Synthesis and Characterization of Binuclear Complexes of Some Transition Metal in Addition to Zinc with bis (2-pyridoyl –6– carboxylic acid) thiourea ligand.

L.J. Najem
Department of Chemistry. College of Science , University of Mosul, Mosul , Iraq

(Received / / 2007, Accepted / / 2008)

Abstract

A new complexes of Fe(II), Co (II), Ni (II), Cu (II) and Zn (II) were synthesized with new Tridentete ligand L= bis (2 pyridoyl –6– carboxylic acid) thiourea in 2:1 and 2:2 Metal : ligand molar ratios.The resulting complexes were of general formula $[M_2(L)Cl_4]$ and $[M_2(L)_2Cl_4]$. All complexes were characterized physiochemical with spectral methods by IR , UV –Visible . Two types of structures were suggested square planner and binuclear octahedral .

Introduction

Metal complexes play an important role in plant and animal life due to their physicochemical properties and exhibit a wide range of biological properties (1). In the other hand scientists were interested in the study of thiourea and thioacetamide ligands for medical and pharmaceutical significance (2,3). They are used as preserving materials and compositions for treatment of tuberculosis and antibiotics against bacterial a infection. The presence of the metallic ions such as Zn(II), Cu (II), Ni(II), Co(II) increases their activity as antibiotics for flu, fever an analgesic treatment for ulcer pains an inhibitor for the growth of skin cancer cells . Some thiourea compounds derivatives have anesthetic traits besides its various industrial and agricultural importance(4,5).

Experimental

1. Materials :

All the starting materials and solvents used throughout this work of BDH and Fluka are used without further purification, the ligand L = bis (2-pyridoyl) -6- carboxylic acid) thiourea has been synthesized according to the reported procedure (6).

2. Analysis and Physical Measurements

Melting point or decomposition temperature were determined on a Buchi 510 melting point apparatus and were uncorrected. Infrared spectra in the range 4000 – 200 cm^{-1} were recorded on a Perkin Elmer 580 B spectrophotometer, as KBr, or CsI discs. Electronic spectra were obtained with a Shimadzu UV/VIS. Recording UV-160 spectrophotometer at room temperature. The measurements were recorded at concentration of 10^{-3} M of the complex in DMF. Conductivity measurements have been carried out with an electrical conductivity measuring set model PCM_3-Jenway using 10^{-3} M in DMF solution at room temperature.

3. Preparation of ligand :

The ligand had been synthesized according to the following method: a solution of 2,6 pyridine dicarboxylic acid (0.534g 0.002 mol) in methanol (20 ml) was added to solution of thiourea (0.0761 g. 0.001 mol) in methanol (20 ml). The mixture was stirred under reflux for 3 hours. After cooling to room temperature a rosy precipitate formed which was filtered off, washed with cold methanol and dried under vacuum

4. Preparation of complexes

1- Complexes of $[M_2(L)Cl_4]$

All the complexes were prepared by the same general method :

(0.480 g. 0.002 mol) of metal (II) chloride hydrate dissolved in 20 ml (50% ethanol + 50% methanol) this solution mixed with a solution composed of ligand (0, 374 g – 0.001 mol) in 20 ml (50% ethanol + 50% methanol) then the mixture was stirred under reflux for 3 hours. After cooling to room temperature the precipitated complex was filtered off washed with (50% ethanol + 50% methanol) and then dried under vacuum.

2- Preparation of $[M_2(L)_2Cl_4]$

These complexes were prepared by using the same above procedure except that the weight was (0.7487 g. 0.002 mol) of the ligand. The mixture was refluxed 3 hours. The precipitate was filtered off, washed with (50% methanol + 50 ethanol). And dried under vacuum

Where M= Fe (II), Co (II), Ni (II), Cu (II) and Zn (II)

Results and Discussion

The resulting complexes were coloured solids stable at room temperature and unaffected by moisture. Their given formulae are in good a agreement with the analytical data shown in table(1).Their molar conductance in the DMF indicate that all complexes were non-electrolyte.

Table 1 : Physical and Properties analytical of the ligand and its compounds

No.	Compound	Colour	M.P (C°)	Yield %	Molar conductous (Ω^{-1} cm^2 mol^{-1})	Metal %	B.M μ_{eff} (25°C)
	L	Rosy	169	77	–		
1	$[Co_2(L)Cl_4]$	Light Violet	219-217	60	10	18.58 (18.40)	2.0
2	$[Ni_2(L)Cl_4]$	Dark Green	170-180	66	7	18.42 (18.03)	Dia
3	$[Cu_2(L)Cl_4]$	Blue	200-202	80	5	(19.68) (19.98)	1.7
4	$[Fe_2(L)Cl_4]$	Dark Brown	187-196*	50	13	(17.64) (18.00)	Dia
5	$[Zn_2(L)Cl_4]$	White	185-187*	60	9	20.06 (19.88)	–
6	$[Co_2(L)_2Cl_4]$	Dark Violet	200-204	60	20	11.68 (11.90)	3.5
7	$[Ni_2(L)_2Cl_4]$	Green	183-185	60	3	11.59 (11.22)	3.9
8	$[Cu_2(L)_2Cl_4]$	Light Green	220-224	77	19	12.46 (11.97)	1.8
9	$[Fe_2(L)_2Cl_4]$	Brown	150-152*	66	10	11.05 (11.44)	6.0
10	$[Zn_2(L)_2Cl_4]$	White	130-135*	70	19	12.72 (12.39)	–

* = Decomposition Temperature

The bonding sites of the ligand were inferred by studying the infrared spectra of the complexes and compared them with spectra of the free ligand (Table2). In IR spectra of the complexes in the ν (N-H) band locationed at, 3335cm^{-1} , the ligand didn’t show any displacement indicating that they are not involved in the coordination.the absorption band ν (c-s) that appeared in at (1200 cm^{-1}) in the ligand appeared in the complexes deviated to a lesser wavelength by (25-100cm^{-1}) indicate their involvement in coordination while the absorption band Amid (ν (C=O)) in the ligand was shown at(1666cm^{-1}).This band appeared in the complexes which are deviated to a lesser wavelength by (20-80 cm^{-1}) which indicates its involvement in coordination .

Table 2 : Electronic and infrared spectral bands of the compounds

No.	Compound Ligand	λ_{max} (cm^{-1}) ------	ν (C=S) 1200	ν (C=O)Amid 1666	ν (M–O) ---------	ν (M–S) -------------	ν (M–Cl) ----------
1	$[Co_2(L)Cl_4]$	15723, 19380	1100 (w)	1640 (s)	450 (w)	330 (M)	275 (S)
2	$[Ni_2(L)Cl_4]$	15152, 25510	1150 (w)	1586 (w)	490 (w)	340 (w)	300 (w)
3	$[Cu_2(L)Cl_4]$	17165	1177 (w)	1590 (w)	497 (w)	328 (w)	260 (w)
4	$[Fe_2(L)Cl_4]$	15574	1170 (w)	1601 (m)	420 (w)	338 (w)	296 (w)
5	$[Zn_2(L)Cl_4]$	27000, 32444	1175 (s)	1625 (m)	442 (s)	342 (s)	311 (w)
6	$[Co_2(L)_2Cl_4]$	10209, 15236, 20608	1111 (s)	1633 (m)	434 (s)	334 (w)	319 (s)
7	$[Ni_2(L)_2Cl_4]$	12850, 15174, 22523	1120 (w)	1640 (w)	445 (s)	345 (s)	250 (M)
8	$[Cu_2(L)_2Cl_4]$	12165	1115 (w)	1600 (w)	–	333 (w)	257 (s)
9	$[Fe_2(L)_2Cl_4]$	11287	1122 (s)	1624 (s)	459 (w)	340 (M)	307 (w)
10	$[Zn_2(L)_2Cl_4]$	10204, 11287, 33784	1159 (m)	1646 (s)	437 (w)	344 (w)	310 (s)

The ligand also has additional bands due to pyridine and (C=O) (ν (OH) of the carboxyl group which appeared at 1640 cm^{-1} ’ 1700 cm-^{1} , 2990 cm^{-1} respectively . These bands do not exhibit any changes in position in all complexes which indicate that these groups do not involve in coordination with metal ion (7) .

In IR spectra , new bands appeared for the complexes due to (M-O),(M-S)(9), (M-Cl)(10) being at (420-497 cm^{-1}) , (328-345 cm^{-1}) and (250-319 cm^{-1}) respectively (7), (8).

The electronic spectra of the Co (II) complex (1) show maximum absorption in the range (15723) and (19380) cm^{-1} due to the band to $^{2}A_{1}g \rightarrow {}^{2}Eg$ (ν_1) transition and the magnetic moment was found to be (1.0 B.M) is substantially in line with expectation for low spin Co(II) in square planer geometry (11). The electronic spectra Co (II) complex (6) at (10204, 15236, 20680) cm^{-1} corresponding to the transitions $^{4}T_{1}g$ (F) → $^{4}T_{2}g$ (F) ν_1, $^{4}T_{1}g$ (F) → $^{4}A_{2}g$ (F) (ν_2) and → $^{4}T_{1}g$ (F) $^{4}T_{1}g$ (P) (ν_3) respectively and the magnetic moment was found to be (3.9) B.M an examination of these bands indicate that the complex has high spin octahedral geometry(12).

For the Ni (II) complex (2) the observed bands at (15152, 25510) cm^{-1} correspond to the transitions $^{1}A_{1}g \rightarrow {}^{1}A_{2}g(\nu_1)$ and $^{1}A_{1}g \rightarrow {}^{1}B_{1}g$ (ν_2) respectively and diamagnetic is show square planer geometry (13).

The Ni (II) complex (7) shows maximum absorption at (12850, 15152, 25510) cm^{-1} correspond to the three spin allowed transition $^{3}A_{2}g(F) \rightarrow {}^{3}T_{2}g(F)(\nu_1)$, $^{3}A_{2}g$ (F) → $^{3}T_{1}g$ (F)(ν_2) and $^{3}A_{2}g(F) \rightarrow {}^{3}T_{1}g(P)(\nu_3)$ respectively and a magnetic moments (3.3) B.M at room temperature, these values are in turn with a configuration and shows the presence of an octahedral environment around Ni(II) ions in the complex.

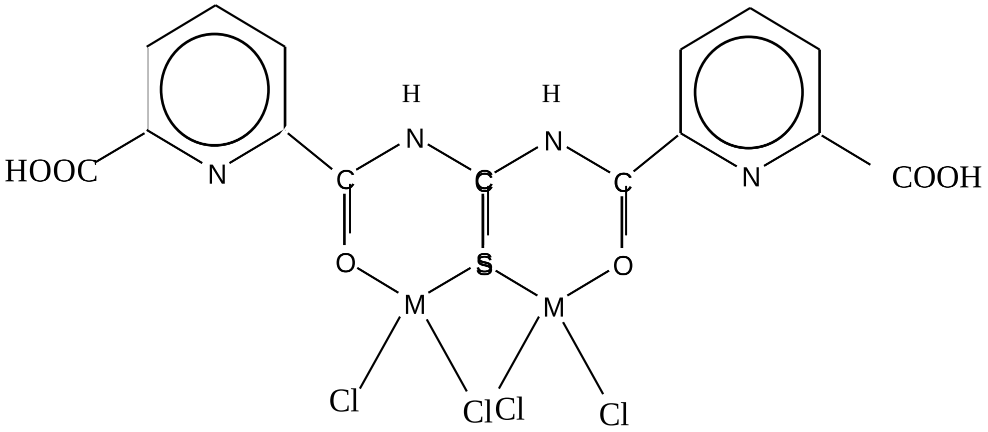
Electronic spectra of copper (II) complex (3) show one band at (17165),cm^{-1} corresponding to the combined transition $^{2}B_{1}g \rightarrow {}^{2}Eg$ and $^{2}B_{1}g \rightarrow {}^{2}A_{1}g$ arising from square planer geometry. The magnetic moment measurements of Cu (II) complex (3) has (1.7) B.M show square planer geometry (14).

The electronic spectra of Cu (II) complex (8) displays bands in the rang (12165) cm^{-1} which may be assigned to $^{2}B_{1}g \rightarrow {}^{2}A_{1}g$, $^{2}B_{1}g \rightarrow {}^{2}B_{2}g$ and $^{2}B_{1}g \rightarrow {}^{2}Eg$ transition this show that the complex has distorted octahedral geometry. The magnetic moment measurements of Cu (II) complex (8) (1.8) show octahedral geometry.

Electronic spectra of Fe (II) complex (4) shows one bands at (15574) cm^{-1} transition d-d-spectra and the magnetic moment measurements of Fe (II) (4) at diamagnetic show the presence of square planer geometry (15).

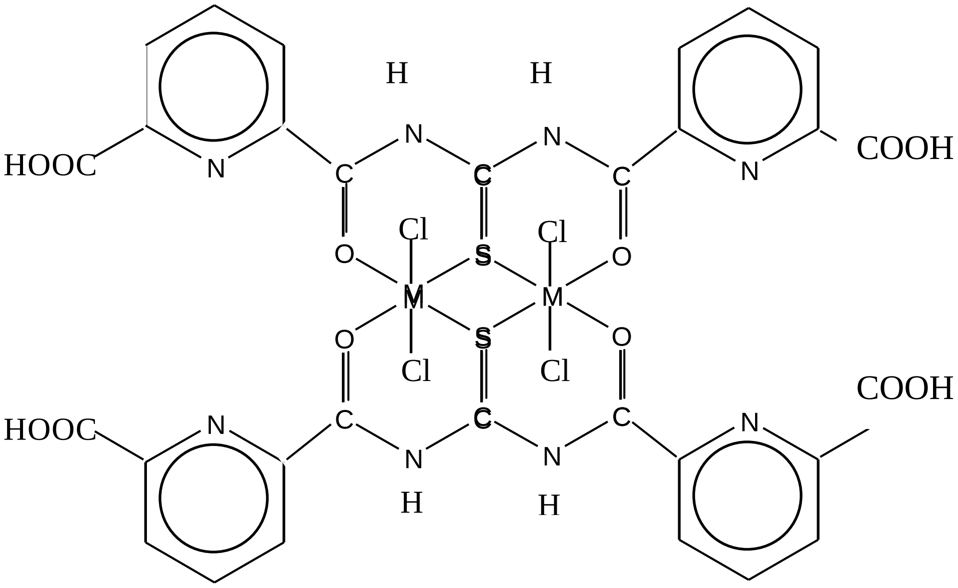
The electronic spectra of Fe (II) complex (9) shows one bands at (11287) cm^{-1} which attitude to the ($^{5}T_{2}g \rightarrow {}^{5}Eg$) transition and could be assigned to a distorted octahedral structure and the magnetic moment values at room temperature (6.0) B.M where well in accord with these having distorted octahedral structure (16).

On the basis of the above discussion the prepared structure of the complexes as shows in fig (1) and fig (2)



M= Fe (II), Co(II), Ni (II), Cu (II), Zn (II)
The Complexes (1-5)

Fig (1)



M= Fe (II), Co (II), Ni (II), Cu(II), Zn(II)
The Complexes (6–10)

Fig (2)

References

1- Auupama Arova, Cl. Arora. Asion Journal of Chemistry. Vol. 15. No. 1 (2003). 144-150.

2- A.A.S. Alwan, Y.Z. Abou, Iraqi Drug Guide 15, ed. 144. (1990).

3- N. Jordena and A. Aloni, JncI, 75, 5, (1985), Abs, 104. 395 y (1986).

4- S. Tadashi; Kojima and N.Osumi, JPAPPI, 87, 112 Chem Abs. 111: 1148849, (1989).

5- M. Akio and K. Osamu., Sumitamo Chemical Co. Ltd Jpn, 63, 280, 053, (1987), chem.. Abs. 111: 77660, (1986).

6- S. Chandra, and L.K. Gupta, Spectrochimica Acta, A 60 (2004), 2767.

7- C. Psharama, N. Kumar, S. Chandra and B.S. Grage J. Indian Chem. Soc., 65 (1988), 434.

8- R.S. Sharma and S.C. Bahel, J. Indian Chem. Soc. 59, 877, (1982).

9- K. Nakamoto, “Infrared and Raman Spectra of Inorganic and coordination compounds”, 5th Edn., Wiley – Interscience, New York (1997).

10- S.E. Livingston and A.E. Mijkelson Inorg. Chem. 9, 2545(1970).

11- J.C. Bailar, H.J. Emelus, Sir R. Nyholmand A.F. Trotman-Dickenson “Comprehensive Inorganic Chemistry”. Programon Press, Oxford. Vol. 115 (1973).

12- M-Sharkir, S.P. Varkey, P.S. Hameed, Polyhedron, 12, (1993), 2775.

13- R.C. Aggar, B. Singh and M.K. Singh, J. Indian Chem. Soc. LIX, 269-373, (1982).

14- A.C. Massey. B.F.G. Johnson, “The chemistry of copper Silver and Gold” Programon Pergamin press. Oxford, 41, (1975).

15- D. Nicholls “The Chemistry of Iron and Nickel” Pergomon Press, Oxford, 1st Ed., (1973).

16- F.A. Cotton and M.D. Myers. J. Am. Chem. Soc., 82, 5023, (1960).

17- R.K. Parihri, R. K. Patel and R.N. Patel, Oriental J. Chem., 15, 397, (1999).

تحضير وتشخيص معقدات ثنائية النوى لعدد من العناصر الانتقالية فضلا عن الخارصين مع ليكاند (٢- بيريدول -٦- حامض الكاربوكسليك) ثايويوريا

ليلى جمعة نجم

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

(تاريخ الاستلام: / /٢٠٠٧ ، تاريخ القبول: / / ٢٠٠٧)

الملخص

يتضمن البحث تحضير معقدات جديدة ذوات الصيغ العامة $[M_2(L)Cl_4]$ $[M_2(L)_2Cl_4]$ حيث $L =$ (بريدويل – ٦ – حامض كابوكسليك) ثايويوريا و $M= Fe(II), Co(II), Ni(II), Zn(II)$ تم تشخيص المعقدات بقياسات التوصيلية الكهربائية وقياسات الاطياف الالكترونية وطيف الاشعة التحت الحمراء وقياسات المغناطيسية وقياسات الامتصاص الذري حيث اظهرت هذه القياسات ان بعض المعقدات كانت رباعية التناسق لها بنية المربع المستوي في حين كان القسم الاخر سداسي التناسق ذات بنية ثماني السطوح الاكثر احتمالا بموجب القياسات اعلاه .