Synthesis and Characterization of some New Binuclear Complexes of Schiff base ligand derived from Isatin and p-phenylenediamine

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Abstract

New series of complexes of general formula $[MLCdCl_4(H_2O)_2]$; where M= Mn, Fe , Co and Ni and L= BIPDA(bisisatin-*p*-phenylenediamine). These complexes were identified by several physiochemical methods including melting points, molar conductance and elemental analyses (CHN), magnetic moments as well spectral such as electronic and infrared spectral measurements. These studies revealed that the Ligand (BIPDA) was behaved as a tetradentate, neutral bridged and bonded to the M(II) ions through the nitrogen and oxygen atoms from one isatin and another nitrogen with two oxygen atoms of the other isatin molecule. As well, the presence of two chloride ions and two aqua molecules around M(II) give the most probable octahedral geometry around it, and the existence of two chloride ions around Cd(II) give the tetrahedral geometry around it . The elemental analysis(CHN) and the infrared spectra agreed well with the proposed structures. Their molar conductance measurements revealed the non-electrolytic behavior of the synthesized complexes.

Keywords: Isatin, p-phenylenediamine, Schiff base, Complexes

Introduction

A considerable interest was paid for the preparation of binuclear complexes using bridging ligands with transition metal ions, particularly, the ligands containing the bridging oxygen atom such as the hydroxo, alkoxo and phenoxo groups and the ligands possessing the nitrogen donor atoms. They had been vastly used to synthesis the poly-nuclear, especially the copper(II) complexes (Venegas-Yazigi *et al*.,2010; Anbu and Kandaswamy , 2011; Vafazadeh *et al* 2011; Saha *et al*., 2014 and Das *et al*., 2016). A relevant amount of work of symmetrical and asymmetrical complexes with bridging hydroxo, alkoxo and phenoxo forming di-copper(II) centers were also synthesized and their structures were estimated (Venegas -Yazigi *et al*., 2010; Vafazadeh *et al*.,2011; Crawford *et al*.,1976 ; Merz and Haase,(1980); Doman *et al*.,1990; Dutta *et al*., 2011; Kahn ,1993).

The Schiff bases prepared from the reaction of salicylaldehyde or β- diketone reagent with amino substrates in equimolar ratio under suitable conditions, upon bi-deprotonation forming the dinegative, tridentate ONO-donor ligands, were reacted with cupric salts to produce the multinuclear complexes on existing the co-ligands (Bhowmik *et al*.,2013 ; Zhang *et al*.,2013. Moreover, the ligand 4,4′- bipyridine was also used to synthesis many homo-binuclear copper(II) complexes (Zhang *et al*.,2013; Biswas *et al*., 2007).

The development in the bioinorganic chemistry increases the attention toward the complexes containing Schiff base ligands and many of these complexes serve as models for biologically important species (Chohan and Sherazi ,1999 ; Dharmaraj *et al*., 2000 ; Jayabalakrishnan and Natarajan , 2001; Al-Shaalan, 2011 and Lianming *et al*., 2011 and Lekha L. and Kanmaniraja K.,2017).

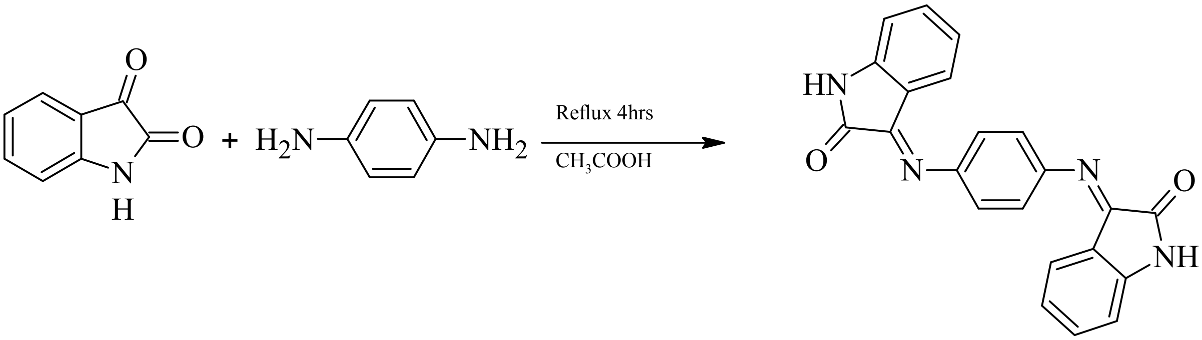
A plausible control to synthesize the multinuclear complexes for transition metal ions is important to design them with the favorable merits. Some of these applications require the presence of multi-metal centers in the certain complexes which have different activities comparing with the mononuclear complexes of same compositions. Some of the homo- binuclear complexes containing Schiff base ligands with other co-ligands were evaluated for their antibacterial activity and found to be more energetic and inhibit the bacterial growth (Vaiana *et al.*,2011 and Usharani *et al.*, 2013).

We attempt, in the present work, to widen the scope of multinuclear complexes by synthesizing new series of hetero binuclear types using Schiff base prepared from the condensation of *p*-phenylenediamine with isatin then their reaction with different metal ions to form the desired binuclear complexes.

Experimental

Synthesis of the ligand

The ligand was synthesized according to the reported procedure (Hassani and Mohammed , 2011) by refluxing the mixture of a hot ethanolic solution of isatin (0.29g, 2mmole) and hot ethanolic solution of *p*-phenylenediamine (0.11g, 1mmole) for 4hrs with few drops of glacial acetic acid. The product obtained after the evaporation of the solvent was filtered and recrystallized from ethanol. Schematically, the synthesis of ligand(BIPDA) is present in Scheme (I).



Scheme(1) The reaction involves the synthesis of the ligand (BIPDA)

Synthesis of the Complexes

The ethanolic solution (20ml) of each one of the following metal chloride (1mmole), $MnCl_2.4H_2O$, $FeCl_2.4H_2O$, $CoCl_2.6H_2O$ and $NiCl_2.6H_2O$, was added to the ethanolic solution (20ml) of (0.36g, 1mmole) of the ligand with stirring. The mixture was refluxed for 2 hrs. Another ethanolic solution (20ml) of cadmium chloride (1mmole) was added and refluxed for an extra 2 hrs. The product was filtrated off, washed with hot ethanol several times and then dried. Some of the chemical and physical data for the synthesized ligand and its complexes are shown in Table I.

Table I
The elemental analyses and physical properties of the synthesized complexes

Compound	Color	M.p. °C	Elemental Analysis: Calc. (Found)%		
			C	H	N
L=BIPDA	Yellow turmeric	225	72.13(72.09)	3.82(3.88)	15.30(15.12)
$[MnLCdCl_4(H_2O)_2]$	Red brown	244d	37.13 (37.11)	2.55(2.54)	7.87(7.84)
$[FeLCdCl_4(H_2O)_2]$	brown	223d	37.09(37.06)	2.55(2.52)	7.87(7.81)
$[CoLCdCl_4(H_2O)_2]$	Deep brown	263d	36.93(36.63)	2.58(2.55)	7.83(7.80)
$[NiLCdCl_4(H_2O)_2]$	Reddish brown	243d	36.94(36.51)	2.54(2.51)	7.83(7.82)

Result and Discussion

The synthesized complexes were prepared according to the following equation:-

$$MCl_2.nH_2O + BIPDA \xrightarrow{CdCl_2} [M(BIPDA)CdCl_4(H_2O)_2]$$

Elemental Analysis

The elemental analyses and the physical properties of the synthesized ligand and its complexes are showed in Table (I). Both, the ligand and its complexes are stable while solid .They are soluble in dimethylformamide (DMF) and dimethylsulfoxide (DMSO) at room temperature. The molar conductivity values in DMF at10^{-3}M were lying in the range (30-47) Ω^{-1}. $mol^{-1}.cm^{-1}$ indicating the non- electrolytic behavior of all complexes (Geary,1974) as shown in Table II.

The Infra-Red Spectra

The coordination sites of the ligands with the M(II) ion had been determined by cautious comparison of the infrared spectra of the synthesized complexes with that of the original ligand as shown in Table(II). The free ligand showed important spectra in the regions 3415,1739 and 1614 cm^{-1} assigned to the stretching of (N-H), (C=O) and (C=N) respectively. The spectra for the (N-H) of isatin group was found unchanged or slightly changed ($\Delta\upsilon$=1-5) comparing with that of the complexes and hence no indication of the coordination of the N-H with the metal ion (Singh *et al*., 2011). The C=O and the azomethine (C=N) spectra of the isatin group in the ligand were showed a significant changes to a lower values ($\Delta\upsilon$=33-49) and ($\Delta\upsilon$=17) respectively in comparison with that of the complexes as shown in Table(II) suggesting the participation of both, the nitrogen and the oxygen, atoms in the coordination with the metal ion(II) ions(Ignat , 2012 and Manan *et al*.,2012).
The presence of the coordinated water molecules in the prepared complexes was indicated by the existence of broad bands in the range 3356-3365 cm^{-1}.Two somewhat weaker bands assigned as the OH rocking(r) and wagging(ω) vibrations at 757-763 and 628- 665 cm^{-1} respectively were found in the spectra of the complexes(Ignat , 2012 and Osman *et al*.,2014). The M-Cl bond usually appears in

the region 200-300 cm^{-1} and this region is beyond the limit of the apparatus. In the low-frequency region, the spectra of the synthesized complexes Table(II) exhibited new bands which were not present in the corresponding ligand, were located at 500-628 and 420-460 cm^{-1} attributed to υ(M-O) and ν(M-N) stretching respectively (Ignat , 2012 and Osman *et al.*,2014).

Table II
Selected I.R. absorption bands of the ligand and its complexes

Compounds	υN-H	υC=O	υC=N	υM−O	υM−N	Coordinated water		
						ν(OH)	r(OH	ω(OH)
L(BIPDA)	3415	1739	1614	----	----	-----	-----	-----
$[MnLCdCl_4(H_2O)_2]$	3400	1705	1597	590	420	3355	761	628
$[FeLCdCl_4(H_2O)_2]$	3409	1706	1597	628	440	3355	761	628
$[CoLCdCl_4(H_2O)_2]$	3402	1690	1597	586	445	3365	757	665
$[NiLCdCl_4(H_2O)_2]$	3412	1704	1597	500	460	3357	763	630

The electronic spectra

The electronic spectra for the original ligand showed absorption bands at 33333 and 22026 cm^{-1} which can be assigned to the π-π* transition of the aromatic ring and n-π* transition in the C=O and C=N chromophores groups respectively(Manan *et al.*, 2012). In the prepared complexes, the second band was found to be shifted to a longer wavelength with higher intensity. This shift may be interpreted as due to the donation of electron density from the lone pair of electrons of the nitrogen of Schiff base to metal ions (Nagajothi *et al.*,2013).

The electronic spectra of Mn(II) complex had the ligand bands in addition to many weak absorptions characteristic for d^5 electronic configuration in the octahedral high spin complex(μeff. 5.77 BM.) d-d transitions due to spin and Laporte forbidden. The very weak bands arise from the promotion of an electron to give various excited states containing only three unpaired electrons displayed a very low intensities and are hidden by the intraligand transitions. The absorption band at 21459,35335 cm^{-1} can be assigned to the $^6A_1g\rightarrow{}^4T_2g(G)$ and the charge transfer of ligand to metal respectively (Osman *et al.*, 2014).

A broad band was observed at 10940 cm^{-1} in the spectrum of the Fe(II) complex and attributed to $^5T_2g\rightarrow{}^5Eg$ transition which is in a good agreement with the octahedral arrangement around the Fe(II) ion (Fayad *et al.*,2013 and Olanrewaju *et al.*,2016).

Two spins allowed transitions were found in the spectrum of the Co(II) complex designated as ν_1 and ν_3 absorption bands at 9210 cm^{-1} and 21882 cm^{-1} respectively as due to the $^4T_1g(F)\rightarrow{}^4T_2g(F)$ and $^4T_1g(F)\rightarrow{}^4T_1g(P)$ transitions respectively. This is a clear indication that the complex has six coordination octahedral geometry(Osman *et al.*, 2014 and Das *et al.*,2016).

The Ni(II) complex exhibits three absorption bands, 9728, 13054 and 21456 cm^{-1} and attributed to the (ν_1) $^3A_2g(F)\rightarrow{}^3T_2g(F)$, ($\nu_2$) $^3A_2g(F)\rightarrow{}^3T_1g(F)$ and (ν_3) $^3A_2g(F)\rightarrow{}^3T_1g(P)$ transitions respectively in accordance with the octahedral arrangement (Vaiana *et al.*, 2010 and Osman *et al.*, 2014).

Finally, Cd(II) did not showed any d-d electronic transition in the visible region but showed absorption bands at 40160 ,40000 , 40650 and 42016 cm^{-1} in the complexes containing the Mn(II), Fe(II), Co(II) and Ni(II) ions respectively, which are attributed to the charge transfer (MLCT) (Ignat , 2012 and Fayad *et al.*,2013). All these bands were tabulated in Table III.

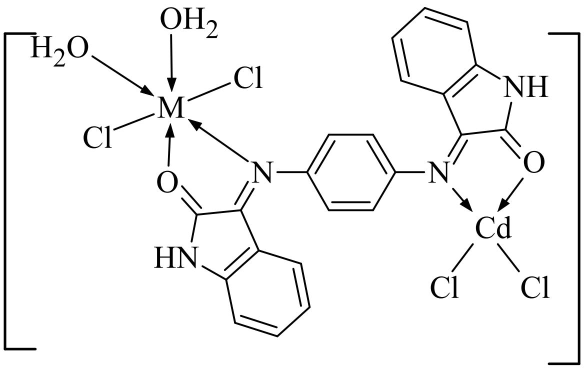
Table III
Spectra, Molar Conductance in (DMF) and Magnetic Moments (B.M.) for the ligand (L) and the Complexes with their Geometries

Compounds	Bands cm^{-1}	Assignment	Λ(DMF)	μ_{eff} B.M	Geometry	
					M	Cd
L=BIPDA	23474 33898	$n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	-	-	-	-
$[MnLCdCl_4(H_2O)_2]$	21459 35335 40160	$^{6}A_{1}g\rightarrow{}^{4}T_{1}g(G)$ C.T.(Mn) C.T.(Cd)	36	5.77	Oct.	Td
$[FeLCdCl_4(H_2O)_2]$	10940 35087 40000	$^{5}T_{2}g\rightarrow{}^{5}Eg$ C.T.(Fe) C.T.(Cd)	30	4.80	Oct.	Td
$[CoLCdCl_4(H_2O)]$	9210 ------ 21882 35587 40650	$^{4}T_{1}g\rightarrow{}^{4}T_{2}g(F)$ $^{4}T_{1}g\rightarrow{}^{4}A_{2}g(F)$ $^{4}T_{1}g\rightarrow{}^{4}T_{1}g(P)$ C.T.(Co) C.T.(Cd)	45	4.09	Oct.	Td
$[NiLCdCl_4(H_2O)_2]$	9728 13054 21456 37593 42016	$^{3}A_{2}g(F)\rightarrow{}^{3}T_{2}g(F)$ $^{3}A_{1}g(F)\rightarrow{}^{3}T_{1}g(F)$ $^{3}A_{1}g(F)\rightarrow{}^{3}T_{1}g(P)$ C.T.(Ni) C.T.(Cd)	47	3.32	Oct.	Td

The magnetic susceptibilities

The magnetic susceptibilities for the synthesized complexes are lying in the range (3.32-5.77 B.M.) and indicative for their consistency of the octahedral arrangement around Mn(II), Fe(II), Co(II) and Ni(II) ions and the tetrahedral geometry for the diamagnetic Cd(II) ion in each complexes (Ignat , 2012 ; Olanrewaju *et al.*,2016).

In conclusion, the synthesized ligand behaved as a neutral tetradentate, coordinated to the metal ions(M) through the nitrogen and the oxygen atoms and to the Cd(II) ion through the other oxygen and nitrogen atoms .The presence of two chloride ions and two coordinated water molecules besides two sites from the tetradentate ligand gave the most probable octahedral geometry around M(II) ion and the other two sites from the ligand with two chloride ions around Cd(II) to give the probable tetrahedral structure in each complex as depicted below in Figure(1).



M= Mn, Fe, Co, Ni

Figure (1) The Structure of the Prepared Complexes

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