

Synthesis and Characterization of Some Aluminum Complexes with Schiff Bases

Salih H. Abbas

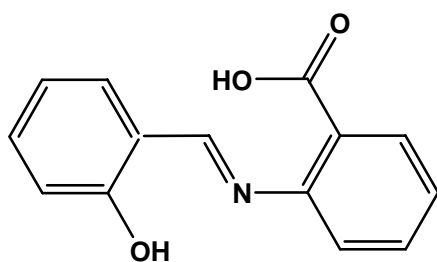
Department of Chemistry, College of Science, University of Basra, Basra, Iraq

E-mail: salihhabbas@yahoo.ca

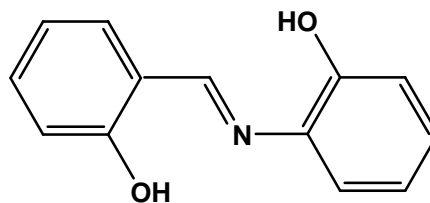
Abstract

Two Schiff bases LH_2 obtained by condensation of salicylaldehyde with anthranilic acid and o-aminophenol have been reacted with $AlCl_3 \cdot 6H_2O$ in neutral and basic medium. Two type of complexes were separated out cationic $[M(LH_2)Cl]$ and anionic $K[ML_2]$ complexes. The characterization of these complexes was obtained by use infrared spectrophotometer and molar conductivity.

Keywords: Aluminum; Schiff base; Molar conductivity.



AASA



APSA

1. Introduction

The Schiff base derived from amino acid with aldehyde, especially hydroxyl aldehyde are quite important due to their important role in biological system (1-4), these Schiff bases act as multidintate ligands with various elements (5). In present work we report the preparation and characterization of some Aluminum complexes formed with Schiff bases derived from anthranilic acid and aminophenol with salicylaldehyde in neutral and basic medium.

2. Material and Methods

2.1. Preparation of ligands

Two Schiff bases were prepared similarly as described elsewhere (5-6) by reacting a mixture of equimolar quantities of anthranilic acid and o-aminophenol with salicylaldehyde in ethanol.

2.1.1. Preparation of (AASA) Schiff base

A solution of anthranilic acid (2.742 g, 20 mmol) in ethanol and (2.13 ml) of salicylaldehyde was refluxed for 2-3 hours and an orange product was separated out after cooling in ice bath, filtered off, washed with cold ethanol and dried in a vacuumed desiccator, the yield product about (4.32 g).

2.1.2. Preparation of (APSA) Schiff base

A solution of o-aminophenol (2.182 g, 20 mmol) in ethanol and (2.13 ml) of salicylaldehyde was refluxed for 2-3 hours and a brown product was separated out after cooling in ice bath, filtered off, washed with cold ethanol and dried in a vacuumed desiccator, the yield product about (3.5 g).

2.2. Preparation of complexes

2.2.1. Preparation of complexes in neutral medium

A solution of $\text{AlCl}_3 \cdot \text{H}_2\text{O}$ (0.318 g, 2 mmol) dissolved in a minimum amount of ethanol was added with stirring to (0.602 g) of AASA ligand dissolved in a minimum amount of ethanol (1:2 metal to ligand), complete precipitation was achieved after refluxing the mixture for 1 hour, the precipitation product was filtered off, washed with cold ethanol and dried in a vacuumed desiccator.

In similar way a solution of $\text{AlCl}_3 \cdot \text{H}_2\text{O}$ (0.318 g, 2 mmol) was added with stirring to (0.53 g) of APSA ligand dissolved in ethanol (1:2 metal to ligand) and the complex was obtained.

2.2.2. Preparation of complexes in basic medium

A solution of $\text{AlCl}_3 \cdot \text{H}_2\text{O}$ (0.159 g, 1 mmol) dissolved in ethanol was added with stirring to (0.301 g) of AASA ligand dissolved in ethanol (1:2 metal to ligand) and 0.1 M of KOH was added slowly to the mixture of reaction, complete precipitation of complex was achieved at pH 7.5-8.5. The precipitation product was filtered off, washed with cold ethanol to removing any unreacted material and dried in a vacuumed desiccator.

In similar way a solution of $\text{AlCl}_3 \cdot \text{H}_2\text{O}$ (0.159 g, 1 mmol) dissolved in ethanol was added with stirring to (0.53 g) of APSA ligand dissolved in ethanol (1:2 metal to ligand). The precipitation product was collected and dried in a vacuumed desiccator.

2.3. FT-IR spectrophotometry

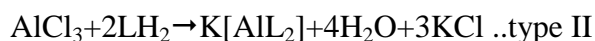
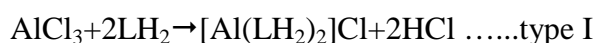
The infrared spectra were recorded on Philips sp-300s (200-4000) cm^{-1} spectrophotometer using KBr disc as shown in Fig. 1, 2.

2.4. Conductivity

The molar conductivity of the prepared complexes were determined by using an electrolytic conductivity measuring apparatus model Konduktoskop E365B Metrohm having a cell of cell constant ($K = 0.78$).

3. Result and Discussion

The reaction of aluminum chloride with ligands was carried on in both neutral and basic medium to give cationic and anionic complexes.



All complexes are fairly stable in air and insoluble in water and most organic solvents and soluble in some organic solvents so we have been measured the molar conductivity values for 10^{-3} M in dimethyl formamide and acetonitrile, they are in rang 85-78 and 166-156 $\text{cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$ respectively (Table 1), which indicate that both type of complexes are 1:1 electrolytes.

Table (1): Yield, melting point and molar conductivity of the prepared complexes.

Complex of	Yield%	Color	M.P. °C	M. conduct. $\text{cm}^2 \text{ ohm}^{-1} \text{ mol}^{-1}$ at 25 °C of 10^{-3} M	
				DMF	acetonitrile
AASA type I	65	yellow	360 decomp.	82	166
APSA type I	82	Greenish Yellow	230 decomp.	76	154
AASA type II	71	Yellow	240 decomp.	83	163
APSA type II	80	Greenish yellow	270 decomp.	78	156

The coordination of the ligands was characterized by comparison of infrared spectra of free ligands and their complexes (Table 2). In the type I complexes the stretching bands of the azomethine group $-\text{CH}=\text{N}-$ (appears at 1610-1600 cm^{-1} in the free ligands) shifting to lower

frequencies by about $45\text{-}30\text{ cm}^{-1}$ that is indicate coordination through the nitrogen atom of this group (7). In free anthranilic ligands two bands were appeared at 2700 cm^{-1} and 1535 cm^{-1} assigned to -OH and asymmetric stretching vibrations of the carboxylic group (8). Disappearance of -OH bands and lowering of OCO^- asymmetric vibration by about $50\text{-}40\text{ cm}^{-1}$ may attributed to coordination of carboxylic group with metal ion through deprotonation (8). The stretching frequency of the phenolic OH group appeared in the region $3400\text{-}3370\text{ cm}^{-1}$ (while in the ligands, $3500\text{-}3450\text{ cm}^{-1}$) showing lowering in frequencies by about $100\text{-}70\text{ cm}^{-1}$ due to complexation with metal ion.

Figure 1: The FT-IR spectra of ligand AASA and its complexes type I and II, respectively.

In the complexes type II the infrared spectra appears similar behavior of azomethane and the asymmetric OCO^- stretching frequency suggesting similar coordination of ligands. The bands of the phenolic -OH stretching vibrations of the free ligands were disappeared in all spectra of the complexes that is indicate deprotonation in basic medium of the phenolic OH groups of salicylaldehyde and aminophenol component of ligands. Both types of the complexes show the appearance of new bands of $420\text{-}365\text{ cm}^{-1}$ and $370\text{-}345\text{ cm}^{-1}$ corresponding to M-N and M-O stretching vibrations, respectively.

4. Conclusion

In present study the ligands in neutral medium act as tridentate monobasic and coordination through azomethine nitrogen, phenolic oxygen and carboxylic oxygen atoms, while in alkaline medium they act as tridentate dibasic ligands, these results are in a good agreement with molar conductance measurements and suggesting hexa-coordination of the metal ion in all complexes which may octahedral structures complexes.

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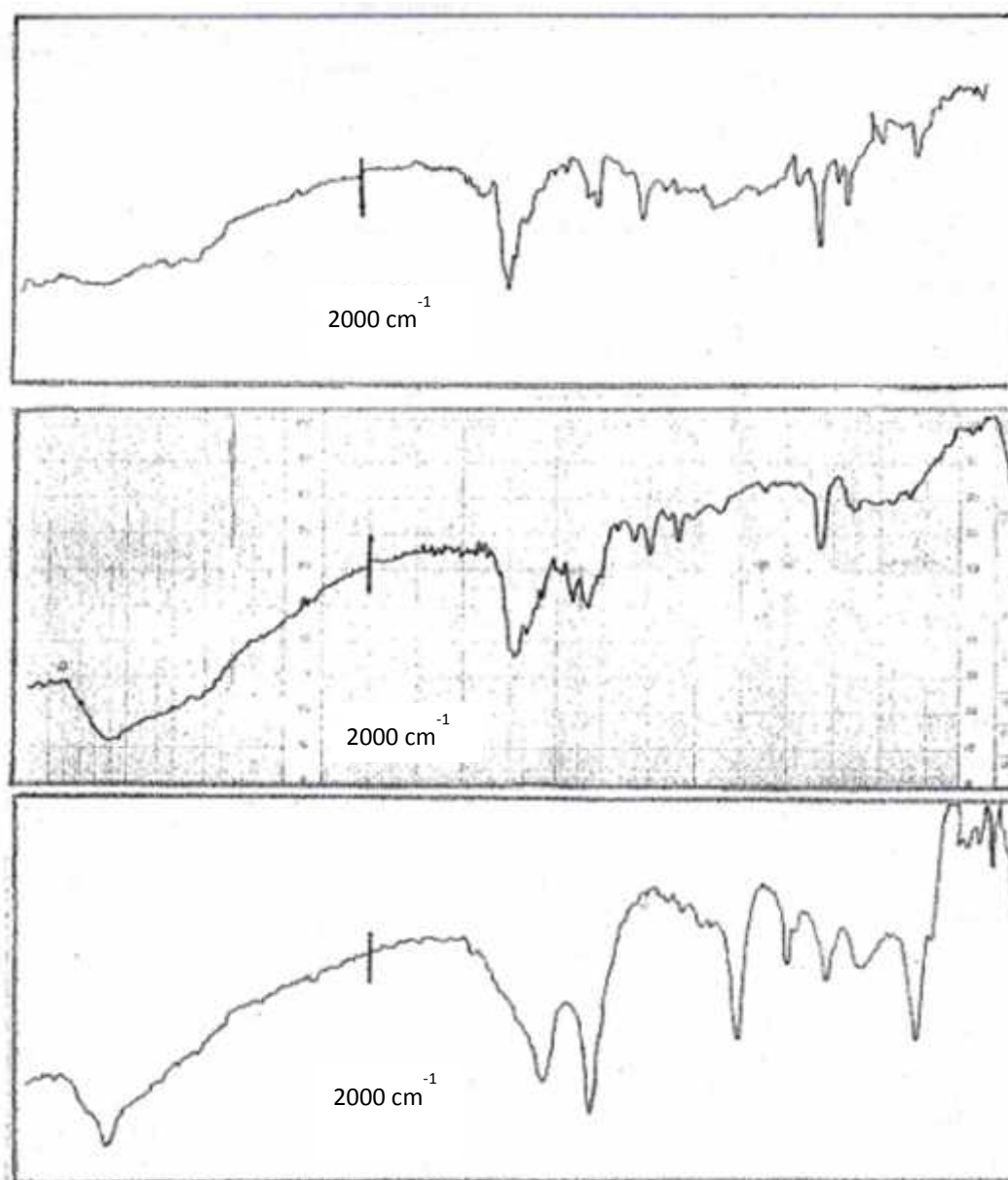


Figure 1: The FT-IR spectra of ligand AASA and its complexes type I and II, respectively.

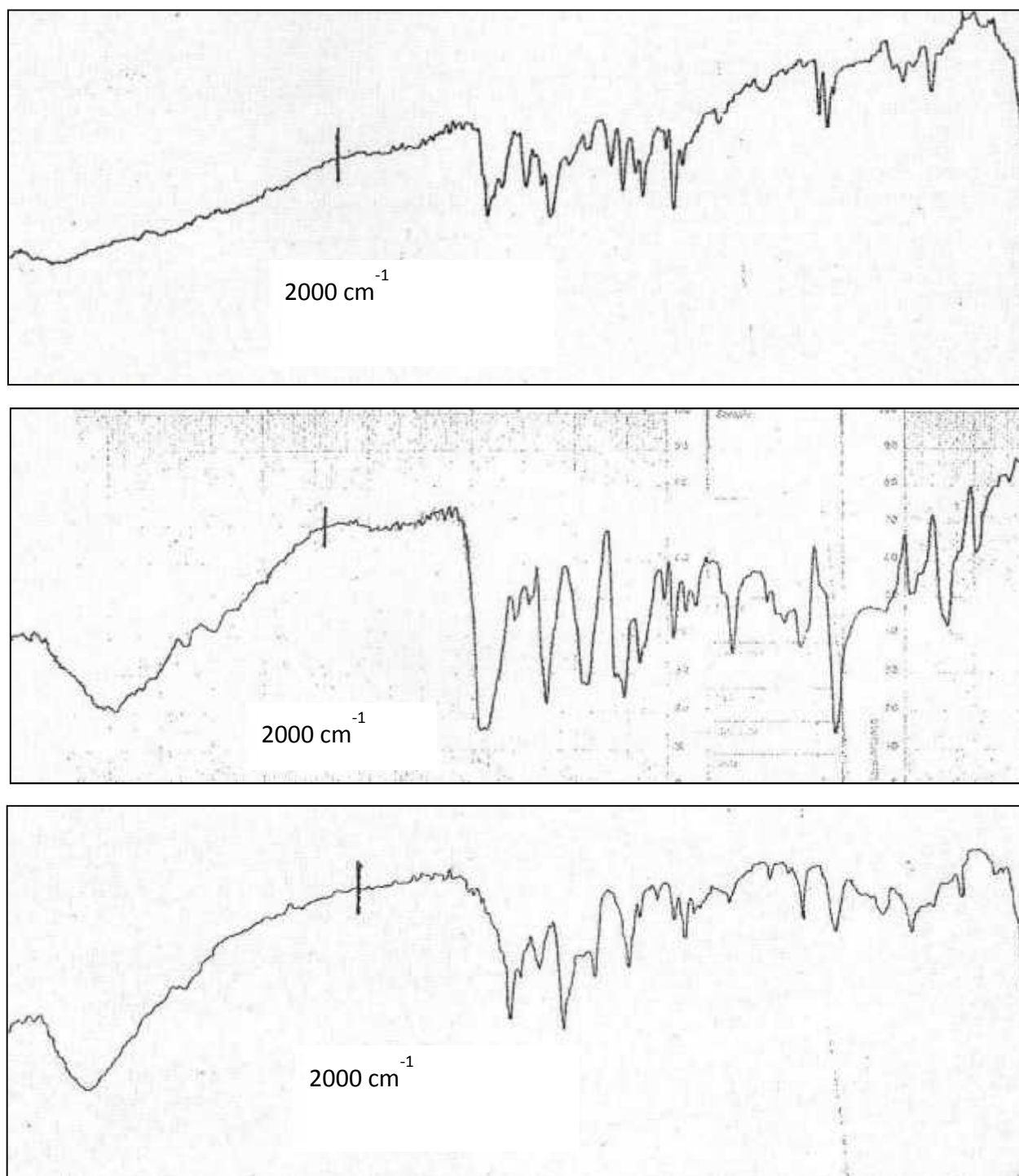


Figure 2: The FT-IR spectra of the ligand APSA and its complexes type I, II, respectively.

تحضير وتشخيص بعض معقدات الألمنيوم الثلاثي لقواعد شف

صالح حمزة عباس/ كلية العلوم –

تم تحضير إثنان من قواعد شف من مفاعلة السالسيلايديهايد مع حامض الأنثرانيلك والأوثوفينول وتعقيدها مع عنصر الألمنيوم الثلاثي بإستخدام ملح $Al_3Cl_3.6H_2O$ حصول على نوعين من المعقدات ، معقد أيوني موجب $[M(LH_2)Cl]$ أيوني سالب $K[ML_2]$ على التوالي ، وقد تم تشخيص هذه المعقدات بطيف الأشعة تحت الحمراء وقياس التوصيل المولاري لـ محاليلها.