equimolar amounts of Salicyladehyde and desired p-substituted aniline in ethanol for about half an hour, then cooling the reaction product in ice-bath followed by filteration and recrystalization[8]. The schiff bases were characterised by NMR and IR.



Where X = H SB(1) ; OCH_3 SB(2) ; CH_3 SB(3) ; NO_2 SB(4)

Solution for mole - ratio method:

In each experiment a number of solutions containing constant amount of Co(II) ion (0.4 ml of $1x10^{-2}$M) and variable amount of the schiff base (0.2 -1.4 ml of $1x10^{-2}$M) was prepared. A suitable amount of solid KNO_3 was added to keep the ionic strength at 0.019M. After diluting each solution with 50% ethanol / water to 9 ml, its pH was adjusted to 9 using disodiumtetraborate solution. Finally the volume of each solution completed to 10 ml. Then the solution's thermostated at 22°C ± 0.5 for two hours and their absorbances were measured at desired wavelength.

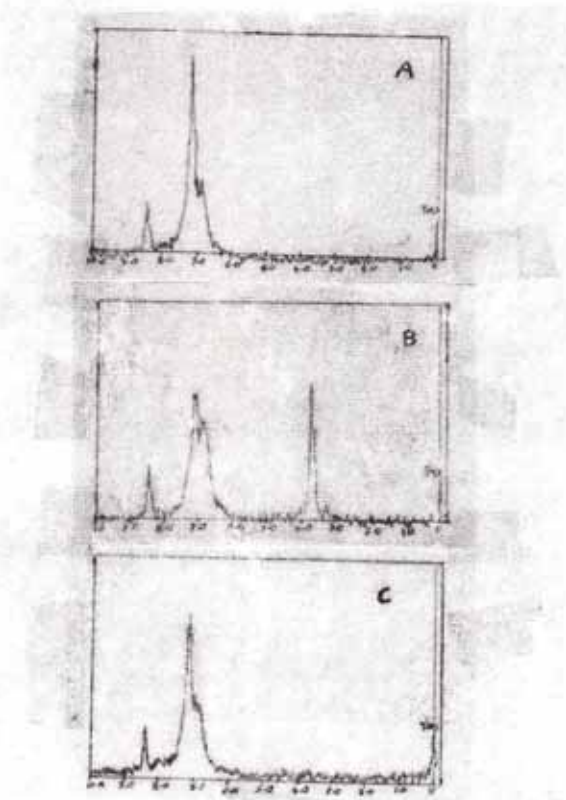
Solutions for maximum absorbances of excess reagent:

A series of solutions containing constant amounts ($4x10^{-3}$M) of Co(II) nitrate and variable excess of the schiff base ($1x10^{-2}$M) was prepared. After adjusting their pH 9 by disodiumtetraborate solution, ionic strength to 0.019 M (KNO_3) and thermostating to 22 ± 0.5°C for two hours, their absorbances were measured at desired wavelengths: 401nm Co(II)-SB(1), 400nm Co(II)-SB(2), 390nm Co(II)-SB(3) and 399nm Co(II)-SB(4).

Results and Discussion:

^{1}H -n.mr. spectra of the prepared schiff bases:

The ^{1}H-n.m.r. spectra of the schiff bases were measured using $CDCl_3$ as a solvant and TMS as a reference. The shifts of the protons are tabulated in table (1) and ^{1}H-n.m.r. spectra of three schiff bases are shown (Fig. I).



Fig(1): ^{1}H-n.m.r. spectra of the schiff bases: A-SB(1); B-SB(2); C-SB(4)

Table (1): ^{1}H-n.m.r. chemical shifts (δ in ppm) of the prepared schiff bases.

Schiff bases	δ N = CH	δ OH	δ H_s	δ H_3
SB(1)	8.46	7.20	6.89	--
SB(2)	8.45	7.15	6.92	3.37
SB(3)	8.51	7.16	7.04	2.36
SB(4)	8.40	7.14	6.95	--

There is a singlet signal for the azomethine proton at the expected position (8.4 - 8.51δ) [9.10]. The singlet signal (7.14 - 7.20 δ) is attributed to the proton af the (OH) group[11]. The doublet signal at (6.80 - 7.04δ) is assigned to phenyl protons and the singlet signals at (3.73δ) and (2.36δ) are attributed to the methyl protons of SB(2) and SB(3)respectively[11].

Absorption Spectra:

The electronic absorption bands of the schiff bases, Co(II) nitrate and Co(II) schiff base complexes are measured and arranged in Table (2). The appearance of new bands which are neither present in the spectra of the individual schiff bases nor in the spectra of Co(II) nitrate, are indications of the complexation reaction between Co(II) ion and the schiff bases.

Table (2): Electronic absorption bands(nm) of the schiff bases (in ethanol), Co(II) schiff base complexes, (ethanol/water) and Co(II) nitrate (in ethanol and in water).

Compounds	λ_1	λ_2	λ_3	Co(II) schiff base complexes	λ
SB(1)	264	315	334	Co(II) - SB(1)	401
SB(2)	264	--	348	Co(II) - SB(2)	400
SB(3)	268	320	340	Co(II) - SB(3)	390
SB(4)	272	318	340	Co(II) - SB(4)	399
Co(II) nitrate in ethanol	--	319	510		
Co(II) nitrate in water	--	311	501		

Mole-ratio method[12]:

The absorbances of the solutions prepared for this method were measured at desired wavelength. Plots of the absorbances versus [schiff base] / [Co(II)] which are shown in Fig.(2) indicate that the Co(II)-schiff base complexes are of the nature 2:1 (ligand / metal). The sharp decrease of absorbance may be due to that, an excess of schiff base can cause a decrease in absorbance, probably because of formation another complex which has smaller ε value[13].

Maximam absorbance of excess reagent:

The absorbances of the solutions prepared, described in experimental section, are measured and maximum absorbances are obtained at 1.0, 1.2, 1.3 and 1.1 ml of the schiff bases SB(1), SB(2), SB(3) and SB(4) respectively.

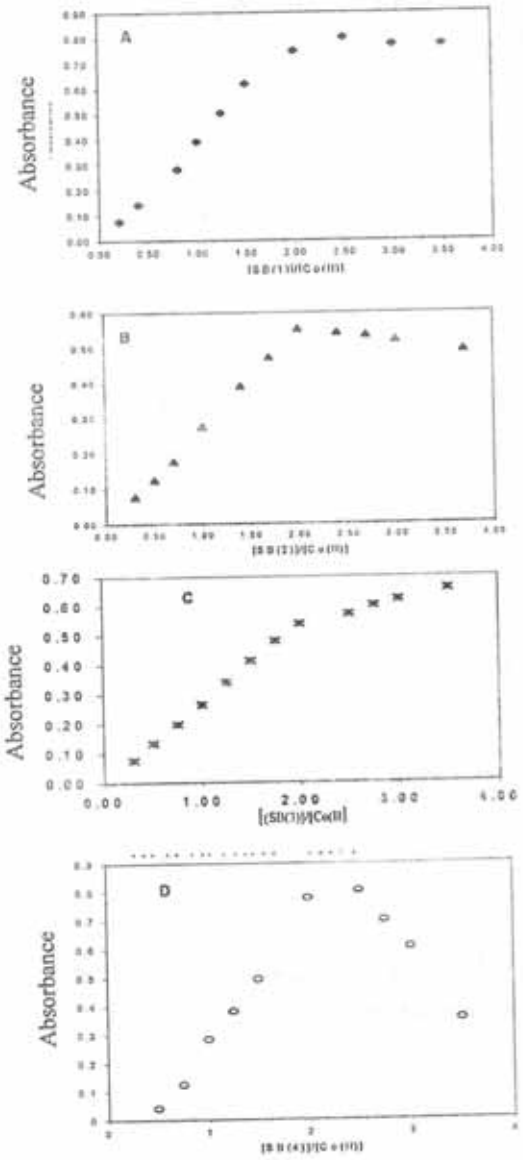


Fig.(2):- Mole-ratio plots for A:Co(II) SB(1), B: Co(II) SB(2), C: Co(II) SB(3), D: Co(II) SB(4)

Determination of stability constants

Stability constants of the Co(II) schiff base complexes are determined by two methods:

Method (A):

Solutions containing stoichiometric amounts of Co(II) ion and schiff base to one containing excess of the schiff base are prepared and thermostated at 22+ 0.5°C, pH=9 , I = 0.019 M (KNO_3) for two hours. The solutions absorbances are measured and stability constants are calculated [14] as follow:

Let ML_2 is the Co(II) schiff base complex

$M + 2L = ML_2$ ..... (1) Where M = Co(II) , L = schiff base

$$K = \frac{[ML_2]}{[M]\,[L]^2} \quad \text{.....(2)}$$

K = Stability constant

The degree of dissociation of the complex can be measured:

$$\alpha = \frac{Am - As}{\quad} \quad \text{..... (3)}$$

Where :

As = Absorbance of stoichiometric solution.

Am=Absorbance of solution with excess reagent.

Eq (2) can be written as:

$$K = \frac{C(1-\alpha)}{\alpha C.\ 4\alpha^2 C^2} = \frac{1-\alpha}{4\alpha^3 C^2} \quad \text{..... (4)}$$

Where C is the concentration of Co(II) nitrate which is equal to the concentration of the complex ML_2. The Stability constant values (Log K) are tabulated in Table (3).

Method B [15]:

By this method both stability constant and the nature of the Co(II) schiff base complexes were determined:

If we suppose that a mononuclear complex of the formula ML_n is formed according to the equation:

$M + n\,L = ML_n$ ..... (1)

The equilibrium constant can be expressed as follow:

$$K = \frac{[ML_n]}{[M]\,[L]^n} \quad \text{.....(2)}$$

Then

$$K = \frac{[ML_n]}{[M_T - ML_n]\,[L_T - ML_n]^n} \quad \text{.....(3)}$$

Where :

M = uncomplexed conc. of Co(II)

L = uncomplexed conc. of the schiff base.

L_T= Total conc. of the schiff base.

M_T= Total conc. of Co(II)

$[ML_n] = A_t - A_o$ A_o= absorbances of blank solution

$A\alpha$ = Maximum absorbance.

$M_T - ML_n = (A\alpha - A_o) - (A_t - A_o) = (A\alpha - A_t)$

Plot of $\log \frac{A_t - A_o}{A\alpha - A_t}$ Versus $\log [L_T]$

gives a straight line with a slope equal to n and an intercept equal to log K. For each experiment, a series of solutions was prepared contained constant amount of Co(II) ion and variable amount of the schiff base. The solutions thermostated at 22 ± 0.5°C for two hours and their pHs and ionic strengths, were adjusted to the experimental condition. Then their absorbances were measured at desired wavelength. From the plots of $\log \frac{A_t - A_o}{A\alpha - A_t}$ versus $\log [L_T]$, Fig(3), the values of log K and n were obtained.

Table (3) : Stability constants of Co(II) schiff base complexes in 50% ethanol at 22 ± 0.5°C, pH = 9 ionic strength = 0.019 M and time = 2 hours.

Co(II) - schiff base complexes	λ1 nm	Volume of Co(II) / 10 ml 2.5x10⁻³M	Absorbance with stochiometric amount of 2.5x10⁻³M SB As	Absorbance with excess of 2.5x10⁻³M SB Am	Degree of Dissociation ∝	Stability constant K x 10⁷	Average log K
Co(II) - SB(1)	401	0.4	0.088	0.492	0.8211	0.80747	6.76
		0.4	0.070	0.514	0.8638	0.52829	
		0.4	0.067	0.530	0.8735	0.47450	
Co(II) - SB(2)	400	0.4	0.039	0.231	0.8311	0.73554	7.23
		0.4	0.082	0.219	0.6255	3.8256	
		0.4	0.062	0.225	0.7244	1.8125	
Co(II) - SB(3)	390	0.4	0.110	0.598	0.8160	0.8466	7.09
		0.4	0.113	0.385	0.7064	2.0823	
		0.4	0.083	0.376	0.7792	1.1667	
Co(II) - SB(4)	399	0.4	0.063	0.444	0.8581	0.56144	6.82
		0.4	0.072	0.458	0.8427	0.65712	
		0.4	0.081	0.438	0.8150	0.85435	

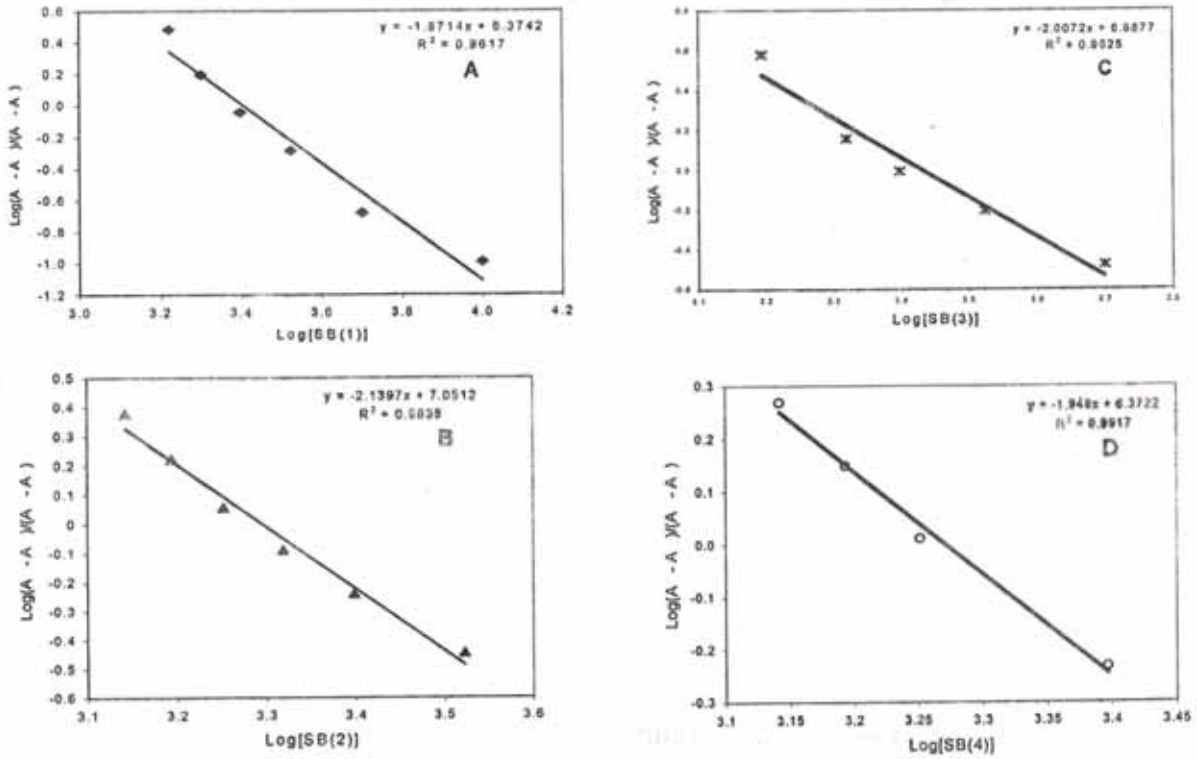


Fig.(3):- Plots of Log At-Ao/A - At vs. log [schiff base] at pH=9, I=0.019M, temp. = 22 +0.5oC, Co(II) = 4 x 10-3 M and Time = 2 hrs. for complexation reaction between Co(II) and schiff bases. A: SB(1) A = 0.824, B: SB(2)= 1.136

The values of logK and n of both methods were tabulated in Table(4).

Table (4) : The values of The stability constants (logK) and n of both methods: A and B.

Complexes	Method A	Method B	
	logK	logK	n
Co(II) - SB(1)	6.76	6.37	1.87
Co(II) - SB(2)	7.23	7.05	2.14
Co(II) - SB(3)	7.09	6.88	2.01
Co(II) - SB(4)	6.82	6.34	1.94

These stability constants values are lower than of Co(II) complexes with other bidentate (N, O) ligands such as glycine ($logK_2$= 8.60), L - Cysteine ($logK_2$ = 17.4), Histidine ($logK_2$ = 12.1) [16] and 8 - hydroxyquinoline ($logK_2$ = 19.7) [17], ∝-alanine ($logK_2$ = 8.48) and picolinic acid ($logK_2$= 10.44)[18]. This lowering can be attributed to the steric dffect caused by the phenyl rings of both benzaldehyde and aniline part of the schiff bases[19].

Also the coordination of the schiff bases to the Co(II) ion may be through the N atom of the azomethine group and oxygen of the aldehyde part.

The variation in the stability constants values of the studied complexes (Table. 4) could be explained on the basis of electronic property of the substituents $-OCH_3$, $-CH_3$ and $-NO_2$.

The substituents $-OCH_3$ and $-CH_3$ are electron donating groups while $-NO_2$ is an electron withdrawing group. The complex Co(II) - SB(2) has the highest stability value due to $-OCH_3$ group which is stronger donating group than - CH_3 [19], keeps the electronic density, around the N atom more available resulting in an increase of its basicity. Also, the resonance contribution from - OCH_3 increases stability [20].

The stability value of Co(II) - SB(3) is higher than that of Co(II) - SB(1) due to the presence of $-CH_3$ in the aniline part of SB(3).

it is expected that the Co(II) - SB(4) stability constant value would be lower than of Co(II) - SB(1) due to the electron withdrawing property of - NO_2, but their difference is very slight, which indicates that - NO_2 group has not significant effect on the basiscity of N atom of the azomethine group.

It is concluded that the stability of the chelate complexes increases with increasing basicity of the N atom of the azomethine group and vice versa.

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جیگیری هاوسەنگی ئالۆزەکانی ن ـ سالسیلیدین ـ پارا ـ X ـ ئەنیلین (NO_2, OCH_3, CH_3, H = X) و کۆبالت (II)

بایزید حسن عبدالله

بەشی کیمیا ـ کۆلیجی زانست ـ زانکۆی سلیمانی- هەریمی کوردستان – عیراق

پوختە

جیگیری هاوسەنگی ئەو ئالۆزانەی کە کۆبالت (II) لەگەڵ ن ـ سالسیلیدین ـ پارا ـ X ـ ئەنیلین (NO_2, OCH_3, CH_3, H = X) دروستیان دەکات پیورا بە دوو ریگەی شەپەنگی لە گیراوەی 50 % ئیتانۆڵ لە 22 ± 0.5 س° و pH = 9 هیزی ئایۆنی 0.019 M (KNO_3) . هەروەها لە بەهای جیگیری هاوسەنگیەکان کۆلرایەوە.

ثوابت استقرارية معقدات ن ـ سالسيليدين ـ بارا ـ X ـ ئەنيلين (NO_2, OCH_3, CH_3, H = X) و كوبالت (II)

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الخلاصة

تم قياس ثوابت استقرارية معقدات الكوبالت (II) مع ن ـ سالسيليدين ـ بارا ـ X ـ ئەنيلين (NO_2, OCH_3, CH_3, H = X) بطريقتين طيفيتين في محلول 50 % ايثانول عند 22 ± 0.5 م° و pH = 9 والقوة الايونية 0.019 M (KNO_3) . وتم مناقشة قيم ثوابت استقرارية المعقدات.

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پەسەند کرا لە ٢٠٠٠/٨/٢١ دا