Synthesis and Characterization of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) Complexes with Hexa azamacrocyclic Ligands Derived from Thiosemicarbazide

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الخلاصة:

تم تحضير بعض معقدات عناصر السلسلة الانتقالية الأولى مع نوعين من الليكاندات المشتقة من الثايوسي ميكاربازايد L_1= ثنائي سايكلوهكسان [15,14,9,7,6,1] سداسي ازا [3,10,5,2] رباعي اون [13,8] ثنائي ثاياهكسادكين الحلقي وكذلك L_2= ثنائي هكسيل الحلقي [15,14,9,7,6,1] سداسي ازا [3,10,5,2] رباعي اون [13,8] ثنائي ثاياهكسادكين الحلقي. هذه المعقدات شخصت ودرست بالتحليل الدقيق للعناصر والتوصيلية المولارية والقياسات المغناطيسية وقياسات الأشعة تحت الحمراء والاطياف الالكترونية . ان قياسات التوصيلية المولارية دلت على كون هذه المعقدات غير الكتروليتية وانها قد تعطي شكل ثماني السطوح.

Abstract:

Some transition metal (II) complex are synthesized with thiosemicarbazide Ligands L_1= dicyclohexen [1,6,7,9,14,15] hexaaza [2,5,10,3] tetra one [8,13] dithiacyclohexadecane and L_2= dicyclohexyl [1,6,7,9,14,15] hexaaza [2,5, 10, 13] tetraone [8,13] dithiaCyclohexadecane. These complexes are characterized by elemental analysis, molar conductance magnetic susceptibility measurements, IR, electronic spectral studies. The molar conductance measurements of the complexes in DMSO correspond to non-electrolytic nature and the complexes may have octahedral geometry.

Introduction:

The semicarbazides are very versatile ligand's, they can coordinate to metal as neutral molecules or, after deprotonation, as anionic ligand's, and can adopt a variety of different coordination modes [1].Heterocyclic thiosemicarbazides with a functional group attached at the 2-position have been the subject of extensive investigation. A review was published by Lobana *et.al* [2].

The metal complexes show more activities as compared to the free thiosemicarbazides and semicarbazides. It may have numerous application e.g, anticancer, fungicides, antibacterial, antiviral, antifungal, antitumour activity and other biological activities [3]. Particularly, first row transition metal complexes with such ligands have a wide range of biological activities [4,5].

The activity of these compounds is strongly dependent upon the nature of the hetero atomic ring and the position of attachment to the ring as well as the form of thiosemicarbazide moiety [6].

In view of the above applications, it is highly desirable to synthesize and characterize transition metal complexes with such ligands.

In the present paper, we report the synthesis and characterization of complexes with thiosemicarbazides (L_1) and (L_2) derived from two types of dicarboxylic acid Fig (1).

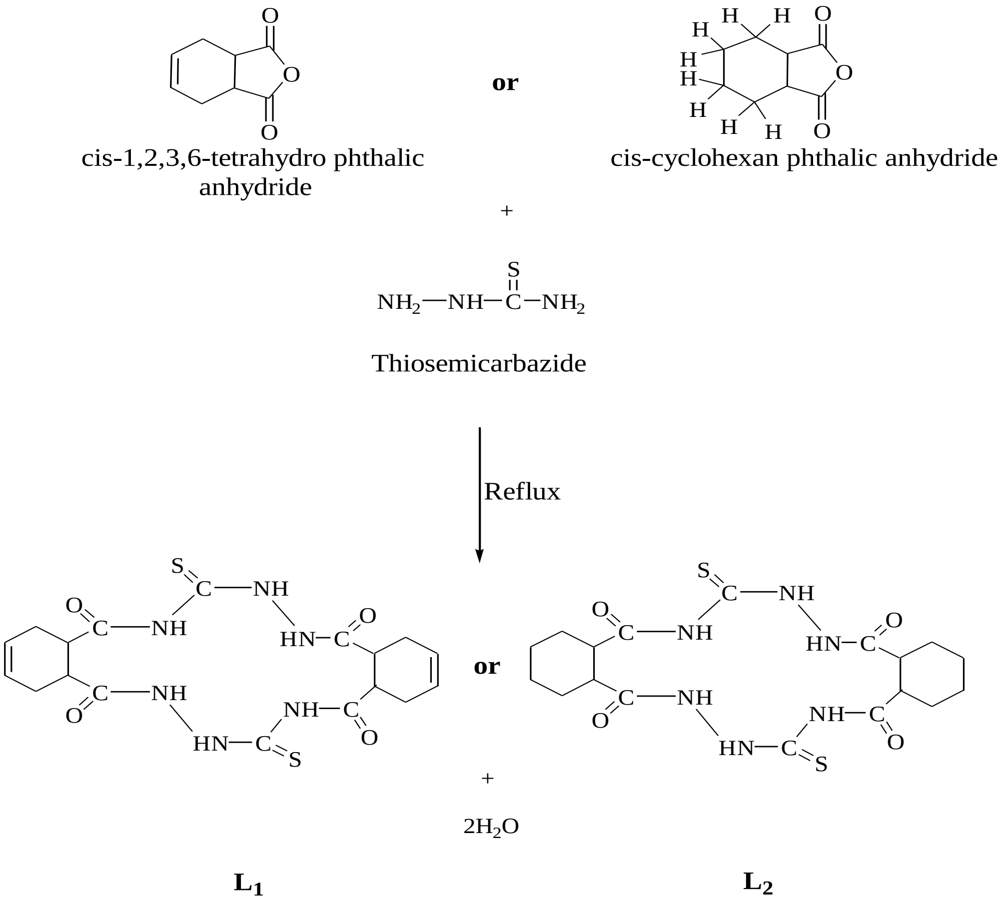


Fig (1): Preparation and structure of the ligand L_1 and L_2

Experimental

The ligand L_1 and L_2 have been synthesized according to the following procedure [7].

Phthalic anhydride (1.04g, 7mmol) dissolved in DMF (5ml) was added dropwise to a thiosemicarbazide solution dissolve in ethanol (0.78g, 7mmol). The reaction refluxed for about 7h in the presence of 2ml conc. HCl, after that the solution was concentrated to about 1/3 of its volume, the formed white solid was filtered off and washed with cold ethanol and dried under vacuum.

The same procedure carried out in preparation L_2 ligand.

A: preparation of the metal complexes:

Hot ethanolic solution of ligands L_1 or L_2 (0.001 mol /20ml) (0.45, 0.454g) respectively and ethanolic solution of the corresponding metal salt (0.01 mol /20ml) were mixed together with stirring. The mixture were refluxed for 4h at ~80˚C. On cooling coloured precipitates were obtained (Table 1),these products were filtered off washed with cold EtOH and dried under vacuum.

B. Physical measurements:

Analyses of the ligands and complexes were carried out using standard method CHNS analysis using Perkin Elmar 2400, CHN analyset in AL-albaet University, Jordan. Infrared spectra in the rang 4000-400 cm were recorded on a Perkin-Elmer 580 B spectrophotometer, as KBr discs. Electronic spectra were obtained with Shimadzu UV/Vis recording UV 160 spectrophotometer at room temperature. The measurement were recorded using a concentration of 10^{-3} M of the complexes in DMSO. The magnetic measurements were carried out at 25˚C by a Farady's mothod using Bruker-BM6 instrument. Conductivities were measured using a conductivity meter mode PCM3 –Jenway. These measurements were obtained using DMSO over concentration of 10^{-3}M at 25˚C.

Results and discussion:

IR spectra:

IR spectra of L_1 and L_2 Table (3) exhibited absorption frequencies assignable to the fundamental ν(N–H) stretching vibration as a strong doublet in the range (3303-3201 cm^{-1}) and (3371–3202 cm^{-1}) respectively, ν(R–CO–N) as a medium intensity band at 1726 and 1730 respectively too. ν(C=S) for L_1 and L_2 ligands appears in the range 1171 and 1173 cm^{-1} respectively, also ν(N–N) stretching vibrations appears at 1180-1190 respectively too. The siplity of some of the fundamental band especially for ν(N–H) stretching vibration probably the result of the resonance coupling [8].

Fundamental frequencies due to (C–H) (C–N), (C=C), or aliphatic (C-C) bands have also been observed in the IR spectra of the compounds.

The disappearance of bands due to ν(C–O–C) stretching frequencies characterized for anhydride's as a doblet at 1850 and 1779 cm^{-1} for phthalic and 1845 and 1769 cm^{-1} for cyclohexyl anhydride and appearance of new bands characteristic of ν(N–N), ν(R–CO–N). and ν(C=S) stretching frequencies confirm the condensation reaction between the anhydride and thiosemicarbazide, resulting a 16 membered cyclic hexaamides macrocycle L_1 and L_2 as show in Fig (1).

In the IR of the complexes the position of ν(N–H) and ν(N–N) stretching vibration shifted to lower frequency after complexation. However the position of ν(R–CO–N) and ν(C–S) stretching vibration did not change much from that observed in free macrocycle Table (3).

This may indicate that the coordination to the metal ions is through the nitrogen rather than the oxygen atoms of the amide functions. The appearance of a band of medium intensity at $\simeq$ 400 cm^{-1} in the complexes is due to ν(M–N) bond vibration which support the coordination with the metal ions.

Electronic spectra & Magnetic measurements:

Manganese (II) Complexes:

The two manganese complexes have a magnetic moment values 5.96–5.98 B.M corresponding to five unpaired electrons having a octahedral structure. The electrons spectral bands were 2787-35640 cm^{-1} may be due to charge transfer [10].

Iron (II) Complexes:

The non electrolytic nature of the two iron complexes indicates that they are in accord with octahedral structure. This fact supported by the magnetic movement values which were 4.63–4.65 B.M as well as the electronic spectra which showed a band at 11960–11870 cm^{-1} attributed to the $^5T_2g \longrightarrow {}^5Eg$ transition[10,11].

Cobalt (II) Complexes:

The magnetic moment values at room temperature for Co (II) complexes 5.10–5.32 B.M corresponding to three unpaired electrons Table (2).

The electronic spectra showed band in the positions 10430, 11045cm^{-1}, 14155, 13870cm^{-1} and 18950, 18740 cm^{-1} the two Cobalt(II) complexes respectively due to the transition $^4T_1g\,(F) \longrightarrow {}^4T_2g\,(F)\ (\nu_1)$, $^4T_1g\,(F) \longrightarrow {}^4A_2g\,(F)\ (\nu_2)$ and $^4T_1g\,(F) \longrightarrow {}^4T_1g\,(p)\ (\nu_3)$.

The other band may be due to charge transfer finally the structure of these complexes may be distorted octahedral in accord with their tentative structure [12,13].

Nickel (II) complexes:

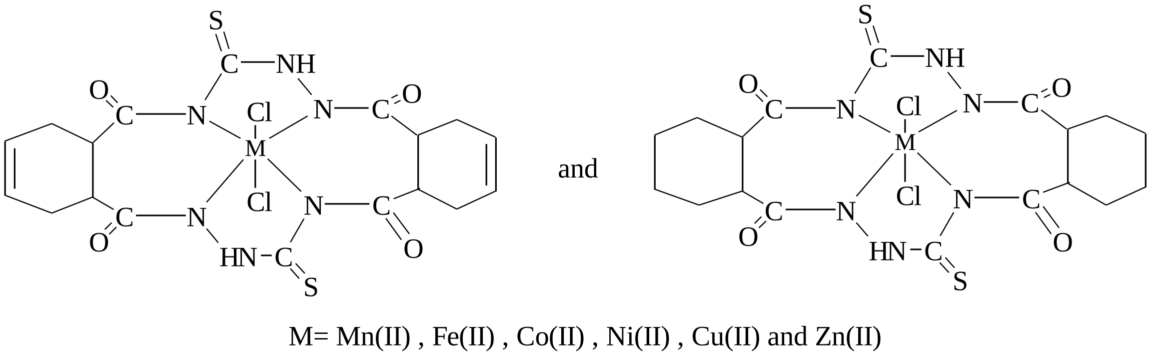
The electron spectrum of the nickel (II) complex shows three bands (1) 1087, 10785 cm^{-1} (2) 15660, 16125 cm^{-1} (3) 24730, 25335 cm^{-1} corresponding to three spin allowed transition ^3A_2g (F) ⟶ ^3T_2g (F) (ν_1), ^3A_2g (F) ⟶ ^3T_1g (F) (ν_2) and ^3A_2g (F) ⟶ ^3T_1g (p) (ν_3) respectively. Also the magnetic moment were 3.05-3.12 B.M, these values are in turn with high-spin configuration show the presence of an octahedral environment around Ni(II) ions [14].

Copper (II) Complexes:

The magnetic moment of the Cu(II) complexes at room temperature lie in the range 1.91 and 1.89 B.M for the two copper (II) complexes corresponding to one unpaired electron electronic spectra display bands in the rang 11991, 10431 cm^{-1} and 14450, 16434 cm^{-1} assigned to the ^2E_2g (F) ⟶ ^2T_2g transition in distorted octahedral structure around Cu(II) ions[15] Fig (2).

As the spectrum of Zn(II) complexes is not well resolved it is not interpreted but its µeff values show that they were diamagnetic as expected.

On the basis of the above discussions we propose the following structures for the metal (II) complexes as in Fig (2).



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

Fig (2): Suggested structure of the complexes [M L_1Cl_2] and [M L_2Cl_2]

Table (1): Some physical properties including molar conductance and elemental analysis data of the complexes

No.	compound	color	M.p (C^o)	Yield %	Molar conductance $\Omega^{-1}\cdot cm^2.mol^{-1}$	Elemental analysis data Found (Calculated%)				
						C%	H%	N%	S%	Metal%
	Ligand (L_1)	White	148-150	70	----	47.97 (48.00)	4.75 (4.88)	18.59 (18.66)	14.11 (14.22)	----
1.	[Mn L_1Cl_2]	Pale yellow	125-127	62	11	37.51 (37.57)	3.80 (3.82)	14.52 (14.61)	11.10 (11.32)	9.48 (9.54)
2.	[Fe L_1Cl_2]	Brown	156-158	74	12	----	----	----	----	10.01 (9.70)
3.	[Co L_1Cl_2]	Dark green	154-156	72	9	----	----	----	----	10.01 (10.17)
4.	[Ni L_1Cl_2]	Green	130-132	68	7	----	----	----	----	10.02 (10.14)
5.	[Cu L_1Cl_2]	Dark green	172-174	75	10	----	----	----	----	----
6.	[Zn L_1Cl_2]	White	180-182	65	8	----	----	----	----	----
	Ligand (L_2)	Pale yellow	164-166	68	----	----	----	----	----	----
7.	[Mn L_2Cl_2]	Yellow	130-132	57	7	----	----	----	----	9.39 (9.48)
8.	[Fe L_2Cl_2]	Brown	155-157	60	11	----	----	----	----	9.89 (9.62)
9.	[Co L_2Cl_2]	Blue	180-182	76	4	----	----	----	----	10.18 (10.10)
10.	[Ni L_2Cl_2]	Dark green	178-180	80	6.0	36.99 (37.06)	4.38 (4.46)	14.31 (14.41)	10.88 (10.98)	9.98 (10.07)
11.	[Cu L_2Cl_2]	Yellow	163-165	50	13	36.65 (36.76)	4.32 (4.42)	14.10 (14.29)	10.78 (10.89)	10.69 (10.80)
12.	[Zn L_2Cl_2]	White	174-176	58	6	----	----	----	----	----

Table (2): Magnatic moment and electronic spectral data of the complexes.

No.	Compound	μeff B.M (25°C)	λ max (cm^{-1})
1.	[Mn L_1Cl_2]	5.96	27870, 35640
2.	[Fe L_1Cl_2]	4.63	11960, 28433
3.	[Co L_1Cl_2]	5.10	10430, 14155, 18950, 35721
4.	[Ni L_1Cl_2]	3.05	10870, 15660, 24730, 26406, 32543
5.	[Cu L_1Cl_2]	1.19	11991, 14450, 37328
6.	[Zn L_1Cl_2]	diamagnetic	37760, 38646
7.	[Mn L_2Cl_2]	5.98	28450, 35787
8.	[Fe L_2Cl_2]	4.65	11870, 39430
9.	[Co L_2Cl_2]	5.32	11045, 13870, 18740, 34450
10.	[Ni L_2Cl_2]	3.12	10785, 16125, 25339, 29578, 33463
11.	[Cu L_2Cl_2]	1.89	10431, 16434
12.	[Zn L_2Cl_2]	diamagnetic	35783, 36943

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

No.	Compound	υ (N=H)	υ ($R-\overset{\overset{O}{\|}}{C}-N$)	υ (N–N)	υ (C–S)	υ (M–N)
	Ligand (L_1)	3303-3201	1728	1180	849	----
1.	[Mn L_1Cl_2]	3289-3184	1718	1115	887	420
2.	[Fe L_1Cl_2]	3282-3143	1728	1117	886	418
3.	[Co L_1Cl_2]	3282-3163	1724	1164	887	422
4.	[Ni L_1Cl_2]	3259-3190	1728	1151	847	426
5.	[Cu L_1Cl_2]	3292-3171	1718	1163	835	417
6.	[Zn L_1Cl_2]	3292-3186	1718	1165	889	411
	Ligand (L_2)	3371-3202	1730	1190	837	----
7.	[Mn L_2Cl_2]	3287-3158	1742	1138	839	442
8.	[Fe L_2Cl_2]	3311-3185	1728	1166	825	425
9.	[Co L_2Cl_2]	3298-3178	1735	1139	841	455
10.	[Ni L_2Cl_2]	3288-3142	1728	1156	863	428
11.	[Cu L_2Cl_2]	3245-3182	1732	1144	833	410
12.	[Zn L_2Cl_2]	3298-3176	1735	1122	842	435

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