



STUDIES ON BIS(PARA ANISIDINE ACETYLACETONATO) NICKEL (II) COMPLEX

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ABSTRACT

Schiff base was prepared from the reaction of para anisidine and acetylacetone. Bis(para anisidineacetylacetonato)nickel(II) complex was synthesized by the reaction of the prepared para anisidineacetylacetone ligand and nickel(II) chloride. The prepared Schiff base is orange yellow, has a yield of 61.90% and melting point of 86°C. The complex prepared is red, has a yield of 71% and decomposition temperature of 270°C. The para anisidineacetylacetone ligand is soluble in water and most organic solvents, similarly, its nickel(II) complex compound is soluble in most solvents except water and methanol, in which it slightly soluble. The molar conductance of bis(para anisidineacetylacetonato)nickel (II) complex compound determined is $4.70 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, suggesting that the complex is non-electrolyte. The infra-red spectral data of para anisidine and acetylacetone base showed a medium size band in the range $1595 - 1630 \text{ cm}^{-1}$, attributable to $\nu(\text{C}=\text{N})$ stretching vibrations, the same band is observable in the nickel(II) complex, indicating coordination of the ligand to the nickel(II) ion. The broad band in the range $3257 - 3420 \text{ cm}^{-1}$ observed in para anisidineacetylacetone ligand is assigned to $\nu(\text{O}-\text{H})$ stretching vibrations, which is absent in anisidineacetylacetonato)nickel(II) complex, as a result of deprotonation of the para anisidineacetylacetone on coordination to the nickel(II) ion. The dissociation constant (pK_a) of para-anisidine acetylacetone determined is 12.66. The stability constant of anisidineacetylacetonato)nickel (II) complex compound determined is 1.29×10^6 and the corresponding Gibb's free energy of complex is $-3.48 \times 10^4 \text{ KJ per mole}$. The average number of para anisidine ligand coordinated to nickel(II) ion determined using potentiometer is 2, suggesting a four coordinate complex compound.

Keywords: Anisidineacetylacetone, complex compound, stability constant, potentiometry.

INTRODUCTION

Anisidineacetylacetone ligand belongs to a class of chemical compounds called, Schiff bases, which are compounds containing the azomethine ($-\text{C}=\text{N}-$) group. They are usually obtained by the condensation of an aldehyde or ketone with primary amine (Holm *et al.*, 1966). Schiff base is a nitrogen analog of an aldehyde or ketone in which the $\text{C}=\text{O}$ group is replaced by a carbon - nitrogen double bond ($\text{C}=\text{N}$) with the nitrogen atom connected to an aryl or alkyl group (Schiff bases are of the general formula $\text{R}_1\text{R}_2\text{C}=\text{NR}_3$, where R_3 is an aryl or alkyl group that makes the Schiff base a stable imine (Henry and Lange, 1977). Schiff base transition metal complexes have been known, however, there was no comprehensive, systematic study until the preparative work of Pfeiffer and associates (1931), in which they reported a series of complexes derived from Schiff bases of salicylaldehyde and its substitution products. Delephine (1898) prepared complexes by reacting metal acetate, salicylaldehyde and a primary amine in alcohol and demonstrated 2:1 stoichiometry (Holm *et al.*, 1966). Recently, Gupta *et al.* (2002) reported the synthesis and characterization of cobalt (II) N, N' - bis(acetylacetone)ethylenediiminato complex from the interaction of cobalt(II) salt and N, N'-bis(acetylacetone)ethylenediimine Schiff base ligand. In another report, Xishi *et al.* (2003) described the

synthesis and spectroscopic properties of manganese(II), cobalt(II) and copper(II) complexes with novel Schiff base ligand derived from 2, 2' bis(p-methoxyphenylamine) and salicylic aldehyde.

Schiff bases and their complexes have been studied for their important properties, for example, thiazole and benzothiazole Schiff bases show effective antifungal activity (Dash *et al.*, 1984). Some Schiff bases derived from quinazolinones show antifungal activity against *Candida albicans*, *Trichophyton rubrum*, *T. mentagrophytes*, *A. niger* and *Microsporium gypseum* (Rao *et al.*, 1987). Metal complexes of molybdenum(IV) and manganese(II) with Schiff base ligands derived from hydrazine carboxamide and hydrazine carbthiamide show antibacterial activity against *S. aureus* and *xanthomonas compestris* (Singh *et al.*, 1999). In another report, Guar (2003) explained that Schiff base complexes of copper(II) and nickel(II) show antibacterial activities to *Colibacillus* and *Pseudomonas aeruginosa*. This paper reports the studies on bis(para anisidine acetylacetonato) nickel(II) Complex.

MATERIALS AND METHODS

In the preparation of reagents, chemical of analytical grade purity and distilled water were used. All glass wares were well washed with detergent rinsed with distilled water and dried in an oven before use.

All weighings were carried out on electric metler balance model AB 54 of 0.001sensitivity. IR spectral analyses were recorded using as Fourier transformed IR Genesis series model in Nujol in the range 4000 – 400cm⁻¹. pH measurements were carried out using Jenway pH meter model 3320 and electrical conductivity using Jenway conductivity meter model 4010.

Preparation of para-Anisidine Acetylacetone

To a 500cm³ round bottom flask were added 12.3g recrystallized para- anisidine in 20cm³ of ethanol, 10.2cm³ of acetylacetone in 20cm³ of ethanol and a few drops of piperidine as condensing agent. The mixture on ice cooling gave an orange – yellow semisolid which was preserved in a desiccator (Raman, *et al*, 2003).

Preparation of Bis(para anisidine acetylacetonato) Nickel(II) Complex

2.05g (0.01M) of the ligand was dissolved in 20cm³ of ethanol. This was mixed with 0.05 mole of the nickel(II) chloride in 20cm³ of ethanol. The mixture was refluxed for two (2) hours on a water bath and then concentrated and then cooled to 0°C. The Solid product obtained was filtered and washed with ethanol and dried (Raman *et al.*, 2003).

Determination of Dissociation Constant of para-Anisidine Acetylacetone

To a 400 cm³ beaker were added 90 cm³ of distilled water, 100cm³ 0.2M KNO₃, 10cm³ of 0.4M para-anisidine acetylacetone and a magnetic stirring bar before the electrodes of a standardized meter were introduced. A 10cm³ of standardized aqueous NaOH was added dropwise with stirring. After each 0.5cm³ addition, the amount of NaOH solution and the corresponding pH were recorded. Points in the 20 to 80 percent titration range were used to calculate the pKa (Gregory *et al.*, 1978).

Determination of Stability Constant of Bis(para-anisidine acetylacetonato) Nickel(II) complex

Into a 400cm³ beaker were added 90 cm³ of distilled water, 100cm³ 0.2M KNO₃, 10cm³ of 0.1M HNO₃ acid, and one millimole of nickel(II) chloride tetrahydrate, respectively. 0.2cm³ of 0.4M sodium salt of para anisidine acetylacetone was added and after each addition with stirring the corresponding pH reading was recorded. The addition of the sodium salt of para anisidine acetylacetone solution was continued until full 10 cm³ was added. The sodium salt of para anisidine acetylacetone was prepared by exactly

neutralizing a weighed solid para anisidine acetylacetone with a calculated amount of standardized 0.48M NaOH and diluting the solution with dimethylsulphoxide to a total volume of 20 cm³ (Angelici, 1977).

RESULTS AND DISCUSSION

The reaction of acetylacetone and para anisidine formed an orange yellow crystalline para anisidine acetylacetone Schiff base of melting point of 86°C and 61.9% yield (Table 1). The reaction of para anisidine acetylacetone Schiff base and nickel (II) chloride yielded a crystalline red bis(para anisidine acetylacetonato) nickel(II) complex. The decomposition temperature of the complex compound is 270°C, which is quite high, suggesting a stable compound (Table 1). The para anisidineacetylacetone Schiff base is soluble in water and most organic solvents, similarly, its nickel(II) complex compound is soluble in most solvents except water and methanol, in which it is slightly soluble. The molar conductance of the complex compound determined is 4.70 ohm⁻¹ cm² mol⁻¹, revealing that the complex compound is non-electrolyte (Table 2). The infra-red spectral analysis of para anisidine schiff base showed a band in the range 1595 – 1630cm⁻¹, attributable to ν(C=N) stretching vibrations, the same band is observable in the complex formed by the Schiff base with cobalt(II) ion, indicating its coordination to the metal ion ((Jezowska *et al*, 1988; Abdulsamath *et al.*, 1992). The far infrared spectra of the complex showed strong bands at 535cm⁻¹ and 352cm⁻¹, which are assigned to ν(M-O) and ν(M-N) stretching vibrations respectively, confirming the coordination of the ligand to the nickel ion (Silverstein and Bassler, 1967; Koji, 1977). The broad band in the range 3257 - 3420 cm⁻¹ observed in para-anisidine schiff base is assigned to ν(O-H) stretching vibrations, which is absent in the nickel(II) complex compound due to deprotonation of the Schiff base on its coordination to the nickel(II) ion (Table 4). The dissociation constant (pKa) of the Schiff base determined is 12.66 (Table 5). The ratio of nickel (II) ion to Schiff base determined potentiometrically is 1:2, implying that it is a four coordinate complex (Table 6). The stability constant of bis(para-anisidine acetylacetonato) nickel(II) complex compound determined is 1.29x10⁶, and the corresponding Gibb's free energy of the nickel(II) Schiff base complex determined is -3.48 x10⁴ kJ mol⁻¹, which is very low indicating that the complex is quite stable (Table 7).

Table 1: Some physical properties of the schiff base and its nickel(II) complex

Compound	Colour	Melting Point (°C)	Decomposition Temp. (°C)	Percent Yield (%)
Schiff base	Orange yellow	86.0	-	61.9
[NiL ₂]	Red	-	270.0	71.0

Key: L = Anisidine acetylacetonato

Table 2: Solubility of the Schiff base and its nickel(II) complex in some solvents

Compound	Water	Methanol	Ethanol	Acetone	Nitrobenzene	Chloroform	DMSO
Schiff base	S	S	S	S	S	S	S
[NiL ₂]	SS	SS	S	S	S	S	S

Where S = soluble and SS = slightly soluble.

From the analytical results of the complex compound, the structure below is proposed.

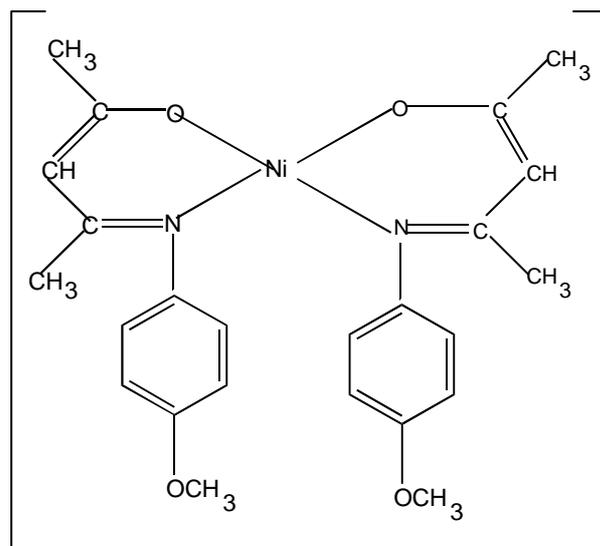


Fig.1: Molecular formula of bis(para-anisidine acetylacetonato) nickel(II) complex

Table 3: Conductivity measurement of the Schiff base and its nickel(II) complex

Compound	Molar Conductance ($\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$)
$[\text{NiL}_2]$	4.7

Table 4: Infra red spectral data of the Schiff base and its nickel(II) complex

Compound	$\nu(\text{C}=\text{N})$ (cm^{-1})	$\nu(\text{O}-\text{H})$ (cm^{-1})	$\nu(\text{M}-\text{O})$ (cm^{-1})	$\nu(\text{M}-\text{N})$ (cm^{-1})
Schiff base	1595 – 1630	3257 - 3420	-	-
$[\text{NiL}_2]$	1570 - 1600	-	535	352

Table 5: Determination of pKa of Para-anisidine acetylacetone

S/No.	Value of NaOH (cm^3)	pH	$10^{-12}[\text{H}^+]$, moldm^{-3}	$10^{-3}[\text{OH}^-]$, moldm^{-3}	$10^{-3}[\text{Na}^+]$, moldm^{-3}	$[\text{A}^-]$, moldm^{-3}	pKa
1	0.5	8.99	684.7000	2.005	1.47	0.0200	10.37
2	1.0	10.46	23.2000	2.006	2.29	0.0199	11.52
3	1.5	10.92	8.0445	2.008	3.42	0.0197	11.78
4	2.0	11.13	4.9602	3.256	4.55	0.0198	11.89
5	2.5	11.27	3.5933	4.495	5.68	0.0197	12.03
6	3.0	11.38	2.7890	5.790	6.80	0.0197	12.18
7	3.5	11.46	2.3200	6.962	7.90	0.0197	12.34
8	4.0	11.54	1.9297	8.370	9.00	0.0196	12.38
9	4.5	11.60	1.6807	9.610	1.00	0.0196	12.39
10	5.0	11.65	1.4980	10.782	11.22	0.0195	12.47
11	5.5	11.70	1.3351	12.098	12.51	0.0195	12.55
12	6.0	11.74	1.2176	13.265	13.40	0.0194	12.68
13	6.5	11.77	1.1363	14.213	14.48	0.0194	12.85
14	7.0	11.80	1.0605	15.230	15.56	0.0193	12.92
15	7.5	11.83	0.9897	16.319	16.63	0.0193	13.11
16	8.0	11.86	0.8821	17.486	17.70	0.0192	13.29
17	8.5	11.88	0.8821	18.311	18.75	0.0192	13.69
18	9.0	11.91	0.2320	19.620	20.31	0.0191	13.98
19	9.5	11.94	0.7683	21.020	21.69	0.0191	14.17
20	10.0	11.96	0.7337	22.010	22.60	0.0190	14.54

Average dissociation constant of Para-anisidine acetylacetone Pka = 12.66

Table 6: Determination of the number of Schiff base (para-anisidine acetylacetone) chelated (n) to nickel(II) ion

S/No.	Vol. of sodium salt Schiff base (cm ³)	pH	10 ⁻³ [H ⁺], moldm ⁻³	10 ⁻¹² [OH ⁻], moldm ⁻³	10 ⁻³ A _{totr} , moldm ⁻³	Log[A ⁻]	10 ⁻³ M _{totr} , moldm ⁻³	n
1	4.2	3.68	1.40	11.55	8.23	-3.08	4.90	0.6
2	4.4	3.70	1.34	12.10	8.61	-3.06	4.89	0.8
3	4.6	3.72	1.28	12.67	8.99	-3.03	4.89	0.8
4	4.8	3.74	1.22	13.27	9.38	-3.01	4.88	0.9
5	5.0	3.76	1.16	13.89	9.76	-2.99	4.88	1.0
6	5.2	3.79	1.09	14.88	10.14	-2.98	4.87	1.1
7	5.4	3.81	1.04	15.59	10.52	-2.96	4.87	1.2
8	5.6	3.83	0.99	16.32	10.89	-2.94	4.86	1.2
9	5.8	3.85	0.95	17.09	11.27	-2.93	4.86	1.3
10	6.0	3.87	0.90	17.89	11.65	-2.92	4.85	1.4
11	6.2	3.90	0.84	19.17	12.03	-2.91	4.85	1.5
12	6.4	3.92	0.80	20.08	12.40	-2.89	4.85	1.6
13	6.6	3.94	0.77	21.02	12.78	-2.87	4.84	1.6
14	6.8	3.96	0.75	22.01	13.15	-2.86	4.84	1.7
15	7.0	3.98	0.70	23.05	13.53	-2.85	4.83	1.8
16	7.2	4.00	0.67	24.14	13.90	-2.83	4.83	1.9
17	7.4	4.02	0.64	25.28	14.27	-2.82	4.82	2.0
18	7.6	4.04	0.61	26.47	14.64	-2.81	4.82	2.0
19	7.8	4.06	0.58	27.71	15.01	-2.80	4.81	2.1
20	8.0	4.08	0.56	29.02	15.39	-2.79	4.81	2.2
21	8.2	4.11	0.52	30.91	16.12	-2.78	4.80	2.4
22	8.4	4.13	0.50	32.38	16.53	-2.77	4.79	2.5
23	8.6	4.15	0.50	34.86	16.87	-2.76	4.79	2.5
24	8.8	4.17	0.47	36.93	17.23	-2.74	4.78	2.6
25	9.0	4.19	0.45	38.21	17.60	-2.73	4.78	2.7
26	9.2	4.21	0.43	40.32	18.02	-2.72	4.78	2.8
27	9.4	4.23	0.41	42.63	18.32	-2.72	4.77	2.8
28	9.6	4.25	0.40	44.73	18.68	-2.71	4.76	2.9
29	9.8	4.26	0.36	46.21	19.07	-2.69	4.76	3.0
30	10.0	4.26	0.36	48.66	19.21	-2.78	4.75	3.0

Where A_{tot} = Total concentration of the dissociated ligand, M_{tot} = Total concentration of the metal salt added.
n = Average number of coordinated Schiff base (2.0)

Table 7: Stepwise formation and the overall stability constants of the complex

Compound	Stepwise stability constant		Overall stability constant	Gibb's free energy
	K ₁	K ₂	K _f	ΔG (kJ Mol ⁻¹)
[NiL ₂]	1.589x10 ³	8.13x10 ²	1.291x10 ⁶	-3.48 x10 ⁴

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