------Raf. Jour. Sci., Vol. 19, No.1, pp 45-51, 2008------

Synthesis and Characterization of Some Cinnamaldehyde Schiff Base Complexes

Najla H. Taher
Department of Chemistry
College of Education for Girls
Mosul University

Akram A. Mohammed
Department of Chemistry
College of Education
Mosul University

(Received 5/6/2007, Accepted 10/9/2007)

ABSTRACT

Metal complexes of the general formula $[M(L)_2]X$ {where M is Cr(III) and Fe(III) and L, N- (cinnamalidene) leucine or N- (cinnamalidene) phenylalanine is a Schiff base formed by condensation of cinnamaldehyde (Cinn) with amino acid, L-Leucine (Leu) or L-Phenylalanine (Phe); X = Cl^- or $NO3^-$}, have been prepared and characterized by analytical, spectral, magnetic and conductance measurements. IR spectra showed that the nitrogen of the azomethine group, carbonyl oxygen and the negatively charged oxygen atoms of the amino acid take part in cardination. Magnetic measurements and electronic spectral studies suggested an octahedral structures for all complexes. Conductance measurements showed a 1:1 electrolytic nature of the complexes.

تحضير وتشخيص عدد من بعض معقدات السينمالديهايد لقواعد شيف

الملخص

يتضمن البحث تحضير عدد من المعقدات ذات الصيغة العامة $[M(L)_2]X$ حيث ان M تمثل ايونات الكروم والحديد الثلاثية الموجبة وان L ، N – (سينماليدين)ليوسين او N – (سينماليدين) فينيل الانين، تمثل قاعدة شيف المشتقة من تفاعل السينمالديهايد مع الحامض الاميني (ليوسين) او (فينيل الانين). تم تشخيص هذه المعقدات بالطرق الكيميائية والفيزيائية والطرق الطيفية المعروفة. اظهرت قياسات الاشعة تحت الحمراء ارتباط الليكاند من خلال ذرة النتروجين لمجموعة الازو ميثاين وذرة الاوكسجين لمجموعة الكاربونيل وذرة الاوكسجين الحاملة للشحنة السالبة للحامض الاميني لجميع المعقدات. اظهرت قياسات المغناطيسية والاطياف الالكترونية بنية ثماني السطوح لجميع المعقدات. دلت قياسات التوصيلية الكهربائية لهذه المعقدات بانها موصلة بنسبة 1 : 1.

INTRODUCTION

Schiff bases and their metal complexes played an important role in the development of coordination chemsistry, resulting in an enormous number of publications, ranging from pure synthetic work to physicochemical (Tuncel and Serin, 2005; Kureshy et al., 1999; Abu-Hussen, 2006; Khandar et al., 2007) and biochemically relevant studies of metal complexes (Panchai et al., 2006; Raman et al., 2001) and found wide range of applications (Taggi et al., 2002; Zhang et al., 1997; Sasaki et al., 1991). Schiff bases which contain cinnamaldehyde moieties are an important class of ligands in the coordination chemistry and widely reported (El-Sonbati et al., 1993; El-Sonbati et al., 2004; Raman et al., 2006). Number of papers dealing with the synthetic, analytical or biomedical applications of Schiff bases complexes containing an amino acid has significantly increased in the past few years (Liang et al., 2005; Sakiyan and Yilmaz, 2003; Shaker et al., 2003; Nath an Goyal, 2002).

Keeping this in view, it was considered worthwhile to synthesize Schiff base complexes and the main aim of the present work is to find new Schiff bases complexes by interacting Cr(III) and Fe(III) salts and Schiff bases formed by condensation of cinnamaldehyde(Cinn) with L-Leucine(Leu) or L-Phenylalanine(Phe).

EXPERIMENTAL

Materials:

All chemicals used in the present work such as amino acids, cinnamaldehyde, $CrCl_3.6H_2O$, $Cr(NO_3)_3.9H_2O$, $FeCl_3.6H_2O$ and $Fe(NO_3)_3.9H_2O$ were of Analytical Reagent (A.R.) grade (B.D.H. and Fluka).

Preparation of the ligands:

Preparation of N-(cinnamalidene)leucine:

Ethanolic solution of cinnamaldehyde (1.321 gm, 0.01 mol.) was added to aqueous solution of L-leucine (1.312 gm, 0.01 mol.). the mixtures were heated under reflux for ~ 6 h. the resulting ligands were precipitated, filtered off, washed with ethanol and air dried.

Preparation of N-(cinnamalidene)phenylalanine:

The method is same as described above. The amino acid used was L-phenylalanine with 1.652 gm (0.01 mol).

Preparation of the metal complexes:

The metal complexes were prepared by adding a hot aqueous solution of metal salts (0.01 mol.) to an ethanolic solution of the ligands (0.02 mol.), heated under reflux for ~ 12 h. the reaction mixtures were concentrated to a small volume by evaporation. On cooling, the complexes were precipitated, filtered off, washed with aqueous ethanol and air dried.

Analysis and physical measurements:

The metal contents were determined according to the standard procedure (Vogel, 1972). Melting points were determined using Richerk Jung Heizbank melting point apparatus. Molar conductivities of the complexes have been measured in an electrolytic conductivity measuring set LF-42 using 10^{-3}M of the complexes in N,N-dimethylformamide (DMF) solutions at room temperature. IR spectra were recorded on a Bruker (tensor 27) spectrophotometer in the 4000-400 cm-1 range using KBr disc. Electronic spectra were recorded on a Shimadzu 160 spectrophotometer in DMF at 25°C for 10^{-3} solution of the compounds using a 1 cm quartz cell. Magnetic susceptibility measurements of the complexes in the solid state were determined by the Fraday method at room temperature using a Bruker BM6 apparatus.

RESULTS AND DISCUSSION

The chemical analytical data of the synthesized chromium (III) and iron (III) complexes were listed in Table (1), suggest that the proposed formulae $[M(L)_2]X$ where L = cinnamaldehyde – amino acid Schiff base. The molar conductances of the complexes in DMF were in the range 67-84 ohm^{-1} cm^{2} mol^{-1} (Table 1) indicating a 1:1 electrolytic nature, (Geary, 1971).

Table 1 : Analytical and some physical properties of the complexes.

Compound	**m.p.^{0}C**	**Colour**	**Yield %**	**% Metal Found (Calcd.)**	**ΛM cm^2 ohm^{-1}mol^{-1}**
(Cinn – Leu)	233	Yellow	76	------	------
(Cinn – Phe)	242	Yellow	71	------	------
$[Cr(Cinn\text{-}Leu)_2]Cl$	251	Brown	62	9.32 (9.03)	76
$[Cr(Cinn\text{-}Leu)_2]NO_3$	258	Brown	67	8.15 (8.64)	79
$[Fe(Cinn\text{-}Leu)_2]Cl$	250	Brown	79	9.22 (9.63)	67
$[Fe(Cinn\text{-}Leu)_2]NO_3$	246	Yellow	82	9.29 (9.21)	80
$[Cr(Cinn\text{-}Phe)_2]Cl$	265	Dark Brown	59	7.77 (8.08)	78
$[Cr(Cinn\text{-}Phe)_2]NO_3$	252	Dark Brown	63	8.04 (7.76)	83
$[Fe(Cinn\text{-}Phe)_2]Cl$	249	Dark Brown	66	8.97 (8.62)	84
$[Fe(Cinn\text{-}Phe)_2]NO_3$	266	Pale Yellow	68	8.09 (8.28)	81

The IR spectra of the Schiff bases (Table 2) showed characteristic absorption bands at the ranges 3445-3451, 1698-1716 and 1630-1646 cm^{-1} due to (OH), (-C=O) and (-C=N) stretching vibrations, respectively. The appearance of the new bands at 1630-1646 cm^{-1} due to the Schiff base azomethine linkage confirmed the formation of the ligands (Cinn-Leu) and (Cinn-Phe). The bonding of the ligand to the metal ion was investigated by comparing the infrared spectra of the free Schiff bases with their metal complexes (Table 2) indicating that the ligands were coordinated to the metal atom in tridentate fashion. It indicated that ν(-C=N) band in the spectra of the Schiff bases at 1630-1646 cm^{-1} due to azomethine linkage was shifted towards lower frequency in the spectra of all the complexes, indicating that the ligands were coordinated to the metal atoms through azomethine nitrogen. Further proof of the coordination to the N atom was provided by the appearance of the bands (M-N) in the 420-431 cm^{-1} region in the IR spectra of the complexes (Abd-Elzaher, 2001; Narula et al., 1982; Panchai et al., 2006). Also, in the spectra of the Schiff bases the bands due to ν(COO) at 1698-1716 cm^{-1} shifted towards lower frequency side and the band due to ν(OH) at 3445-3451 cm^{-1} disappeared which was an evidence for the bidentate coordination of these groups with the metal atom {it is worthwhile mentioning here that the amino acids exist as zwitter ions, NH_3^+ AA. COO^- (AA means Amino Acid) and in the complexes NH_3^+ gets deprotonated and binds the metal through the neutral NH_2 group}. Moreover, the non ligand bands appeared at 455-470 cm^{-1} assigned to M-O mode, conclusively indicated that the ligands are coordinated to the metal ions through these groups (Puri and Asplund, 1982; Bellamy, 1966). The other new bands located at 1381-1392cm^{-1} and 553-574 cm-1 for nitrate and chloride groups, respectively. The positions of these bands suggested the ionic nature and the non-involvement of these groups in coordination (Nakamoto, 1978) and therefore remained outside the coordination sphere. These observations were in good agreement with the conductance values which have been supported the given formulation of the complexes.

Table 2 : Important I.R. spectral bands (cm^{-1}).

Compound	**ν (C=N)**	**ν (COO)**	**ν (OH)**	**ν (M-N)**	**ν (M-O)**
(Cinn – Leu)	1630	1698	3445	------	------
(Cinn – Phe)	1646	1716	3451	------	------
$[Cr(Cinn\text{-}Leu)_2]Cl$	1621	1682	------	420	470
$[Cr(Cinn\text{-}Leu)_2]NO_3$	1610	1683	------	429	469
$[Fe(Cinn\text{-}Leu)_2]Cl$	1612	1688	------	424	455
$[Fe(Cinn\text{-}Leu)_2]NO_3$	1620	1687	------	431	468
$[Cr(Cinn\text{-}Phe)_2]Cl$	1631	1693	------	424	457
$[Cr(Cinn\text{-}Phe)_2]NO_3$	1636	1687	------	424	458
$[Fe(Cinn\text{-}Phe)_2]Cl$	1632	1692	------	423	457
$[Fe(Cinn\text{-}Phe)_2]NO_3$	1632	1697	------	423	458

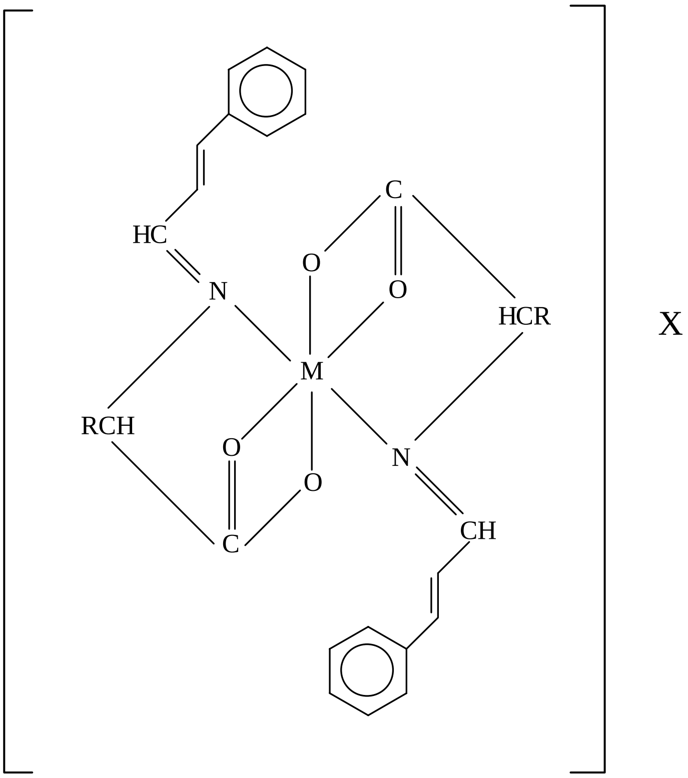
The electronic spectra of the chromium (III) complexes recorded in DMF (Table 3), show two bands in the ranges 13513-14409 and 24271-24937 cm^{-1}, corresponding to $^4A_2g(F) \rightarrow {}^4T_2g(F)$ and $^4A_2g(F) \rightarrow {}^4T_1g(F)$ transitions, respectively. The transition $^4A_2g(F) \rightarrow {}^4T_1g(P)$ is usually not observed in the visible region since it was hidden under the strong charge transfer band at the range 34364-35087 cm^{-1}, the position of the bands indicated that these complexes exhibited octahedral geometry (Lever, 1984). Also chromium (III) complexes exhibit magnetic moments of 3.84-3.98 B.M., corresponding to three unpaired electrons. These moments were close to the spin only magnetic values, suggesting an octahedral geometry around the chromium (III) ion (Figgis, 1978). The electronic spectra of iron (III) complexes (Table 3), show three bands at 15698-16556, 19230-20080 and 33444-34722 cm^{-1}, which might be assigned to transitions $^6A_1g \rightarrow {}^4T_1g$, $^6A_1g \rightarrow {}^4T_2g$ and the charge transfer transition, respectively.

The positions of the important bands indicate a six coordinate octahedral geometry (Lever, 1984). The magnetic moments obtained for iron (III) complexes (Table 3) were in favor to infer the presence of high spin octahedral geometry around the central iron (III) (Figgis, 1978).

Table 3 : The magnetic moments and the electronic spectral data (cm^{-1}).

Compound	**μ eff B.M**	**d-d transitions and charge transfer (C.T) bands (cm^{-1})**
$[Cr(Cinn\text{-}Leu)_2]Cl$	3.84	13513 , 24937 , 35087 (C.T)
$[Cr(Cinn\text{-}Leu)_2]NO_3$	3.91	14265 , 24271 , 34364 (C.T)
$[Fe(Cinn\text{-}Leu)_2]Cl$	5.77	15698 , 19230 , 33444 (C.T)
$[Fe(Cinn\text{-}Leu)_2]NO_3$	5.63	16556 , 20080 , 34722 (C.T)
$[Cr(Cinn\text{-}Phe)_2]Cl$	3.98	14064 , 24570 , 34843 (C.T)
$[Cr(Cinn\text{-}Phe)_2]NO_3$	3.90	14409 , 24752 , 34965 (C.T)
$[Fe(Cinn\text{-}Phe)_2]Cl$	5.98	16366 , 19305 , 34602 (C.T)
$[Fe(Cinn\text{-}Phe)_2]NO_3$	5.91	16286 , 19723 , 34013 (C.T)

It could be deduced, from the above, that the cinnamaldehyde-amino acid Schiff base ligands behave as a monobasic tridentate chelating agent towards the central Cr (III) and Fe (III) via the three bonding sites of the azomethine nitrogen atom, carboxyl oxygen and the negatively charged oxygen atoms of the amino acid. Thus hexacoordinated octahedral geometry was suggested for the chromium (III) and iron (III) complexes as shown in figure (1).



M = Cr (III) or Fe (III) ion
R = - CH_2Ph or $(CH_3)_2\text{-}CH\text{-}CH_2^-$
X = Cl^- or NO_3^-

Fig. 1 : The proposed structure of the complexes.

REFERENCES

Abd-Elzaher, M.M., 2001. Spectroscopic Characterization of Some Tetradentate Schiff Bases and their Complexes with Nickel, Copper and Zinc, J. Chin. Chem. Soc., Vol. 48, pp.153-158.

Abu-Hussen, A.A.A., 2006. Synthesis and Spectroscopic Studies on Ternary Bis-Schiff Base Complexes having Oxygen and/or Nitrogen Donors, J. Coord. Chem., Vol. 59, No. (2/20), pp.157-176.

Bellamy, L.J., 1966. The Infrared Spectra of Complex Molecules. Methuen, 3rd. ed., London, 95 p.

El-Sonbati, A.Z., Al-Shihri, A.S. and El-Bindary, A.A., 2004. Polymer Complexes XLV. Spectral Studies on Metal-Ligand Bonding in Novel Poly-Schiff Base Complexes, J. Inorg. And Organomet. Poly., Vol. 14, No. 1, pp.53-71.

El-Sonbati, A.Z., El-Bindary, A.A., Diab, M.A. and Mazrouh, S.A., 1993. Polymer Complexes, XXIII: Synthesis and Physicochemical Studies on Transition Metal Complexes of Symmetric Novel poly (N, N-́O-O-phenylenediamine) - Bis (Cinnamaldehyde), Monatshefte fur Chemie, Vol. 124, No. (8/9), pp.793-801.

Figgis, B.N., 1978. Introduction to Ligand Field Theory, Wiley, New York.

Geary, W.J., 1971. Use of Conductivity Measurements in Organic Solvents for the Characterization of Coordination Compounds, Coord. Chem. Rev., Vol. 7, pp.81-122.

Khandar, A.A., Yazdi, S.A.H., Khatamian, M., McArdle, P. and Zarei, S.A., 2007. Synthesis, Characterization and Structure of Nickel (II) Complexes of a 16-Membered Mixed-Donor Macrocyclic Schiff Base Ligand, Potentially Hexadentate, Bearing Two Pendant Alcohol Functions, Polyhedron, Vol. 26, No. 1, pp.33-38.

Kureshy, R.I., Khan, N.H. and Abdi, S.T., 1999. Synthesis, Physicochemical Studies and Solvent Dependent Enantioselective Epoxidation of 1,2-dihydronaphthalene Catalyzed by Chiral Ruthenium(II) Shiff Base Complexes, J. Mol. Catal., Vol. 150, pp.163-173.

Lever, A.B.P., 1984. Inorganic Electronic Spectroscopy, Elsevier, Amsterdam.

Liang, Y., Su, B., Zhao, J. and Sun, W., 2005. The Synthesis of New Asymmetric Double Schiff Bases Containing A New O-Amino Benzoic Acid Derivative, Synth. Commun., Vol. 34, No. 17, pp.3235-3242.

Nakamoto, K., 1978. Infrared and Raman Spectra of Inorganic and Coordination Compounds. John Wiley, 3rd ed. , New York.

Narula, A.K., Singh, B. and Kappor, R.N., 1982. Anthranilic Acid Hydrazide Complexes of Aluminum (III) and Titanium (IV), J. Indian Chem. Soc., Vol. 59, 1296 p.

Nath, M. and Goyal, S., 2002. Synthesis, Characteristic Spectral Studies and in vitro Antimicrobial Activity of Organosilicon(IV) Complexes of N-(2-hydroxynaphthalidene) -Amino Acid Schiff Bases, Phosphorus, Sulfur, and Silicon and the Related Elements, Vol. 177, No. 2, pp.447-463.

Panchai, P.K., Pansuriya, P.B. and Patel, M.N., 2006. In-vitro Biological Evaluation of Some ONS and NS Donor Schiff’s Bases and their Metal Complexes, J. Enzy. Inhib. Med. Chem., Vol. 21, No. 4, pp.453-458.

Puri, R.N. and Asplund, R.O., 1982. Preparation and Properties of Tri-µ3-Oxo-Triaquotris (L-Aminoacid) Tris (Dihydrogen Phosphito) Triiron (III) Nitrates : Synthetic Probes for the Ferritin Iron Co Re, Inorg. Chim. Acta, Vol. 66, pp.49-56.

Raman, N., Kulandaisamy, A. and Jeyasubramanian, K., 2001. Synthesis, Spectroscopic Characterization, Redox and Biological Screening Studies of Some Schiff Base Transition Metal (II) Complexes Derived from Salicylidene-4-Aminoantipyrine and 2-Aminophenol/2-Aminothiophenol, Synth. and React. in Inorg. Met. Org., and Nano-Met. Chem., Vol. 31, No. 7, pp.1249-1270.

Raman, N., Raja, S.J., Joseph, J. and Raja, J.D., 2006. Molecular Designing, Structural Elucidation, and Comparison of the Cleavage Ability of Oxovanadium (IV) Schiff Base Complexes, Russ. J. Coord. Chem., Vol. 33, No. 1, pp.7-11.

Sakiyan, I. and Yilmaz, H., 2003. Managanese (III) Complexes of Some Amino Acid (L-Serine, L-Methionine, L-Cystein) Schiff Bases Derived from 2-Hydroxy-1-Naphthaldehyde, Synth. and React. in Inorg., Met.-Org., and Nano-Met. Chem., Vol. 33, No. 6, pp.971-983.

Sasaki, C., Nakajima, K. and Kojima, M., 1991. Preparation and Characterization of Optically Active Quadridentate Schiff Base - Titanium (IV) Complexes and the Catalytic Properties of these Complexes on Asymmetric Oxidation of Methyl Phenyl Sulfide with Organic Hydroperoxides, Bull. Chem. Soc. Jpn., Vol. 64, pp.1318-1324.

Shaker, A.M., Awad, A.M. and Nassr, L.A.E., 2003. Synthesis and Characterization of Some Novel Amino Acid Schiff Base Fe (II) Complexes, Synth. and React. in Inorg., Met.-Org., and Nano-Met. Chem., Vol. 33, No. 1, pp.103-117.

Taggi, A.E., Hafez, A.M., Wack, H., Young, B., Ferraris, D. and Lectka, T., 2002. The Development of the First Catalysed Reaction of Ketanes and Imines : Catalytic Asymmetric Synthesis of µ-Lactams , J. Am. Chem. Soc., Vol. 124, pp6626-6635.

Tuncel, M. and Serin, S., 2005. Synthesis and Characterization of Copper (II), Nickel (II) and Cobalt (II) Complexes with Azo-Linked Schiff Base Ligands, Synth. and React. in Inorg. Met-Org. and Nano-Met. Chem., Vol. 35, No. 3, pp.203-212.

Vogel, A.I., 1972. A Textbook of Quantitative Inorganic Analysis, Longman Inc., 3rd ed., New York.

Zhang, J.X., Zhou, Y. and Cai, G., 1997. Preparation of Schiff Base-Cu Complex and their Application in the Asymmetric Synthesis of Chrysanthemate, J. Mol. Catal., Vol. 11, pp.41-44.