

Investigation of New Tetra Dentate Macrocyclic [N₄] Ligand and it's Complexes with Transition Metal's

Saad K. Dawood

Sahbaa A. Al-Sabaawi

Department of Chemistry / College of Science
University of Mosul

Received
28 / 07 / 2010

Accepted
09 / 02 / 2011

الخلاصة:

البحث يتضمن تحضير ودراسة عدد من معقدات العناصر الانتقالية Cu(II), Ni(II), Mn(II), Fe(II), Co(II) بالإضافة إلى Zn(II) مع الليكاند (٩,٢-ثنائي امين- الحلقي) L₁. تم مفاعلة ا حد القواعد النايتروجينية ٤-مثيل بريدين (٧-بكولين) L₂ مع هذه المعقدات لتكوين معقدات جديدة (معقدات إضافة) بنسبة مولية ٢:١ حيث كان الليكاند احادي السن. شخصت المعقدات بالتحليل الدقيق للعناصر (M%) واستخدام التوصيلية المولارية والقياسات المغناطيسية وتحت الحمراء والطيف الالكتروني للتوصل إلى الصيغ المتوقعة لهذه المعقدات.

Abstract :

This paper describes the preparation and study of a number of transition metal Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) with the ligand (2,9-diamin-5,7,12,14-tetraazo-1,4,8,11-tetra oxo-6,13-dithiacyclotetra-decane)L₁.

These complexes also reacted with 4-methyl pyridine (γ -picoline) L₂ to form 1:2 adducts in which the ligand act as a monodentate ligand. All these complexes and the adduct characterized by microanalytical (M%), molar conductance measurements, magnetic susceptibility measurements, IR, and electronic spectral.

Introduction :

Thiourea and their complexes have been extensively studied during recent years mainly because of their various biological properties^(1,2,3). Thiourea usually act's as chealating ligand with transition metal ions, bonding through the sulfur or nitrogen atoms⁽⁴⁾. Macrocyclic ligands are

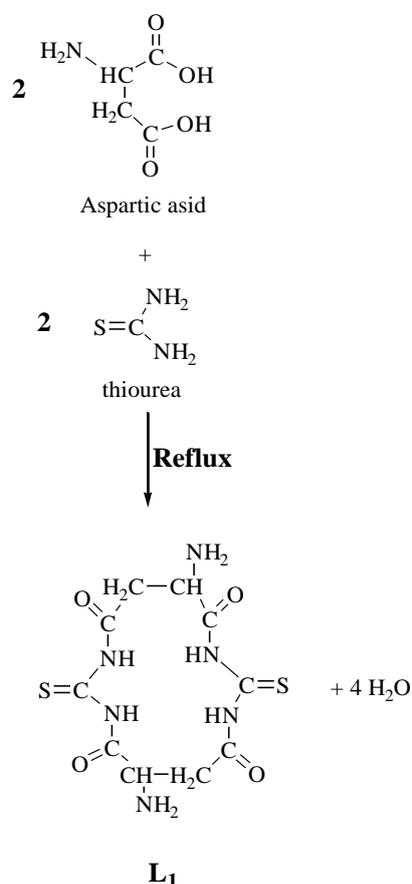
known and recognized as examples of organic skeleton containing cyclic structures in which their arrangements of the ligands molecule are sufficiently constrained to influence, often dramatically, the properties of the complex formation with metal^(5,6). Such ligands frequently show selectivity in their complexation properties, coordinating behavior of anions and may modify the redox chemistry of the formed metal complex⁽⁷⁾.

As part of our continuous research work pertaining to the synthesis, characterization of metal complexes from thiourea, we describe here some new transition metal complexes obtained from Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) chlorides.

Experimental :

The ligand L₁ has been synthesized according to the following procedure⁽⁸⁾.

Aspartic acid (6.6 g , 0.05 mol) was dissolved in hot ethanol (20 ml) and mix with hot ethanolic solution (20ml) of thiourea (3.8 g , 0.05 mol) with stirring. The mixture then reflux at ~80 °C for 7h in the presence of (2 ml) concentrated hydro- chloric acid, on standing over night, a white precipitate formed which was filtered off washed with cold ethanol and dried under vacuum Scheme (1) some of its physical properties are listed in Table (1) .



Scheme (1) : preparation and structure of the ligand L₁ .

A- Preparation of the metal complexes :

The hot solution of the ligand L_1 (0.01 mol, 0.42 g) in 20 ml ethanol and ethanolic solution of the corresponding metal salt (0.01 mol/20 ml) were mixed together with stirring. The mixture was refluxed for 6h at $\sim 80^\circ\text{C}$, on cooling gives a colored precipitate of the complexes which was filtered off washed with cold EtOH and dried under vacuum .

B- Preparation of the base adducts :

These complexes were prepared by adding excess 4-methyl pyridine dissolved in ethanol and mixed with every complex alone and refluxed at $\sim 80^\circ\text{C}$ for about 3h. On cooling gives coloured precipitate Table (1) which was filtered off washed with cold EtOH and dried under vacuum .

C- Physical measurements :

Metal analysis of all complexes were carried out using standard method. (atomic absorption method) .Infrared spectra ($4000-400\text{ cm}^{-1}$) were recorded on Perkin-Elmen 580B spectrophotometer, as KBr discs. Electronic spectra were obtained with Shimadzu UV/Vis, recording UV/160 spectrophotometer at room temperature. The measurements were recorded using in DMSO as a solvent . The magnetic measurements were carried out at 25°C on solid by the Faraday method using Bruker BM6 instrument.

Conductivities were measured using conductivity meter mode PCM3-Jenway using 10^{-3}M DMSO at 25°C of the complexes.

Results and discussion :

Four new bands appear in the spectrum of free ligand (L_1) assignable to amid I [$\nu\text{ C=O}$], amid II [$\nu\text{ (C-N)} + \delta\text{ (N-H)}$], amid III [$\delta\text{ (N-H)}$] and amid IV [$\delta\text{ C=O}$] bands respectively^(9,10). The spectrum also show a splitting band due to $\nu\text{(-C=S)}$ at 1175, 1122 cm^{-1} . A sharp band's observed at 3250 and 3385 cm^{-1} which may be assigned to -NH and -NH_2 group respectively, Table (3)⁽¹⁰⁾.

Complexes :

The molar conductance measurements in DMSO show's two types of complexes, a nonelectrolyte nature for Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) while 1:2 electrolyte for the base adduct complexes. Thus these complexes may be formulated as $[\text{ML}_1\text{X}_2]$ and $[\text{ML}_1(\gamma\text{-pic})_2]\text{Cl}_2$ respectively. On complex formation the shifting to word lower side of $\nu\text{(NH)}$ bands and also the bands of amide II suggest a coordination through the nitrogen (NH) group [N4] core, also the band positions due to $\nu\text{(C=S)}$ did not change and $\nu\text{(NH}_2)$ indicating un coordinated behavior of C=S and NH_2 groups. A further supported by the

appearance of a medium intensity band in the range of 450-475 cm^{-1} attributed to $[\nu(\text{M}-\text{N})]$.

Manganese (II) complexes :

The electronic spectra exhibit bands 30303, 38776 cm^{-1} may be due to charge transfer ^(11,12). The magnetic moment values at room temperature 5.89, 5.99 BM for the manganese (II) complexes were well in accordance with those having octahedral structure with five unpaired electrons ^(9,10) Fig (1).

Iron(II) complexes :

The electronic spectra of iron (II) complexes at room temperature showed a band at 10162 and 9842 cm^{-1} which attributed to the ${}^5\text{T}_{2g} \longrightarrow {}^5\text{E}_g$ transition and could be assigned to a distorted octahedral structure ^(11, 12). The values of the Fe(II) complexes magnetic moment at room temperature was 4.56, 4.68 were well in accord with those having distorted octahedral structure ⁽¹¹⁾.

Cobalt (II) complexes :

The two Co(II) complexes exhibit magnetic moment values lie in 4.78 and 4.85 BM corresponding to three unpaired electrons higher value due to orbital contribution Table (2).

The electronic spectra of these complexes showed an absorption in the region(1) 10183, 10708(2) 14810, 15737(3) 18571,25325 and 32258, 33333 cm^{-1} these bands may be assigned to the transition ${}^4\text{T}_{1g}(\text{F}) \longrightarrow {}^4\text{T}_{2g}(\text{F})\nu_1$, ${}^4\text{T}_{1g} \longrightarrow {}^4\text{A}_{2g}(\nu_2)$ and ${}^4\text{T}_{1g}(\text{F}) \longrightarrow {}^4\text{T}_{1g}(\text{P})\nu_3$ respectively ⁽¹¹⁾. The fourth band and it may be due to charge transfer. The position of these bands indicates that these complexes have distorted octahedral geometry ^(9,10,12) Fig.(1) .

Nickel (II) complexes :

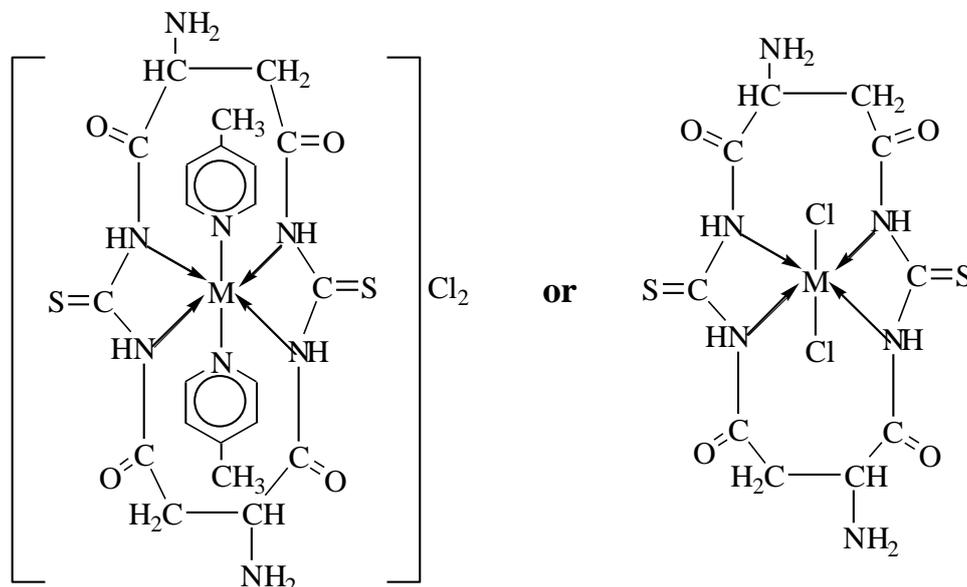
The magnetic moment value's of the two nickel (II) complexes showed 3.04 and 3.17 BM, these values are in turn with high-spin configuration and shows the presence of an octahedral environment around Ni(II) ion in complexes ⁽¹³⁾. The electronic spectrum of the complexes shows three bands at(1)10162,10893, (2) 15185, 15364 and (3), 25641, 26397 cm^{-1} correspond to ${}^3\text{A}_{2g}(\text{F}) \longrightarrow {}^3\text{T}_{2g}(\text{F}) \nu_1$, ${}^3\text{A}_{2g}(\text{F}) \longrightarrow {}^3\text{T}_{2g}(\text{F}) \nu_2$ and ${}^3\text{A}_{2g}(\text{F}) \longrightarrow {}^3\text{T}_{2g}(\text{P}) \nu_3$ respectively. These band indicate the complexes has octahedral geometry Fig.(1).

Copper (II) complexes :

The magnetic moment values of Cu(II) complexes are 2.05, 1.95 BM which are corresponding of one unpaired electron.

Electronic spectra of the two complexes display one bands which assigned to the ${}^2E_{2g} \rightarrow {}^2T_{2g}$ transition in distorted octahedral structure around the Cu (II) ions^(7,10,12) Fig.(1) .

On the basis of the above discussion we propose the following structure of the metal (II) complexes as in Fig.(1) .



Fig(1) : Suggested structures of the complexes.

Where :

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

Table (1): Molar conductance and metal analysis of the complex

No.	Compound	Colours	M.P °C	Yield %	Molar conductance $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{Mol}^{-1}$	Salts	Metal analysis Found (calculated)%
1.	[Mn(L ₁)Cl ₂]	White	235	74	21.5	MnCl ₂	11.21 (11.64)
2.	[Mn(L ₁)(γ -pic) ₂] Cl ₂	Yellow	234	68	81.0	MnCl ₂	9.25 (9.73)
3.	[Fe (L ₁)Cl ₂]	Brown	217	70	16.8	FeCl ₂	11.14(11.90)
4.	[Fe (L ₁)(γ -pic) ₂] Cl ₂	Deep yellow	231	82	83.0	FeCl ₂	9.12(9.91)
5.	[Co (L ₁)Cl ₂]	Green	230	64	13.0	CoCl ₂ .6H ₂ O	11.86 (12.40)
6.	[Co (L ₁)(γ -pic) ₂] Cl ₂	Brown	254	63	85.0	CoCl ₂ .6H ₂ O	10.01 (10.37)
7.	[Ni (L ₁)Cl ₂]	Brown	241	58	12.0	NiCl ₂ .6H ₂ O	11.65 (12.36)
8.	[Ni (L ₁)(γ -pic) ₂] Cl ₂	Dark brown	300	86	72.0	NiCl ₂ .6H ₂ O	9.98 (10.33)
9.	[Cu (L ₁)Cl ₂]	Gray	219	81	19.0	CuCl ₂	12.94 (13.24)
10.	[Cu (L ₁)(γ -pic) ₂] Cl ₂	Gray	239	67	82.9	CuCl ₂	10.80 (11.09)
11.	[Zn (L ₁)Cl ₂]	Pink	233	83	14.6	ZnCl ₂	12.82 (13.58)
12.	[Zn (L ₁)(γ -pic) ₂] Cl ₂	Brown	271	80	76.5	ZnCl ₂	10.87 (11.38)

Table (2) : Magnetic moment and elemental spectra data of complexes

No.	Compound	μ_{eff} B.M 25 C	λ max cm^{-1}
1.	[Mn(L ₁)Cl ₂]	5.89	32258 , 38776
2.	[Mn(L ₁)(γ -pic) ₂] Cl ₂	5.99	30303 , 36768
3.	[Fe (L ₁)Cl ₂]	4.56	10162 , 32258
4.	[Fe (L ₁)(γ -pic) ₂] Cl ₂	4.68	9842 , 27027 , 32258
5.	[Co (L ₁)Cl ₂]	4.78	10183 , 15737 , 18571 , 33333
6.	[Co (L ₁)(γ -pic) ₂] Cl ₂	4.85	10708 , 14810 , 25325 , 32258
7.	[Ni (L ₁)Cl ₂]	3.04	10162 , 15364 , 26397 , 32456
8.	[Ni (L ₁)(γ -pic) ₂] Cl ₂	3.17	10893 , 15185 , 25641 , 32470
9.	[Cu (L ₁)Cl ₂]	1.95	10183 , 34482
10.	[Cu (L ₁)(γ -pic) ₂] Cl ₂	2.05	10893 , 30303
11.	[Zn (L ₁)Cl ₂]	----	28162 , 32786
12.	[Zn (L ₁)(γ -pic) ₂] Cl ₂	----	29708 , 28985

Table (3) : Selected I.R bands and their assignment in cm^{-1}

No.	Compound	ν (-C=S)	Amid II	Amid III	ν NH	ν NH ₂	M-N
	Ligand	1175, 1122	1500	1297	3250	3385	----
1.	[Mn(L ₁)Cl ₂]	1174, 1122	1393	1231	3208	3385	470
2.	[Mn(L ₁)(γ -pic) ₂] Cl ₂	1175, 1121	1457	1232	3210	3384	462
3.	[Fe (L ₁)Cl ₂]	1175, 1120	1366	1275	3197	3384	470
4.	[Fe (L ₁)(γ -pic) ₂] Cl ₂	1175, 1121	1384	1272	3208	3418	472
5.	[Co (L ₁)Cl ₂]	1174, 1122	1367	1234	3205	3380	467
6.	[Co (L ₁)(γ -pic) ₂] Cl ₂	1175, 1122	1384	1231	3209	3384	468
7.	[Ni (L ₁)Cl ₂]	1155, 1121	1368	1232	3204	3384	469
8.	[Ni (L ₁)(γ -pic) ₂] Cl ₂	1175, 1110	1387	1230	3204	----	472
9.	[Cu (L ₁)Cl ₂]	1175, 1120	1402	1235	3197	----	450
10.	[Cu (L ₁)(γ -pic) ₂] Cl ₂	1175, 1121	1385	1273	3200	3335	475
11.	[Zn (L ₁)Cl ₂]	1173, 1123	1368	1203	3222	3385	475
12.	[Zn (L ₁)(γ -pic) ₂] Cl ₂	1174, 1121	1386	1274	3215	----	470

REFERENCES :

- 1) H. Beraldo, D. Gambino, Mini-Rev. Chem. 4, 31, 2004 .
- 2) S. Gasas, M. S. Garcia-Tasend, J. Sordo. Coord. Chem. Rev. 209, 197, 2000.
- 3) K. Alomar, M. A. Kan, M. Ahain, G. Bouet, Polyhedron, 28, 1273, 2009.
- 4) T. S. Lobana, P. Kumari, M. Zeller, R. J. Butcher, Inorg. Chem. Commun, 11, 972, 2008 .
- 5) S. Chandra. R. Kumar, Spectrochim. Acta part A, 61, 437, 2005 .
- 6) S. Chandra. R. Kumar, Spectrochim. Acta part A, 62, 518, 2005 .
- 7) S. Chandra. R. Kumar, J. Ind. Chem. Soc. 82, 693, 2005 .
- 8) S. Chandra. And L. K. Gupta, Spectrochim. Acta part A, 60, 2767, 2004 .
- 9) S. K. Dawood, I. A. Hassen, T. Y. Yousif J. Edu. Sci., 18, No.(2), 1, 2006.
- 10) M. Sharkir, S. P. Varkey and P. S. Hameed, Polyhedron, 12, 2775, 1993.
- 11) A. B. P. Lever. "Crystal Field Spectra and Electronic Spectroscopy", Wiley Interscience, New York, 101, 1970 .
- 12) J. Ferguson, Prog. Inorg. Chem., 12, 159, 1970 .
- 13) A. B. P. Lever. "Inorganic Electronic Spectroscopy" Elsevier Amsterdam, 168, 1968.