Synthesis and characterization of some transition metal complexes with new Schiff base ligand (ABATSC)

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Abstract

Six metal complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with new Schiff base *p*-(N,N-dimethyl amino benzaldehyde) acetopheneden thiosemicarbazone (ABATSC) have been synthesized and characterized by elemental analysis, magnetic susceptibility, molar conductance, in addition of IR and electronic spectra. The result show that the functional groups was (–C=S) and (-CH=N-). It has been found that (ABATSC) act as a natural bidentate ligand . The suggest geometry of the complexes appears to be octahedral and expected for non electrolyte.

Key words:- characterization; thiosemicarbazone; variable coordination; five-membered chelate rings.

الخلاصة

تضمن البحث تحضير ستة معقدات لايونات الكوبلت(II), النيكل(II), النحـاس(II), الخارصـين (II), الكادميوم (II) والزئبق (II) مع ليكاند قاعدة شف الجديدة بارا- [(N,N–داي مثيل أمينو بنزاديهايد) أسـيتو فينيدين ثايو سيماكاربازون] (ABATSC) . شخصت الليكاند المحضرة ومعقداتها الفلزية بوسـاطة التحليل الدقيق للعناصر والحساسية المغناطيسية والتوصيلية المولارية بالاضافة الى أطيـاف الاشـعة تحـت الحمراء والاطياف الالكترونية. بينت نتائج الدراسة ان المجاميع الفعالة لليكاند المخلبي هي (-CH=N-) و-(C=S) حيث تسلك كليكاند متعادلة ثنائية المخلب. تم اقتراح الصيغة التركيبية ثمانيـة الـسطوح للمعقـدات الصلبة وقد تبين أنها عديمة التوصيل الكهربائي.

Introduction

Organic compounds containing an azomethine group (-CH=N-) are known as Schiff bases [1]. Thiosemicarbazone are of considerable interest because of their chemistry and potentially biological activities, such as antibacterial[2,3], antitumor[4], antimicrobial[5] and antiviral[6].

A large number of transition metal complexes of thiosemicarbazone have been reported[7]. Thiosemicarbazones usually act as chelating ligand with transition metal ions, bonding through the sulfur and hydrazine nitrogen atoms[8,9] . The synthetic and structural aspects of a number of transition metal complexes of N,S systems have been described[10,11].

This work describe the synthesis and characterization of some transition metal complexes, with new Schiff base ligand (ABATSC) derived from thiosemicarbazone.

Experimental

Materials and measurements

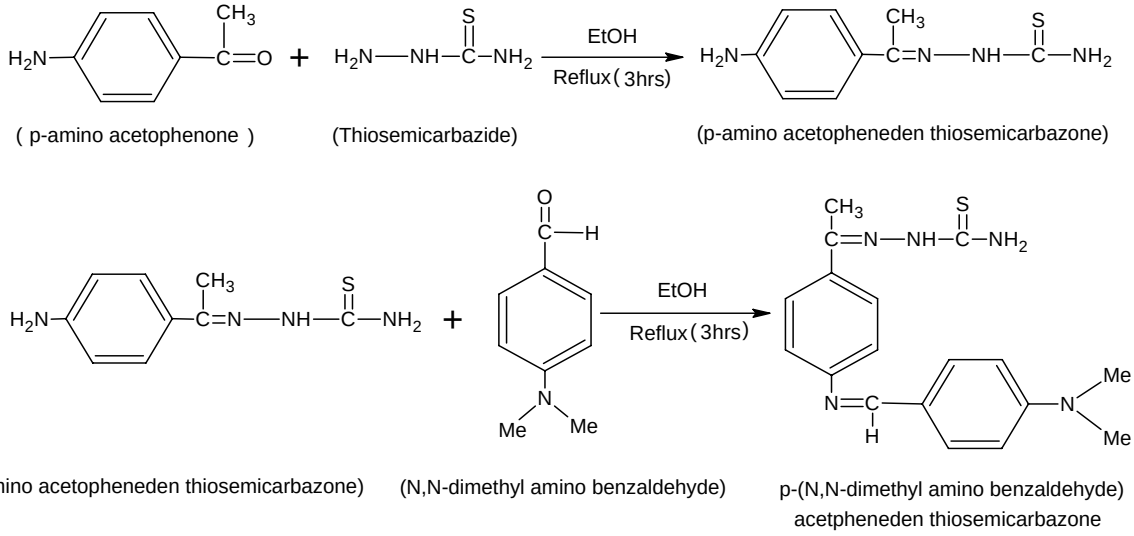
All chemicals are of highest purity and used as supplied. Electro thermal melting point model 9300 was used to measure the melting points of the ligand and its complexes. Elemental Microanalysis (C.H.N) performed using on Thermofinigan Flash Tehran university Iran. IR spectra were recorded using KBr disces 4000-400cm^{-1} on FT-IR Testscan Shimadzu model 8000-Electronic spectra were recorded using Shimadzu Uv-Vis 1700 spectrophotometer. Electrical conductivity was measured by using alpha Digital conductivity meter with solute concentration of (10^{-3}M) in DMSO. The magnetic susceptibilities were measured on powdered samples using faraday method, Balance Magnetic (MSB-MKI) had been employed for this purpose. The diamagnetic corrections were made by Pascal's constant[12].

Synthesis of Schiff base ligand (ABATSC)

The method of preparation was as follows:

The *p*-amino aceto phenone (2.7 gm, 20 mmol) dissolved in ethanol (30 cm^3) was mixed with thiosemicarbazone (1.82 gm, 20 mmol) dissolved in ethanol (30 cm^3). To this solution added three drops from glacial acetic acid and the mixture was refluxed for 3hrs. A clear coloured solution was obtained. The Schiff base ligand was isolated after the volume of the mixture was reduction to half by evaporation and recrystilized by hot ethanol . The crystalline product was dried over anhydrous $CaCl_2$.

The Schiff base ligand (*p*-amino acetopheneden thiosemicarbazone) has been taken and dissolved (4.16 gm, 20mmol) in (30cm^3) of ethanolic solution with the same volume of ethanolic solution of (N,N- dimethyl amino benzaldehyde) (2.98 gm, 20mmol). To this mixture was added three drops from glacial acetic acid. The mixture was refluxed with stirring for 3hrs. the resulting solution was evaporation to half volume and precipitated product was collected by filtered off, purified by crystallization from hot ethanol, and dried over anhydrous $CaCl_2$. Scheme 1.



(p-amino acetophenone) (Thiosemicarbazide) (p-amino acetopheneden thiosemicarbazone)

(p-amino acetopheneden thiosemicarbazone) (N,N-dimethyl amino benzaldehyde) p-(N,N-dimethyl amino benzaldehyde) acetpheneden thiosemicarbazone

Scheme 1: Synthesis of the (ABATSC) ligand

Synthesis of complexes

The chelate complexes have been obtained by adding (0.678 gm, 2mmol) of ligand dissolved in ethanol ($30cm^3$) to a hot solution of metal (II) chloride (1mmol) dissolved in the same solvent ($30cm^3$). The reaction mixture was refluxed for (30min), then concentrated until the solid compounds precipitated. They were filtered off, washed with ethanol ($10cm^3$) to remove there remaining unreacted substances, and dried over anhydrous, $CaCl_2$

Results and Discussion

The new Schiff base ligand (ABATSC) is yellow crystals, but the prepared complexes of this ligand vary in colour depending of metal ion. The complexes are quiet air-stable, insoluble in water, but its soluble in common organic solvents.

Some phesical and chemical properties for Schiff base ligand and its chelate complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) metal ions are listed in table(1). In all cases (1:2) (metal:ligand) solid complexes are isolated, that is agreement with the stoichiometric ratio found using molar ratio method. The complexes are non electrolytes.

Attempts to propose the structure of the isolated complexes come for full investigation using the following studies.

Metal : ligand ratio

The metal : ligand ratios of chelates were determined by the method of molar ratio method at the wavelengths of maximum absorption. The compound (ABATSC) was found to form 1:2 chelates with metal ions under studies, these results are in agreement with the values reported for some Schiff base complexes[13,14].

Infrared spectra

The important infrared bands of free ligand and complexes are summarized in table(2). The weak band in the spectrum of free ligand observed at 3307 cm^{-1} due to $\upsilon(NH_2)$ remained unaffected after complexation[15,16]. The ligand band at 1600 cm^{-1} due to υ(C=N) of imine nitrogen shifted to lower wave numbers on complexation suggests involvement of unsaturated nitrogen atoms of azomethine group in bonding with the metal ion. Other band observed disappearance in some the complexes[17]. The υ(C=S) stretching vibration appears at 1155 cm^{-1} in the spectrum of free ligand, this band appearing at 1166-1145 cm^{-1} with some decrease in intensity, of the complexes spectra. Both shift and reduced in intensity may indicate the formation of the complex[18].

The spectra of chelate complexes showed new weak bands in the region 415-480 cm^{-1}, these bands did not present in the spectrum of ligand may be attributed to vibration υ(M-N) and (M-S) provide evidences concerning the bonding of nitrogen and sulfur to the metal ions [19-21]. Representative example for their spectra is given in Fig.1

Magnetic and electronic spectral studies

The magnetic moments and electronic spectral bands of the complexes are summarized in table (3).

The magnetic moment of the cobalt (II) has been found to be (4.45 B.M), which is the with the range of octahedral cobalt (II) complexes[22]. The electronic spectrum of this complex shows three absorption bands at 14836, 17889 and 22075 cm^{-1}, there are assigned to $^4T_1g(F)\rightarrow{}^4T_2g(F)$ (υ_1). $^4T_1g(F)\rightarrow{}^4A_2g(F)$ (υ_2) and $^4T_1g(F)\rightarrow{}^4T_1g(P)$ (υ_3) transitions, respectively, which are characteristic of octahedral stereo chemistry[23]. For the Nickel (II) complex, its magnetic moment (3,15 B.M), and d-d spectrum of this complex show bands at 14577 and 21367 cm^{-1}, which are suggesting the existence of $^3A_2g\rightarrow{}^3T_1g(\upsilon_2)$ and

$^3A_2g \rightarrow {}^3T_1g(P)(\upsilon_3)$ transitions with an octahedral spatial configuration[23]. The magnetic moment value of the copper(II) complex (1.81 B.M) which may suggest an octahedral structure. Its electronic spectrum shows band centered at 15961 cm^{-1} which may assigned to $^2Eg \rightarrow {}^2T_2g$ transition in octahedral environment[22].

Zinc(II), Cadmium(II) and mercury(II) complexes are diamagnetic moments for d^{10} ions and the electronic spectra of there complexes do not show any d-d band[24].

Conductivity measurement

All chelate complexes prepared in this work showed conductivity values ranged between (7.62-6.42) $S.mol^{-1}.cm^2$, in DMSO at room temperature these values indicating that no conductive species exist[25]. According to these results the structural formulas of these complexes may be proposed in Fig. 2.

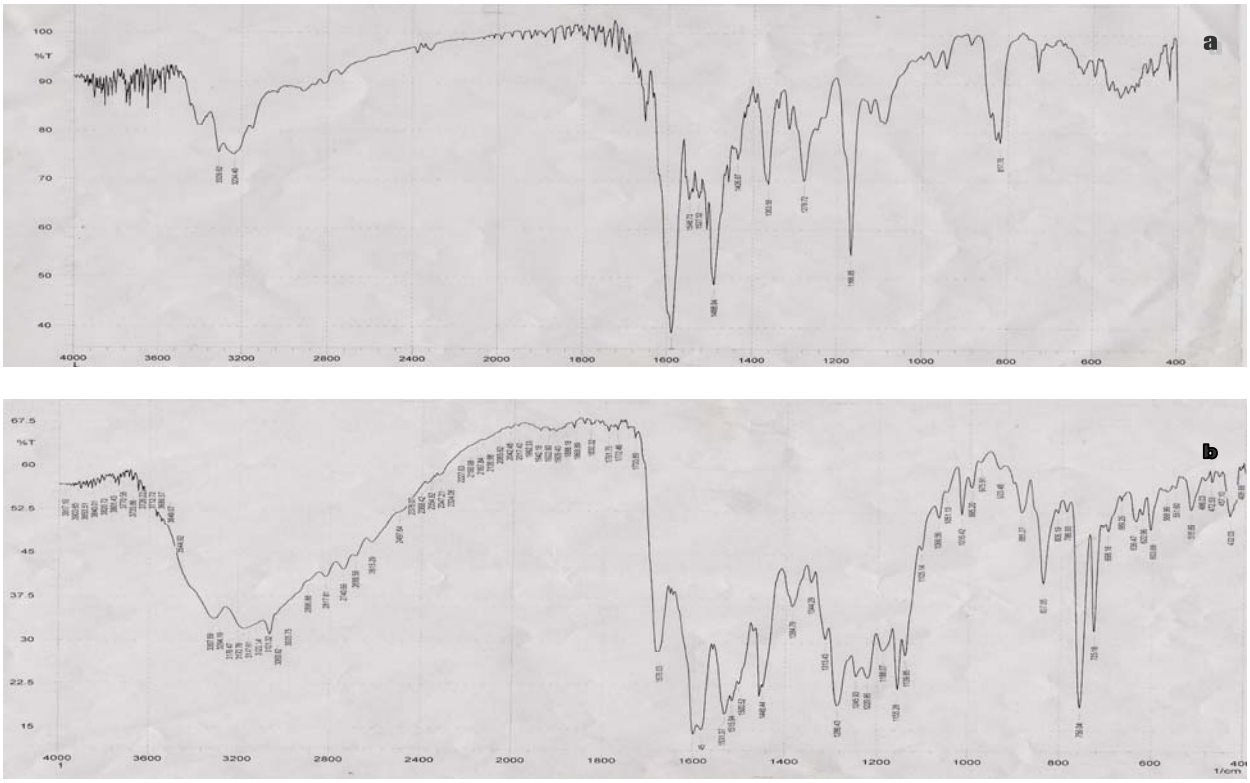


Fig.(1): IR spectra of; (a) $[CuL_2Cl_2]$ & (b) the ligand (ABATS

Table 1: Physical data and analysis of the ligand and its complexes.

No.	compound	Colour	M.P ºC	Yield %	Formula	Found,(calc.)%			
						C	H	N	M
1	L	Yellow	163	91	$[C_{18}H_{21}N_5S]$	63.55 (63.71)	6.25 (6.19)	20.05 (20.64)	----
2	$[CoL_2Cl_2]$	red	182	54.52	$[C_{36}H_{42}N_{10}S_2CoCl_2]$	53.80 (53.46)	5.23 (5.19)	17.63 (17.32)	7.55 (7.29)
3	$[NiL_2Cl_2]$	red	197	47.89	$[C_{36}H_{42}N_{10}S_2NiCl_2]$	53.20 (53.48)	5.45 (5.19)	17.65 (17.33)	7.43 (7.26)
4	$[CuL_2Cl_2]$	green	201	45.56	$[C_{36}H_{42}N_{10}S_2CuCl_2]$	53.52 (53.16)	5.04 (5.16)	17.44 (17.22)	8.12 (7.82)
5	$[ZnL_2Cl_2]$	Yellow	210 d	55.56	$[C_{36}H_{42}N_{10}S_2ZnCl_2]$	52.89 (53.04)	5.65 (5.15)	16.75 (17.19)	7.87 (8.02)
6	$[CdL_2Cl_2]$	Yellow	188	59.69	$[C_{36}H_{42}N_{10}S_2CdCl_2]$	52.34 (52.94)	5.07 (4.87)	16.43 (16.26)	13.47 (13.00)
7	$[HgL_2Cl_2]$	Yellow	203 d	68.89	$[C_{36}H_{42}N_{10}S_2HgCl_2]$	45.88 (45.52)	4.76 (4.42)	15.13 (14.75)	20.85 (21.07)

Ligand = (ABATSC), d= complex metal with decomposition

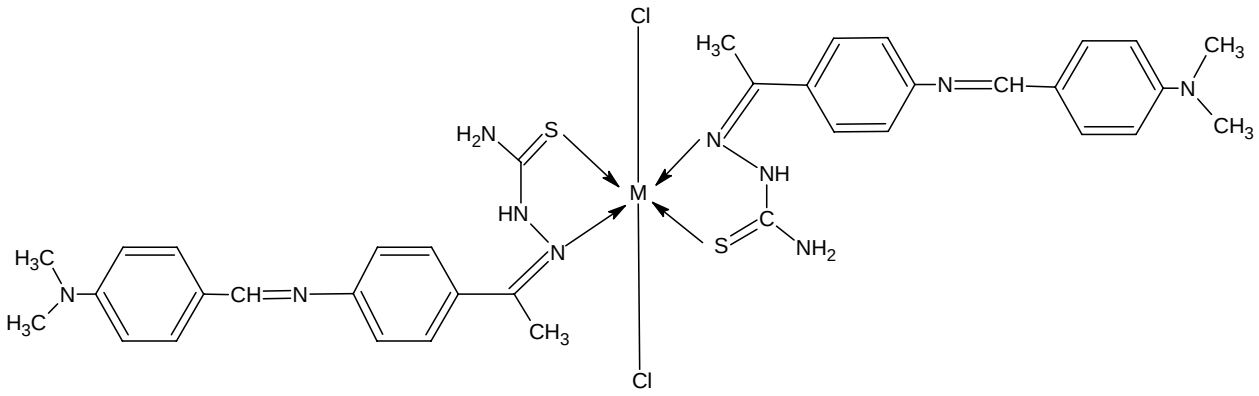
Table.2 : IR spectra frequencies for the ligand and its metal complexes in cm^{-1} units

Compound	υ(NH_2)	υ(N-H)	υ(C=N)	υ(C=S)	υ(NH-C=S)	Y(M-N)	υ(M-S=C)
L=(ABATSC)	3307 w	3101 w	1600 s	1155 s	837 w	----	-----
$[CoL_2Cl_2]$	3305 w	3120 w	1587 m	1148 m	837 w	425 w	480 w
$[NiL_2Cl_2]$	3300 m	3230wbr	1580 m	1160 w	830 w	420 w	480 w
$[CuL_2Cl_2]$	3309 w	3234 w	1585 s	1166 s	830 w	420w	465w
$[ZnL_2Cl_2]$	3309 w	3170 w	1573 m	1150 w	837 w	415 w	475 w
$[CdL_2Cl_2]$	3309 w	3120 w	1577 s	1163 w	830 w	445 w	470 w
$[HgL_2Cl_2]$	3307 w	3170wbr	1583 m	1145 m	837 w	430 w	465 w

L= ligand, s = strong, w = weak, m = medium, br = broad.

Table.3: Electronic spectra and Magnetic moment of complexes.

Complexes	Absorption bonds(cm^{-1})	Transition	μeff(B.M)
$[CoL_2Cl_2]$	14655 16397 23787	$^4T_1g(F)\rightarrow{}^4T_2g(F)$ $^4T_1g(F)\rightarrow{}^4A_2g(F)$ $^4T_1g(F)\rightarrow{}^4T_2g(P)$	4.54
$[NiL_2Cl_2]$	14578 22492	$^3A_2g\rightarrow{}^3T_1g(F)$ $^3A_2g\rightarrow{}^3T_1g(P)$	3.15
$[CuL_2Cl_2]$	15615	$^2Eg\rightarrow{}^2T_2g$	1.81
$[ZnL_2Cl_2]$	----	----	Dia
$[CdL_2Cl_2]$	----	----	Dia
$[HgL_2Cl_2]$	----	----	Dia



M= Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II)

Fig.2: The proposed structural formula of the metal chelate complexes.

Conclusion

Anew Schiff base ligand *p*-(N,N-dimethyl amino benzaldehyde acetopheneden thiosemicarbazone) (ABATSC) and its chelate complexes have been synthesized. All the complexes are stable and nonionic**.** The geometry is proposed for all complexes show octahedral stereochemistry.

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