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Synthesis and Characterization of Some Schiff Base Complexes Containing Heterocyclic Compounds With Cobalt(II) , Nickel(II), Copper(II) and Zinc(II)

Saleh A.Ahmed.

College of science, University of Tikrit, Tikrit.

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Abstract : The Synthesis of Complexes for Cobalt(II) , Nickel(II), Copper(II) and Zinc(II) with New ligands Schiff base ; N-[5-(phenyl)2-(amino)1,3,4-thiadiazolebenzylidene] (L1) and N-[5-(phenyl)2-(amino)1,3,4-thiadiazole-4-N-dimethylbenzylidene] (L2) have been prepared and characterized by, Atomic absorption spectrophotometer (AAS), Infrared spectra , Electronic spectra, Molar conductivity measurements and Magnetic moment measurements ; It has been found that the ligands behave as a neutral bidentate , Ligands forming chelates with 1:2 (metal : ligand), Octahedral structure is suggested for metal Complexes according to the analytical results.

Key words ; Schiff base, Transition metal Complexes, 1,3,4-Thiadiazol .

Introduction:

Schiff base ligands and their transition metal complexes have been extensively studied for many years (1-4). These complexes have been widely used as bidentate ligands in the field of coordination chemistry (5-10). Thiadiazole synthesized and tested for their antifungal (11). Nematocidal(12). Antibacterial(13). Anti-inflammatory activities(14). Besides industrial applications(15). and agricultural used (16). Thus it will be interesting to prepare and study of complexes containing Schiff base derived from 1,3,4 -thiadiazole and benzaldehyde or 4- [N-]dimethyl benzaldehyde, The aim of this work is prepared transition metal complexes of N-5-phenyl 2-amino 1,3,4 -thiadiazolbenzylidene(L1) and N-5-phenyl 2-amino 1,3,4 -thiadiazole 4-N-dimethylbenzylidene(L2).

Experimental Part

All the chemical substances were supplied by BDH and Fluka and of purity more than 99%, Infrared spectra were recorded by a SHIMADZU infrared spectrophotometer FT - IR model 8400S in the 4000-200 cm⁻¹ Range using KBr disc, Ultraviolet spectra were recorded on HITACHI model 2000U spectrophotometer using DMF as a solvent, melting point were determined by an

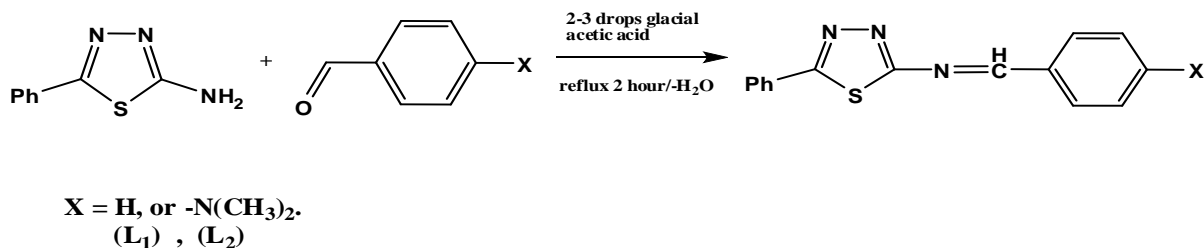
Electrothermal melting point model 9300, Magnetic susceptibilities were measured on instrument type Bruker BM 6 were carried at room temperature by Faraday method , the molar conductivity of complexes (0.001 M) in DMF was measured using HANNA model 214EC conductivity meter, determination of metals percentage by atomic absorption spectrophotometer on Perkin-Elmer model 2280.

• Synthesis of the ligands and complexes

2-amino-5-phenyl-1,3,4-thiadiazole was prepared according to following general procedure (17,18). The ligands (L1) and (L2) are prepared by a same method ; A mixture of benzaldehyde (1.06 g, 0.01 mole) or 4-N-dimethylbenzaldehyde (1.49 g, 0.01 mole) in 30 ml absolute ethanol and 2-amino-5-phenyl-1,3,4-thiadiazole (1.77 g, 0.01 mole) with 2-3 drops of glacial acetic acid was refluxed for 2 hours with continuous stirring, after cooling at room temperature, the precipitate was filtered, dried and recrystallized from ethanol (19) scheme(1). The complexes were prepared by dissolving (0.265 g, 1mmole) of (L1) or (0.308 g, 1mmole) of (L2) in 40 ml absolute ethanol which then added drop wise with vigorous stirring to (0.5 mmole) of MCl₂ metal salts [M=Co(II), Ni(II), Cu(II) and Zn(II)] dissolved in 10 ml hot distilled water the mixture was

heated to 50°C for 30 min. , then left overnight, the solid complex formed was

filtered, washed with 10 ml ethanol and dried.



Scheme (1); show the structure of ligands L1 and L2.

Results and Discussion

• Characterization of ligands and its metal complexes

The ligands and its metal complexes were

insoluble in water but soluble in organic solvent such as DMSO, DMF the metal percentage in complexes and physical data of ligands and complexes are given in table (1).

Table (1): metal percentage and physical data of ligands and its complexes.

Compound	Formula	Color	M.p °C	Yield %	% Metal calc.(found)
L ₁	C ₁₅ H ₁₁ N ₃ S	yellow	238-236	72	---
L ₂	C ₁₇ H ₁₆ N ₄ S	yellow	217-215	75	---
[Co(L ₁) ₂ Cl ₂]	C ₃₀ H ₂₂ N ₆ S ₂ Cl ₂ Co	Deep yellow	268-266	69	8.93 (8.90)
[Ni(L ₁) ₂ Cl ₂]	C ₃₀ H ₂₂ N ₆ S ₂ Cl ₂ Ni	orange	275-273	65	8.90 (8.86)
[Cu(L ₁) ₂ Cl ₂]	C ₃₀ H ₂₂ N ₆ S ₂ Cl ₂ Cu	Brown	256-254	70	9.55 (9.58)
[Zn(L ₁) ₂ Cl ₂]	C ₃₀ H ₂₂ N ₆ S ₂ Cl ₂ Zn	white	251-249	68	9.51 (9.47)
[Co(L ₂) ₂ Cl ₂]	C ₃₄ H ₃₂ N ₈ S ₂ Cl ₂ Co	Deep yellow	245-243	68	7.90 (7.85)
[Ni(L ₂) ₂ Cl ₂]	C ₃₄ H ₃₂ N ₈ S ₂ Cl ₂ Ni	orange	258-256	62	7.87 (7.82)
[Cu(L ₂) ₂ Cl ₂]	C ₃₄ H ₃₂ N ₈ S ₂ Cl ₂ Cu	Brown	239-237	71	8.46 (8.50)
[Zn(L ₂) ₂ Cl ₂]	C ₃₄ H ₃₂ N ₈ S ₂ Cl ₂ Zn	white	232-230	66	9.17 (9.14)

• Infrared spectra

The important infrared spectra data of ligands and its complexes are given in table (2), The bands in region 1637-1626 cm⁻¹ attributed ν(C=N) vibration thiazole ring, This value was increased after Copmplexation (20). The bands ν(C-S-C) in region 755-750 cm⁻¹, This band remains in the same region in free ligands and after Copmplexation that mean is the sulfur atom in thiazole group doesn't coordinate with

metal in complexes (21). The bands in the range 1618-1600 cm⁻¹ due to azomethine group in the ligands and then was shifted to lower frequencies after Copmplexation which are 1595-1574 cm⁻¹, New weak bands in the region 456-415 cm⁻¹ were observed in the spectra of metal complexes, These bands were not present in the spectrum of ligands, and they due to ν(M-N) (22-23)

Table (2): IR absorption bands of ligands and its complexes in cm⁻¹ units.

Compound	ν(C=N) thiazole ring	ν(C-S-C)	ν(C=N) azomithine	ν(M-N)
L ₁	1637	755	1618	---
L ₂	1626	750	1600	---
[Co(L ₁) ₂ Cl ₂]	1658	754	1592	422
[Ni(L ₁) ₂ Cl ₂]	1657	753	1587	415
[Cu(L ₁) ₂ Cl ₂]	1655	754	1586	448
[Zn(L ₁) ₂ Cl ₂]	1649	752	1590	456
[Co(L ₂) ₂ Cl ₂]	1652	751	1573	424
[Ni(L ₂) ₂ Cl ₂]	1651	750	1581	416
[Cu(L ₂) ₂ Cl ₂]	1654	749	1575	450
[Zn(L ₂) ₂ Cl ₂]	1650	752	1578	455

• Magnetic measurement and electronic spectra

The magnetic moment and spectral data of prepared complexes are given in table (3). The magnetic moment of Cobalt (II) has

been found to be (4.57, 4.43 B.M) which is with the range of octahedral Cobalt (II) complexes ⁽²⁴⁾. The electronic spectra of L₁ and L₂ show strong bands in the range 43250-42110 cm⁻¹ and 34520-34310 cm⁻¹ which are attributed $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively, the electronic spectra of this complexes show two absorption bands at 16230-16110 cm⁻¹ and 22870-22650 cm⁻¹ there are assigned to ⁴T_{1g} (F) → ⁴A_{2g} (F) (ν₂) and ⁴T_{1g} (F) → ⁴T_{2g} (P) (ν₃) transitions respectively, which are characteristic of octahedral stereochemistry. For Nickel (II) complexes its magnetic moment (3.30,3.10

B.M) and spectra of this complexes show bands at 16260-16125 cm⁻¹ and 22230-22110 cm⁻¹ which suggesting the existence of ³A_{2g} (F) → ³T_{1g} (F) (ν₂) and ³A_{2g} (F) → ³T_{1g} (P) (ν₃) transitions which an octahedral spectral configuration. The magnetic moment value of Copper (II) complexes (1.73,1.61B.M) which may suggest an octahedral structure. Its electronic spectrum show at 15638-15450 cm⁻¹ which may assigned to ²E_{2g} → ²T_{2g} transition in octahedral structure ^(24,25). Zinc (II) complexes are diamagnetic and electronic spectra of these complexes exhibit high intense charge transfer transition ⁽²⁶⁾.

Table (3): magnetic moment, Electronic spectra, Conductivity of the complexes.

Complexes	Electronic spectra cm ⁻¹			transition	Conductivity cm ² .ohm ⁻¹ .mol ⁻¹	μ eff. (B.M)
	ν ₁	ν ₂	ν ₃			
[Co(L ₁) ₂ Cl ₂]	--	16238	22872	⁴ T _{1g} (F) → ⁴ A _{2g} (F) (ν ₂) ⁴ T _{1g} (F) → ⁴ T _{2g} (P) (ν ₃)	7.32	4.57
[Ni(L ₁) ₂ Cl ₂]	--	16260	22238	³ A _{2g} (F) → ³ T _{1g} (F) (ν ₂) ³ A _{2g} (F) → ³ T _{1g} (P) (ν ₃)	9.41	3.30
[Cu(L ₁) ₂ Cl ₂]	--	15638	--	² E _{2g} → ² T _{2g}	11.19	1.73
[Zn(L ₁) ₂ Cl ₂]	--	--	--	--	10.47	dia
[Co(L ₂) ₂ Cl ₂]	--	16119	22656	⁴ T _{1g} (F) → ⁴ A _{2g} (F) (ν ₂) ⁴ T _{1g} (F) → ⁴ T _{2g} (P) (ν ₃)	8.15	4.43
[Ni(L ₂) ₂ Cl ₂]	--	16125	22110	³ A _{2g} (F) → ³ T _{1g} (F) (ν ₂) ³ A _{2g} (F) → ³ T _{1g} (P) (ν ₃)	9.63	3.10
[Cu(L ₂) ₂ Cl ₂]	--	15456	--	² E _{2g} → ² T _{2g}	10.88	1.61
[Zn(L ₂) ₂ Cl ₂]	--	--	--	--	9.11	dia

• **Conductivity measurements:**

The molar conductance of the complexes 0.001 M in DMF at room temperature show that all complexes are non-electrolytes ⁽²⁷⁾. The

value in the range 7.32-11.19 cm².ohm⁻¹.mol⁻¹ table (3).

According to these results the structural formula of prepared complexes may be proposed in figure (1).

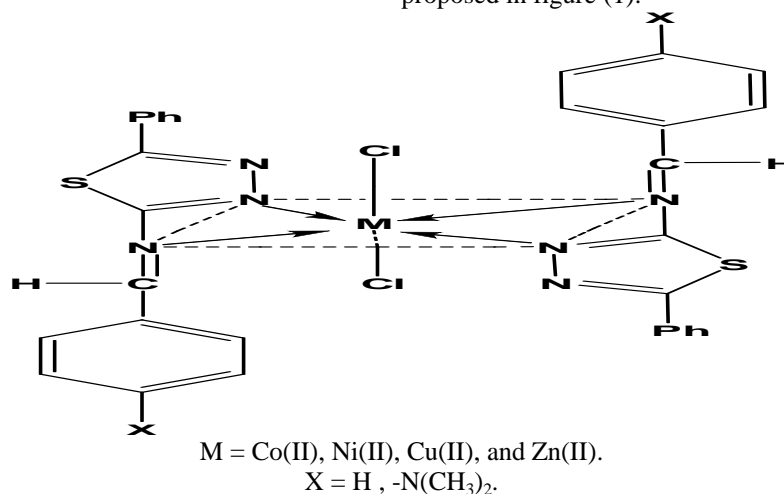


Fig.1: the proposed structural formula of the complexes.

References

- 1- V.Daier, H. Biava, and C. Palopoli ; J. Inorg. Biochem. 98(2004) 1806.
- 2- O.Q.Munro, and G.L Camp ; Acta Crystallogr. 59(2003) 672.
- 3- J.H. Weber; Inorg. Chem. 6 (1967) 258.
- 4- N.J. Long ; Angew. Chem. Int. Ed. Engl. 34 (1995) 21.
- 5- C. Sousa, C. Freire, and B. de Castro; Molecules, 8(2003) 894.
- 6- V. K. Singh, R. Sinha, R. Kant, and B. K. Sinha ; Asian J. Chem. 10(1998) 532.
- 7- L. T. Yildirm, and O. Atakol ; Cryst. Res. Technol. 37(2002)1352.
- 8- A. Pui; Croatia Chemica Acta, 75, (2002) 165.
- 9- A. D. Garnovski, and A. L. Nivorozhkin ; Coord. Chem. Rev., 126(1993) 1.
- 10- D. E. Hamilton, R. S. Drago, and A. Zombeck ; J. Am. Chem. Soc. 109(1987) 374.
- 11- X. Juan, L. Hua, G. Jin and Z. X. Zhang; J. Agric. food. Chem. 50(2002)3757.
- 12- L. Zie , X. Wang, and X. Day ; Synth. Commun. 30(2000)3791.
- 13- S. Akhanum, S. Shashikanth, and B. Sudha; Science Asia La., 383-392(2003).
- 14- A.A.EL-Emam, M.A.Moustafa, S.M. Bayomia, and M.B.EL-Ashmawy ; Journal Chinese Chemical Society ;36(1989)252.
- 15- B. Robret ; Studies In Conservation ,44(1998)121.
- 16- S. Bala, R.P. Gupta, M.L. Sachdeva, A. Singh, and H.K. Pujari; Indian J. Chem. 16B(1978)481.
- 17- M. Hejsek, and I. Wiedermanova ; Acta. Vniv. Chemica, 40(2000)15.
- 18- M.Y.S. Ahmed ; M.Sc. Thesis, University Of Mosul ,2006.
- 19- I.K. Jassim, and H.M. Abdullah ; Iraq J. Of Chemistry, 28(2002)3.
- 20- A.A. EL-Bindary, and A.Z. EL-Sonbati; Spectroscopy Lett., 32(1999)581.
- 21- P. Chattopadhyay , and C. Sinha ; Indian J. Chem. 35A(1996)523.
- 22- K. Nakamoto, " Infrared and Raman Spectra of Inorganic Coordination Compounds " Wiley press, New York , 4th Ed., 1986.
- 23- J. Arpalahiti , and P. Lehtikoinen ; J. Inorg. Chem., 29(1990)2564.
- 24- D. Nicholas ; " Texts in Inorganic Chemistry," Pergamon press, Oxford, 1st Ed., 1973.
- 25- B.N. Figgis, and J. Lewis ; "Modern Coordination Chemistry," Interscience, New York , 1960.
- 26- T. Mathur, U.S. Ray, J.C. Liou, T.H. Lu, and C. Sinha ; Polyhedron , 24(2005)739.
- 27- W.J. Geary ; Coord. Chem. Rev., 7(1971)81.

تحضير وتشخيص بعض معقدات قواعد شيف والمحتوية على حلقات غير متجانسة لايونات الكوبلت والنيكل والنحاس والخاصين الثنائية

صالح عبد الله احمد.

E.mail: scianb@yahoo.com

الخلاصة

يتضمن البحث تحضير معقدات فلزية لايونات الكوبلت (II) ، النيكل (II) ، النحاس (II) والخاصين (II) مع ليكاندات جديدة لقواعد شيف ن [5- (فنيل) 2- (امينو) -1,3,4- ثايادايازول بنزيلدين] (L1) و ن [5- (فنيل) 2- (امينو) -1,3,4- ثايادايازول -4- ن- ثنائي مثيل بنزيلدين] (L2) . شخصت الليكاندات المحضرة ومعقداتها بوساطة التحليل الطيفي الذري والأشعة تحت الحمراء والأطياف الالكترونية كما درست التوصيلية المولارية والخواص المغناطيسية لهذه المعقدات. ومن خلال نتائج البحث تبين أن الليكاندات تسلك سلوك كليكاندات متعادلة ثنائية السن وترتبط مع جميع الايونات الفلزية بنسبة مولية 1:2 (فلز : ليكاند) تم اقتراح الشكل الثماني السطوح لجميع المعقدات الفلزية بالاعتماد على نتائج التحليل التي تم الحصول عليها.