

## Synthesis and Characterization of Co(II), Ni(II) and Cu(II) complexes with amido oxime ligands

S.S. Ezzat

Dept. Chemistry, College of Science, University of Mosul, Mosul, Iraq

(Received: 12 / 5 / 2009 ---- Accepted: 5 / 1 / 2010)

### Abstract

A series of new amidoxime complexes were prepared through direct reactions of the ligands  $\beta$ (p-tolyl mercapto) propionamidoxime ( $L^1$ ) and  $\beta$ (p-toluene sulfonyl)propionamidoxime ( $L^2$ ) with  $(CoCl_2 \cdot 6H_2O, NiCl_2 \cdot 6H_2O$  and  $CuCl_2 \cdot 2H_2O$  in (1:1) or (1:2) metal: ligand molar ratio.

The prepared complexes were characterized by atomic absorption, IR and electronic spectra conductivity measurements and magnetic measurements. Electronic spectra and magnetic moment measurements indicated that these complexes have tetrahedral or octahedral environment.

### Introduction

The chemistry of metal complexes containing both nitrogen and sulfur donors has grown rapidly, largely due to the discovery of metals in mixed nitrogen / sulfur environments as the active sites of many important enzyme. It is therefore important to understand the redox chemistry of metal ions in mixed nitrogen/sulfur coordination environments<sup>(1-3)</sup>.

The first vic-oxime quasi-macrocyclic complexes were prepared by Uhlig and Friedrich<sup>(4)</sup>. Since that time, several  $N_4$  and  $N_2S_2$  quasi-macrocyclic and  $BF_2$ -macrocyclized oximes have been synthesized<sup>(5-7)</sup>.

Lockwood<sup>(8)</sup> prepared some complexes of copper oxime which used to oxidized anthracene, while metal-containing oxime complexes are utilized in medicine as well; technetium(V) and copper (II) containing vic-oximes currently are used as cerebral and myocardial perfusion imaging agent<sup>(9-12)</sup>. Purshan et al.<sup>(13)</sup>, report the synthesis, structure and electronic properties of Ni(II) and Cu(II) oxime complexes with  $N_2S_2$  and  $N_2S_2O$  donor arrays.

A series of four coordinate square planar nickel (II) complexes of o-phenylenebis - ( $N$ -methyloxamidate) ( $L^1$ ) and related o-phenylene ( $N$ -methyloxamidate) ( $L^2$ ) and o-phenylenebis-(oxamidate) ( $L^3$ ) tetradentate ligands have been synthesized and characterized structurally, spectroscopically and electrochemically<sup>(14)</sup>. Mono and homo-dinuclear cobalt (II), nickel (II), and copper(II) complexes of the type  $[M(3fsa)_2-HyAm](H_2O)_n$  and  $[M_2(3fsa)_2-HyAm](H_2O)_n$  respectively, where  $((3fsa)_2-HyAm)$  is a Schiff base derived from 3-formylsalicylic acid and hydroxylamine hydrochloride,  $n=0,1,2$  have been isolated and characterized<sup>(15)</sup>.

According to these interesting results, we report here the preparation of the ligands ( $L^1$ ), ( $L^2$ ) and their complexes with Co(II), Ni(II) and Cu(II) in (1:1) or (1:2) metal:ligand molar ratio.

### Experimental

IR spectra were recorded on a Shimadzu FTIR spectrophotometer in the  $(4000-250) \text{ cm}^{-1}$  range using CsI pellets. The metal content was estimated spectrophotometrically using Shimadzu AA670 spectrophotometer. Electronic spectra were obtained with a Shimadzu UV/Vis. recording UV-160 spectrophotometer at room temperature. The measurements were obtained using a concentration of

$10^{-3} \text{ M}$  of the complexes in dimethylsulfoxide (DMSO). The magnetic measurements were determined at  $25^\circ\text{C}$  by Faraday method using Bruker BM6 instruments. Conductivity measurements were made at concentration of  $10^{-3} \text{ M}$  of the complexes in (DMSO) solvent at ambient temperature using conductivity meter model 4070 Genway.

### Synthesis:

Preparation of the ligands  $\beta$  (p-tolylmercapto) propionamidoxime ( $L^1$ ) and  $\beta$  (p-toluene sulfonyl) propionamidoxime ( $L^2$ ) according to the literature method<sup>(16)</sup>. Their melting point are 95-96 for  $L^1$  and its yield 75% while the melting point  $L^2$  is 165-166  $^\circ\text{C}$ , yield 84%..

### Preparation of $[M(L^1)_2Cl_2]$ complexes $M = Co(II), Ni(II)$ or $Cu(II)$

To an ethanolic solution ( $20 \text{ cm}^3$ ) of the ligand ( $L^1$ ),  $\beta$  (p-tolylmercapto) propionamidoxime (0.21 g, 1mmol) an ethanolic solution of  $CoCl_2 \cdot 6H_2O$  (0.238g, 1mmol),  $NiCl_2 \cdot 6H_2O$  (0.2377g, 1mmol) or  $CuCl_2 \cdot 2H_2O$  (0.1705g, 1 mmol) was added with stirring at  $80^\circ\text{C}$ . A distinct change in colour was observed. The mixture was stirred under reflux for 2h. to ensure the completion of the reaction. The solid products were filtered out, washed with ethanol and diethyl ether and then dried under vacuum.

### Preparation of $[M(L^2)_2Cl_2]$ complexes:

These complexes were prepared according to the above method, by using  $L^2$ , p-toluene sulfonyl propionamidoxime (0.24g, 1mmol).

### Preparation of $[M(L^1)_2Cl_2]$ complexes:

To a stirred solution of ( $L^1$ ) (0.42 g, 1mmol) in ethanol ( $20 \text{ cm}^3$ )  $CoCl_2 \cdot 6H_2O$  (0.238g, 1mmol),  $NiCl_2 \cdot 6H_2O$  (0.2377g, 1mmol) or  $CuCl_2 \cdot 2H_2O$  (0.1705g, 1 mmol) in ethanol ( $10 \text{ cm}^3$ ) were added. Then each mixture of them was refluxed for 2h. with continuous stirring. The precipitate was obtained after reduction of the volume of the solution to about  $10 \text{ cm}^3$  the solid product was filtered off, washed with ethanol and diethylether, then dried under vacuum for several hours.

The  $[M(L^2)_2Cl_2]$  complexes were prepared by using the same method as described for  $[M(L^1)_2Cl_2]$  complexes.

## Results and Discussion

Complexes of both ligands are coloured and they are soluble in dimethylformamide (DMF) and dimethylsulfoxide (DMSO) to a considerable extent, the low molar conductance values in (DMSO) suggest that they are non-electrolytes<sup>(17)</sup>. Most of these complexes melt or decompose above 170 °C. The isolated complexes and their physico-chemical properties are listed in Table 1.

The most important IR assignment of the ligands as well as its bonding sites (Table 2) have been determined by careful comparison of the spectra of the ligands with those of their metal complexes.

The IR spectrum of the ligands (recorded by using CsI), showed bands at 1620-1625, 3400, 3250, 3300, 1310 and 892-930  $\text{cm}^{-1}$  which assigned to  $\nu(\text{C}=\text{N})$ ,  $\nu(\text{OH})$ ,  $\nu(\text{NH}_2)$ ,  $\nu(\text{S}=\text{O})$  and  $\nu(\text{C}-\text{S})$  respectively.

In the complexes of ligands ( $\text{L}^1$ ) the bands due to  $\nu(\text{C}=\text{N})$  show down word shift and it was observed at 1600-1592  $\text{cm}^{-1}$  suggesting the participation of azomethine group in complexation further the band at 1420  $\text{cm}^{-1}$  due to  $\nu(\text{N}-\text{O})$  shows an upward shift and appears as a strong bands at 1440  $\text{cm}^{-1(18)}$ . As well as the band due  $\nu(\text{C}-\text{S})$  was found at lower frequencies in all complexes containing ligand ( $\text{L}^1$ ). The infrared spectra of metal complexes showed new band at 430-470 and 360-380  $\text{cm}^{-1}$  assigned to  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{S})$  respectively<sup>(19)</sup>. They also showed a bands in the region 280-300  $\text{cm}^{-1}$  which may be associated to  $\nu(\text{M}-\text{Cl})$  vibration<sup>(20)</sup>.

In the complexes of the formula  $[\text{M}(\text{L}^2)\text{Cl}_2]$  and  $[\text{M}(\text{L}^2)_2\text{Cl}_2]$  the bands  $\nu(\text{OH})$  and  $\nu(\text{NH}_2)$  were found at lower values indicates the coordination through nitrogen atom of the amide group and the oxygen of the oxime group<sup>(21)</sup>. The  $\nu(\text{S}=\text{O})$  and  $\nu(\text{C}=\text{N})$  were found at same stretching frequencies which means it does not participate in coordination with metal ions. Furthermore the IR spectra showed another bands at (500-510) (450-470) $\text{cm}^{-1}$  which may be due to  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{N})$  respectively.

The U.V-Visible spectra of the ligands and there complexes were recorded at  $10^{-3}\text{M}$  solution in DMSO the results obtained are presented in Table 2. The broads band observed in the range 30789-32573  $\text{cm}^{-1}$  are due to  $\pi-\pi^*$  or in  $\pi^*$  within the ligands.

The values of magnetic moment of Co(II) complexes (1,2) are 3.92 and 3.97 B.M. The electronic spectrum of Co(II) complexes show a bands at 16863 and 14684  $\text{cm}^{-1}$  due to  $^4\text{A}_2 \rightarrow ^4\text{T}_1\text{p}$  ( $\nu_3$ ) transition as result of spin orbit coupling, similar to those reported for  $[\text{CoCl}_4]^{-2}$  and  $[\text{CoI}_4]^{-2}$  suggesting a tetrahedral geometry for Co(II) complexes<sup>(22)</sup>. In tetrahedral

geometry  $\nu_1$  and  $\nu_2$  was observed due to the instrument used.

The Ni(II) complexes (3 and 4) show a magnetic moments of 3.78 and 3.86 B.M, these values agree well with a high spin configuration and indicate the presence of tetrahedral geometry<sup>(20)</sup>. The electronic spectra of these complexes show a bands at 14949 and 15038  $\text{cm}^{-1}$  which correspond to the transition  $^3\text{T}_1(\text{F}) \rightarrow ^3\text{T}_1(\text{p})$  ( $\nu_3$ ) in tetrahedral environment. In tetrahedral geometry  $\nu_1$  and  $\nu_2$  was observed due to the instrument used.

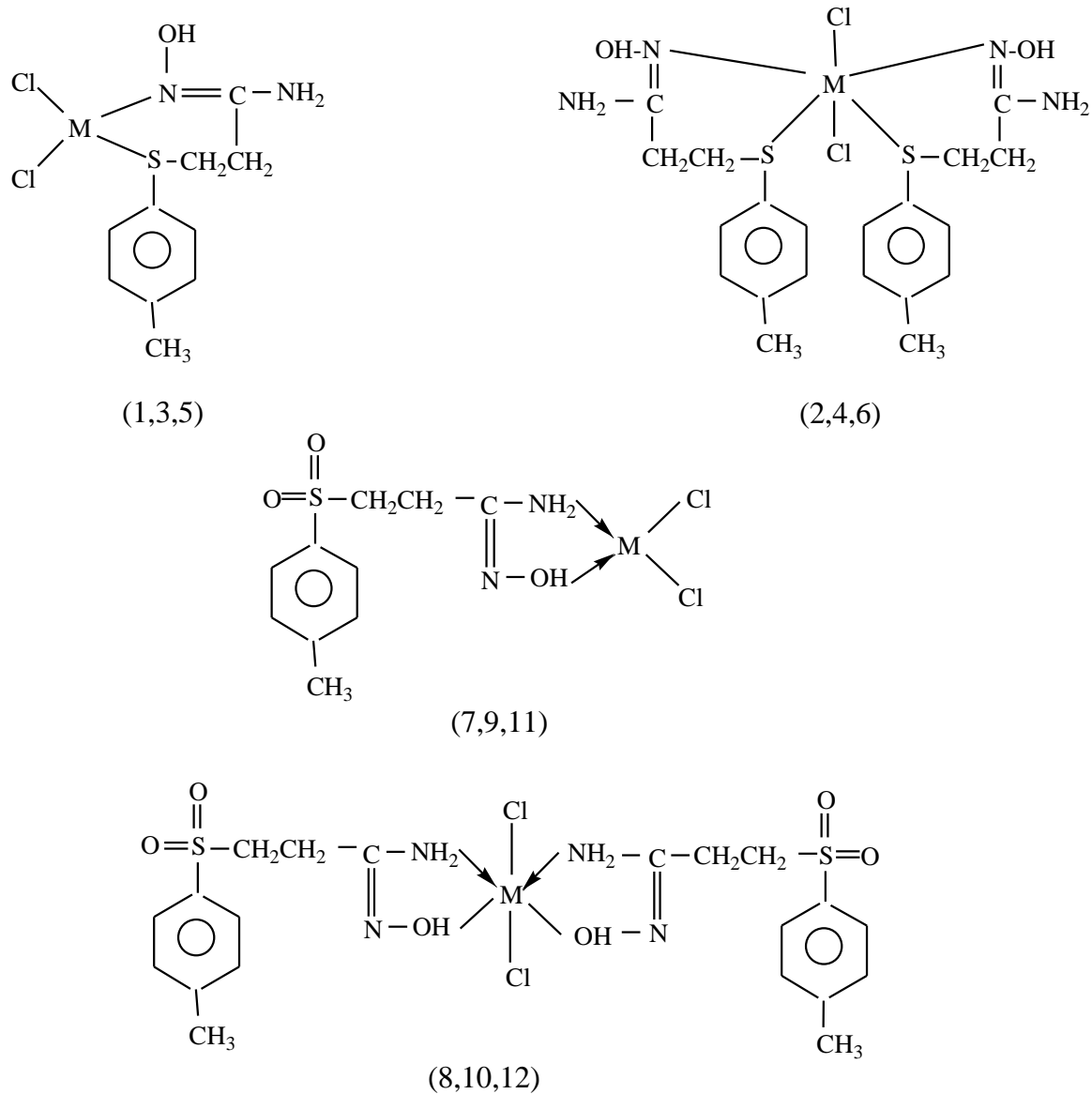
The Cu(II) complexes (5 and 6) show a magnetic moment of 2.17 and 1.93 B.M., the electronic spectra showed a band at 16129 and 14000  $\text{cm}^{-1}$ , which correspond to the transition  $^2\text{T}_2 \rightarrow ^2\text{E}$  and another band at 30000  $\text{cm}^{-1}$  correspond to charge transfer respectively. This show that the Cu(II) complexes have tetrahedral environment<sup>(23)</sup>.

The room temperature magnetic moment of cobalt (II) complexes (7 and 8) are 4.82 and 4.87 B.M<sup>(27)</sup>. The electronic spectrum shows bands at 10500-1100, 14947-16100 and 18656-19300  $\text{cm}^{-1}$ . Thus the spectra resemble those of complexes possessing octahedral geometry and may exhibit  $\text{D}_{4h}$  symmetry<sup>(24)</sup>. Assuming effective symmetry of various bands can be assigned to  $^4\text{T}_1\text{g}(\text{F}) \rightarrow ^4\text{T}_4\text{g}(\text{F})$  ( $\nu_1$ ),  $^4\text{T}_1\text{g}(\text{F}) \rightarrow ^4\text{A}_2\text{g}(\text{F})$  ( $\nu_2$ ) and  $^4\text{T}_1\text{g}(\text{F}) \rightarrow ^4\text{T}_1\text{g}(\text{p})$  ( $\nu_3$ ) transitions respectively.

The magnetic moment of the nickel (II) complexes (9 and 10) at room temperature are 2.85 and 3.12 B.M. The electronic spectrum of the nickel (II) complexes show three spin-allowed transitions ( $\text{cm}^{-1}$ ) at 10000-11000, 14970-15300 and 28300-29000  $\text{cm}^{-1}$  which are assignable to  $^3\text{A}_2\text{g}(\text{F}) \rightarrow ^3\text{T}_2\text{g}(\text{F})$  ( $\nu_1$ ),  $^3\text{A}_2\text{g}(\text{F}) \rightarrow ^3\text{T}_1\text{g}(\text{F})$  ( $\nu_2$ ) and  $^3\text{A}_2\text{g}(\text{F}) \rightarrow ^3\text{T}_1\text{g}(\text{p})$  ( $\nu_3$ ) respectively. Examination of these bands indicate that the complexes have octahedral geometry and might posses  $\text{D}_{4h}$  symmetry<sup>(25)</sup>.

The magnetic moment of copper (II) complexes at room temperature are 2.15 and 1.62 B.M., corresponding to one unpaired electron. The electronic spectrum show a bands at 16000-17100  $\text{cm}^{-1}$  which were assigned to  $^2\text{B}_{1g} \rightarrow ^2\text{A}_{1g}$  and  $^2\text{B}_{1g} \rightarrow ^2\text{E}_g$  respectively. Examination of these bands indicates that the complexes have octahedral geometry<sup>(26)</sup>.

On the basis of the foregoing studies, the ligand used in this study, coordinate to the metal ions in bidentate fashion through S,N or O sits of the ligands forming mononuclear complexes (1-12) as shown in fig 1.



M = Co(II), Ni(II) and Cu(II)

Fig 1: The suggested structure for the prepared complexes

**Table 1: Physical properties of the complexes**

No.	Complex	m.p (°C)	Colour	Analysis % found (calc.) (M%) Found		$\Omega$ ohm <sup>1</sup> .cm <sup>2</sup> .mol <sup>-1</sup>	$\mu_{eff}$ (B.M)
				Found.	Calcd.		
1	[Co(L <sup>1</sup> )Cl <sub>2</sub> ]	280-281	Brown	17.8	17.35	12	3.92
2	[Co (L <sup>1</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	182-185	Pale Brown	10.61	10.72	18	3.97
3	[Ni(L <sup>1</sup> )Cl <sub>2</sub> ]	205-207	Pale Yellow	17.06	17.26	45.4	3.78
4	[Ni (L <sup>1</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	175-177	Pale Brown	10.81	10.67	2.2	3.86
5	[Cu(L <sup>1</sup> )Cl <sub>2</sub> ]	265	Yellow	18.3	18.67	4.4	2.17
6	[Cu (L <sup>1</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	174-177	Pale Yellow	11.08	11.54	15.3	1.93
7	[Co(L <sup>2</sup> )Cl <sub>2</sub> ]	241-245	Pale Yellow	15.28	15.86	6.9	4.82
8	[Co (L <sup>2</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	250-252	Yellow	9.27	9.61	7.7	4.87
9	[Ni(L <sup>2</sup> )Cl <sub>2</sub> ]	219-221	Brownish	15.32	15.79	6.2	2.85
10	[Ni (L <sup>2</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	220-223	Brownish	9.78	9.56	9.8	3.12
11	[Cu(L <sup>2</sup> )Cl <sub>2</sub> ]	234-235	Yellow	16.97	17.08	2.3	2.15
12	[Cu (L <sup>2</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	240-242	Pale Brown	10.11	10.34	6.2	1.62

**Table 2: Selected IR bands electronic spectra data for the ligands and their complexes**

No.	IR band (cm <sup>-1</sup> )										$\lambda_{max}$ U.V. Vis. (cm <sup>-1</sup> )
	$\nu$ (C=N)	$\nu$ (OH)	$\nu$ (NH <sub>2</sub> )	$\nu$ (N – O)	$\nu$ (C – S)	$\nu$ (S=O)	$\nu$ (M – Cl)	$\nu$ (M – S)	$\nu$ (M – N)	$\nu$ (M – O)	
L <sup>1</sup>	1620(s)	3400	3250	1420	982	---	---	---	---	---	30789
1	1592	3400	3250	1440	860	---	293	360	430	---	16863
2	1598	3400	3250	1440	865	---	283	375	470	---	14684
3	1600	3400	3250	1430	862	---	298	360	460	---	14949
4	1595	3400	3250	1435	870	---	281	380	460	---	15038
5	1592	3400	3250	1450	865	---	293	380	450	---	16129
6	1590	3400	3250	1430	873	---	295	365	430	---	14000,30000
L <sup>2</sup>	1625(s)	3400	3300	1420	930	---	---	---	450	---	32573
7	1594	3280	3180	1430	930	1310	287	---	450	510	10500,14947, 18656
8	1595	3265	3190	1440	925	1310	282	---	460	500	11000,16100, 19300
9	1598	3270	3165	1430	930	1310	289	---	470	505	10000,14970, 28300
10	1602	3210	3195	1435	935	1310	294	---	455	505	11000,15300, 29000
11	1592	3255	3170	1435	923	1310	294	---	450	515	16000
12	1597	3260	3190	1440	930	1310	285	---	465	500	17000

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## تحضير ودراسة معقدات الكوبلت (II) والنيكل (II) والنحاس (II) مع لكاندات الاميدو او كزيم

سمير سعد الله عزت

قسم الكيمياء ، كلية العلوم ، جامعة الموصل ، الموصل ، العراق

( تاريخ الاستلام: ١٢ / ٥ / ٢٠٠٩ ---- تاريخ القبول: ٥ / ١ / ٢٠١٠ )

## الملخص

تم تحضير مجموعة جديدة من معقدات الاميدو او كزيم من خلال تفاعل الليكاندات  $\beta$ -(بارا-توليل ميركيتو) بروبوناميدو او كزيم ( $L^1$ ) و  $\beta$ -(بارا-توليل سلفونيل) بروبوناميدو او كزيم ( $L^2$ ) مع الاملاح الفلزية  $NiCl_2 \cdot 6H_2O$  و  $CuCl_2 \cdot 2H_2O$  بنسبة (١:١) او (١:٢) فلز : ليكاند. تم تشخيص المعقدات المحضرة بواسطة اطياف الامتصاص الذري ، اطياف الأشعة تحت الحمراء وفوق البنفسجية كذلك باستخدام التوصيلية الكهربائية والقياسات المغناطيسية. بينت القياسات المغناطيسية واطياف الانتقال الالكتروني بان المعقدات تمتلك بنية رباعية او ثمانية السطوح.