Preparation and Spectral Studies for some Chelate Complexes of Praseodymium.

L.J. Abbas[1] ; F.J. M. Al-Imarah[2] and B. A. Saeed[3]

[1]Pharmaceutical Chemistry Branch, Coll. of Pharmacy

[2]Dept. Chemistry and Marine Environmental Poll., Marine Science Centre,

[3]Chemistry Department, Education College

University of Basra, Basra – Iraq.

Abstract

Chelating complexes between praseodymium metal and each of (I): Salicylaldehyde, (II):β-diketone, Dibenzoyl methane(Ph – C(=O)- CH_2 - C(=O)-ph)(DBM) and (III): Schiff base of the type (ph – C(=O) - CH_2 -C(=N-ph)-ph) have been prepared. The ligands and complexes were identified by their melting points and IR spectra in which complexes showed high melting points exceeded those for the original ligands, and clear differences in the IR spectra especially in the region of bending vibrations at 400 – 800 cm^{-1}. The fluorescence spectra for the ligands and their complexes with praseodymium have been studied in acidic and basic methanol solutions. The influence of pH upon their fluorescence properties was also investigated. For ligand II (DBM) the fluorescence intensity increases as acidity increase gradually, while it does not show any fluorescence emission in basic medium. For the complex DBM- Pr^{3+}, fluorescence intensity increases as the acidity gradually increase similar to that for $1x10^{-3}$ M ligand DBM but to a larger amount for the complex. It is concluded that in acidic medium the fluorescence spectra for all ligands and their complexes to praseodymium are increased with acidity but to a large extent for complexes compared with ligands. In neutral medium, the change is negligible while in basic medium the fluorescence spectra are disappeared for each of ligands and their complexes with praseodymium.

تحضير ودراسة الصفات الطيفية لبعض معقدات عنصر البراسيديميوم المخلبية

ليلى جاسم عباس* ، فارس جاسم محمد الأمارة و بهجت علي سعيد*****

***فرع الكيمياء الصيدلانية, كلية الصيدلة, جامعة البصرة**

****قسم الكيمياء وتلوث البيئة البحرية, مركز علوم البحار, جامعة البصرة,**

*****قسم الكيمياء, كلية التربية, جامعة البصرة,**

الخلاصة

تم تحضير المعقدات بين معدن البرا سيديميوم وكل من الليكاندات المخلبية التالية (I) الساليسالديهايد,(II) بيتا داي كيتون ثنائي بنزوايل الميثان (DBM) ذي التركيب الكيمياوي (Ph – C(=O)- CH_2 - C(=O)- ph) و (III) قاعدة شف ذات التركيب الكيمياوي (ph – C(=O) - CH_2 - C(=N-ph)-ph). شخصت الليكاندات والمعقدات بواسطة تقنيات درجات الانصهار ومطيافية الاشعة تحت الحمراء, حيث أظهرت معقدات البراسيديميوم درجات انصهار عالية جدا" مقارنة بالليكاندات الأصلية واختلافات واضحة في أطياف الاشعة تحت الحمراء خصوصا" في مناطق الاهتزازات الانحنائية للمدى 400 – 800 سم$^{-1}$. درست المعقدات المتكونة بين البراسيديميوم والليكاندات المخلبية باستخدام مطيافية التفلور في أوساط مختلفة الأس الهيدروجيني لتقييم تأثير الأس الهيدروجيني على صفاتها التفلورية. لليكاند (II)(DBM) تزداد شدة التفلور مع الزيادة التدريجية للحامضية ولكنه لم يظهر أي طيف في المحيط القاعدي. وللمعقد DBM- Pr^{3+} تزداد شدة التفلور مع الزيادة التدريجية للحامضية كما للتركيز $1x10^{-3}$ مولاري لليكاند ولكن بحدود ابعد للمعقد. يمكن آن نستنتج انه في المحيط الحامضي تزداد شدة التفلور لكل الليكاندات ومعقداتها مع البراسيدميوم بزيادة الحامضية وبدرجة اكبر للمعقدات مقارنة مع ليكانداتها. ولا يوجد اختلاف في المحيط المتعادل بينما تختفي أطياف التفلور لكل الليكاندات والمعقدات في المحيط القاعدي.

Introduction

Schiff base's could be prepared by condensation of aldehydes or ketones with different amines, hydroxyamines or hydrazines in presence of acetic acid or zinc chloride or boron triflorides as catalyst [G.O.Dudek,1961]

β-diketone Schiff bases of the type benzoyl acetone and dibenzoyl methane with primary amines have been prepared by Saeed

[B.A.Saeed,1989], and their UV, IR, Mass and NMR spectra have been studied. Also, Abood et al. have prepared some Schiff base's derived from β- ketone or aldehyde with aromatic and dialiphatic primary amines and their spectra were studied too.

Schiff base's have the ability to form metal complexes which were recognized before 100 years [Beel,1977] depending upon the main active imino group in which the first metal complex salicylaldehyde imino-Cu(II) was the first to be prepared and identified [Beel,1977]. [Kanatomi et al.,1976], prepared the complexes Cu(II), Ni(II), and Co(II) for Schiff Base's derived from stilpene diamine with acetyl acetone or salicylaldehyde or 5-hydroxyl acetophenone.

Complexes between lanthanides and Schiff bases were prepared by [Jain et al., 1979] . Some of the Schiff base's metal complexes were studied spectrophotometrically and showed some alteration in their spectra compared with Schiff base's themselves [Luo et al.,1998].

Rare earth metals (Eu, Pr,…etc.) are paramagnetic and in certain β-diketone complexes can provide a local magnetic field suitable for use in NMR and can dissolve in CCl_4, $CDCl_3$ and alcohols [Williams et al.,1973]. Normally, paramagnetic ions(usually colored) do not form fluorescent chelate complexes. The fluorescence characteristics can often be made effective by adjustment of pH of the solution. Organic molecules which are nonplaner, no rigid could be used as a fluorometric reagent for metals as a chelates. Schiff bases, such as basic dye rhodamines forming ion associates with complex metal anions, some β- diketones are reagents for rare earth metals [Sandell et al., 1962].

Procedures and Methods

Ligands:

Dibenzoyl methane (DBM, 1,3-Diphenyl propandion-1,3) and Salicylaldehyde were purchased from Riedel-De Haen and Aldrich Chemical companies respectively. Schiff base is prepared by condensation reaction between DBM and aniline for 2 hours, and then crystallized from

Ethanol [Fadel-Almawla, 2001]. The prepared Schiff base was identified by TLC in which it gave one spot, the expected Schiff base has the structure (ph – C(=O) - CH_2 -C(=N-ph)-ph) as it is previously characterized (10) .

Complexes:

Complexes were prepared according to the following procedure [Eiesentranut et al., 1965]: In a thick walled flask fitted with a stopcock connected to a vacuum system, 2.3 g (0.0188 mole Salicylaldehyde, 0.010 mole DBM and 0.00764 mole Shiff base) were dissolved separately in 20 ml 95% ethanol. 1 g (0.025 mole) of sodium hydroxide dissolved in 15 ml of 50% ethanol was added. The reactants were continuously stirred with a magnetic stirrer. Then, 1 g (0.00306 mole) of aqueous praseodymium (III) nitrate dissolved in 15 ml of 50% ethanol was added. Then, the flask was covered and stirred for 2 Hours, the complexes started to form after 5 minutes of stirring. The products were filtered to remove ethanol, then the residues were washed with ethanol to remove any excess ligands, and with hot water to remove unreacted metal salt and NaOH. Then the residues were dried in open air at room temperature. Melting points for complexes were recorded with Melting Point Instrument type Electro thermal Engineering LTD.

Spectroscopic Analysis :

IR spectra were recorded for all ligands and complexes in the Petrochemical complex in Khor Al-Zubair by using Shimadzo FTIR-84005 Spectrophotometer. Spectra recorded for materials as solid by using KBr disc. Fluorescence spectra were recorded in the Marine Science Centre/ Basrah University by using Shimadzo Spectrofluorometer RF 540 fitted with data base and quartz cell of 1 cm bath length.

For fluorescence studies, ligands and complexes solution prepared as follows:

$1x10^{-3}$ M for each material (ligands and complexes) were prepared by weighting the right weight of each material and dissolved in either acidic or basic methanol. After scanning of the fluorescence spectrum for the clear solution, certain amount of either HCl or NaOH were added and the fluorescence spectra were recorded.

Results and Discussion

The prepared complexes are characterized by colors difference from their ligands. Complex I is dark green, complex II is yellow and complex III is yellowish green. Solutions of complexes in methanol is characterized by colors according to the medium whether it is acidic or basic in which all showed light yellowish green colors in basic medium while colors were disappeared in acidic medium. Furthermore, the preparation and identification of prepared compounds were done according to procedures maintained in previous study [J.A.Nasir,2006]. All ligands are dissolving in ethanol while all complexes do not dissolve in this solvent. Therefore, complexes were treated with ethanol to remove any unreacted ligands and treated with water to remove NaOH.

The measured melting points for the ligands and their complexes to praseodymium are presented in table 1.

Table 1. Boiling point for salicylaldehyde and melting points for ligands and complexes prepared in this study.

Materials	Melting Points ° C	
	Ligands	Complexes
Salicylaldehyde	196-197 (boiling point)	390-391
D B M	75-77	> 400
Schiff Base	99-100	> 400

The IR spectra for all compounds, Salicylaldehyde, DBM, Schiff base and their complexes to praseodymium showed identical shapes except a minor differences. The spectra are characterized by stretching frequencies for C=N or C=O around 1400 - 1700 cm^{-1} and different bands around 400 – 1000 cm^{-1} which belong to the bending of different groups in each structure.

For the complexes of these ligands with praseodymium (I, II, and III) the stretching frequencies of the N-H or O-H bonds were disappeared as well as their bending frequencies in addition to appearance of new ligand – metal band in the region 400-800 cm^{-1}. Differences are shown between the IR spectra of each ligand and its complex to praseodymium especially in the region 500 - 1000 cm^{-1}, as shown in fig. 1, which represents the part 400-2000 cm^{-1} of their IR spectra. The structures of the complexes were confirmed by spectrophotometry [Silverstein, 1981]·

For Fluorescence studies [T.Moller], all ligands and complexes were excited by ultra-violate radiation above wavelength of 300 nm. They were excited at about 300 – 400 nm and emite at nearly the same excited wavelengths as shown in fig. 2. Recorded excitation and emission wavelengths were in the limits of 392 and 394 nm respectively.

The fluorescence of the studied chelating complexes showed narrow-lines emission which could be used as special sensors [Hausenstein et al., 1989]. It is appeared that the fluorescence intensities of studied ligands and their complexes to praseodymium decreased from ligand I (salisylaldehyde) to ligand II(DBM) then ligand III(Schiff base). Complexes showed the same behavior like their ligands, they showed increase in intensities for complexes I and III while the intensity of complex II was decreased compared to their ligands. This means that complex I is more stable than complexes II and III. Moreover, the complex III (Schiff base – Pr) recorded the highest increase in the fluorescence intensity. It is about 380% ((Intensity of complex / intensity of ligand) x 100)) compared to ligand III, while complex II (DBM- Pr)recorded a decrease to about 50% compared to ligand II.

The fluorescence intensity of the studied complexes, which were recorded under the same conditions, vary linearly with the increase of acidity . The three ligands and their complexes to Pr behave in a different manners in acidic, neutral and basic media, and the complexes show a certain levels of hydrolysis to give original ligands(15).The fluorescence of studied materials in different media behave in different manner as indicated in table 2.

Table 2. Fluorescence features of the studied materials in different media.

Material	Acidic medium	Neutral medium	Basic medium
I. Salicylaldehyde			
Ligand	Increase intensities with acidity	Low fluorescence	No spectra
Complex	Increase intensities with acidity	Hight fluorescence	No spectra
II. DBM			
Ligand	Increase intensities with acidity	-	No spectra
Complex	Increase intensities with acidity	-	None enhancement
III. Schiff base			
Ligand	Increase intensities with acidity	-	-
Complex	Increase intensities with acidity	-	-

\- = No change in the spectral line.

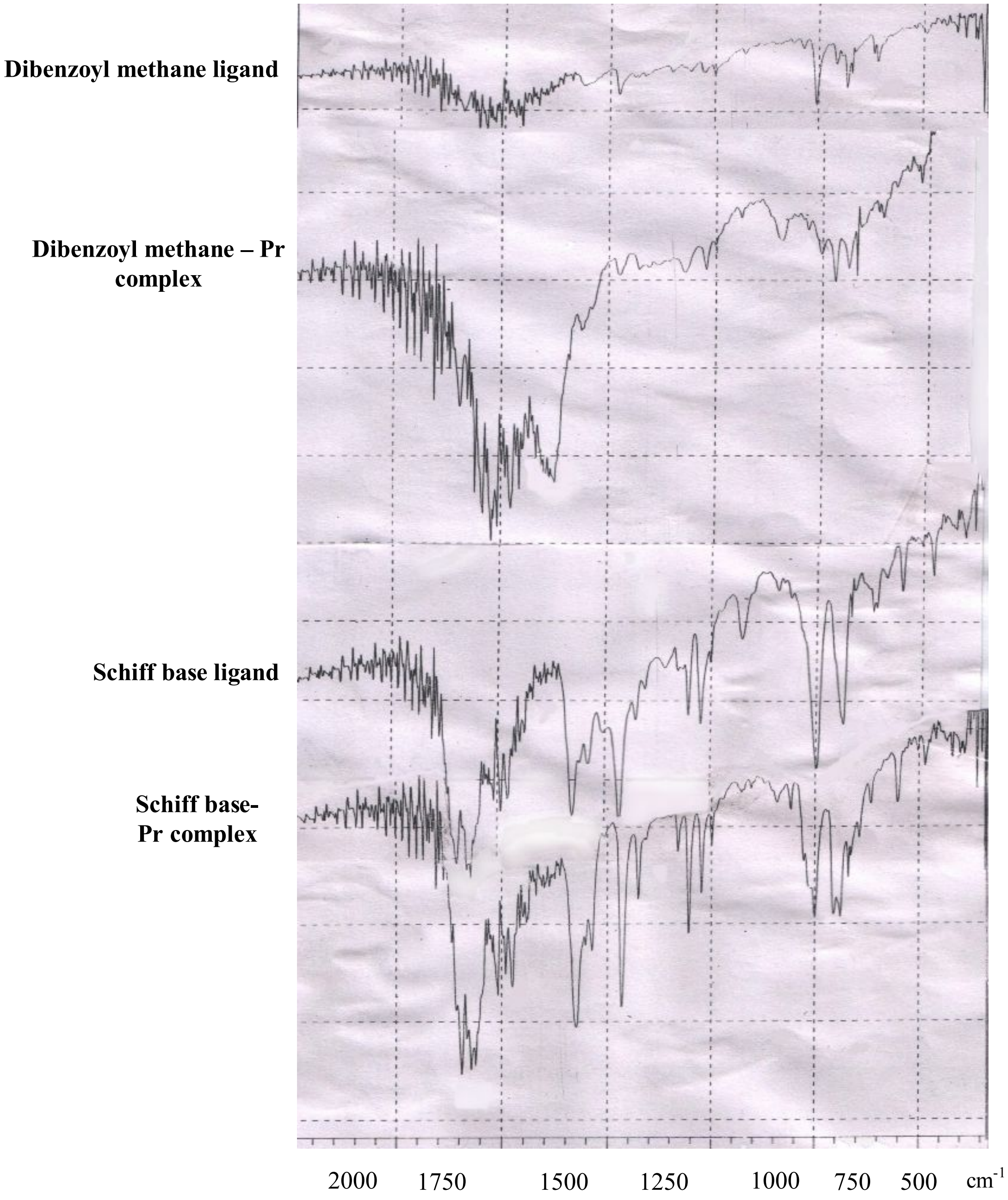

Fig.1. Part of the IR spectra 400-2000 cm^{-1} for the studied ligands and complexes (II) and (III)

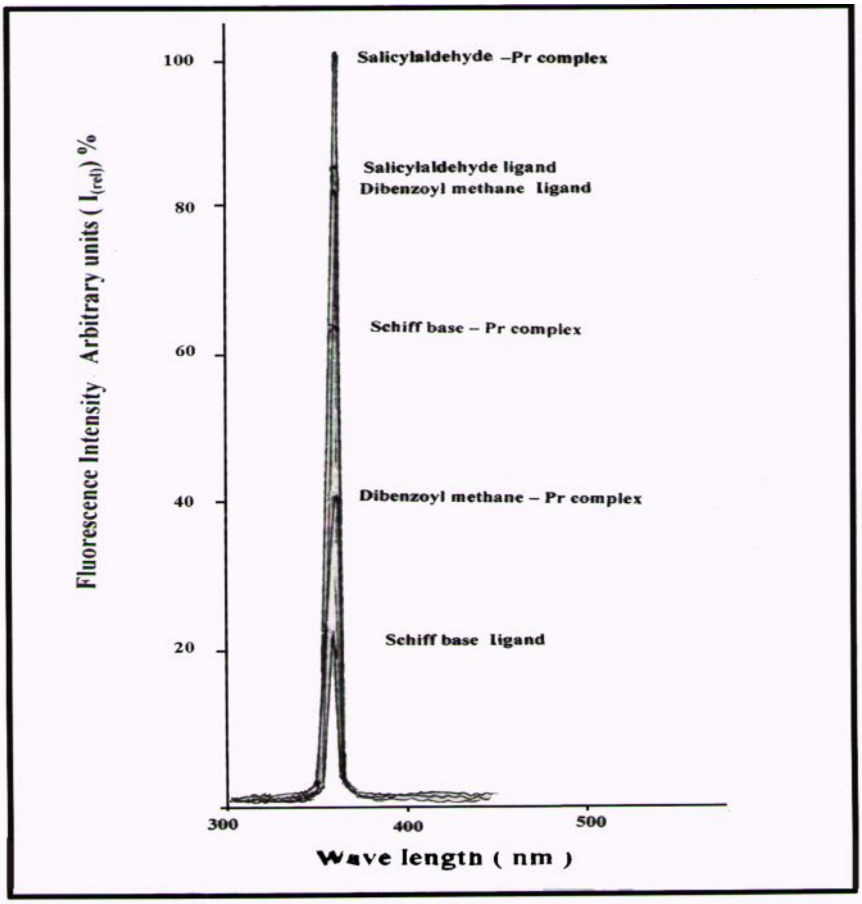

Fig. 2. Fluorescence spectra for ligands and complexes in this study.

Conclusion

It is seemed that in acidic medium the fluorescence intensities for all ligands and their complexes to praseodymium are increased with acidity but to large extent for complexes compared with ligands. In neutral medium the change is negligible while in basic medium there were no spectral bands.

Acknowledgment

The authors would like to thank Mr. Abdul-Hussein Kh.Alaeal, Marine Science Centre for his help by conducting the fluorescence studies.

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