

Synthesis and Study of Spectral Characterization of N₂O₂ Type Schiff Base Metal Complexes

Akram A. Mohammed

Department of Chemistry, College of Education, University of Mosul, Mosul, Iraq

(Received 5 / 11 / 2007 , Accepted 31 / 12 / 2007)

Abstract

Novel N₂O₂ type Schiff base and its metal complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) have been synthesized from the Schiff base (H₂L) 4[N-(2-hydroxyacetophenone)imino]antipyrinyl-2-amino-2-methyl-1-propanol derived from 4-aminoantipyrine, o-hydroxyacetophenone and 2-amino-2-methyl-1-propanol. Structural features of the complexes have been deduced from metal analyses, infrared, electronic spectra, magnetic susceptibility and conductivity measurements. All complexes were found to have the composition of [ML] type. IR spectra show that the ligand is coordinated to the metal ions in a tetradentate manner. The electronic and magnetic susceptibility data of the complexes suggest a square planar geometry around the central metal ion. The molar conductance data reveal that the complexes are non-electrolytes.

Keywords : Schiff base, tetradentate, N₂O₂ type, metal complexes, 4-aminoantipyrine

Introduction

Schiff bases are characterized by the -N=CH-(imine) group which is important in elucidating the mechanism of transamination and racemisation reactions in biological systems [1,2]. Due to the great flexibility and diverse structural aspects, a wide range of Schiff bases have been synthesized and their complexation behaviour studied [3-6]. Literature survey shows that Schiff base complexes have wide range of applications on the industrial scale, such as dyes and pigments [7]. Another area of application of these Schiff bases is analytical chemistry where some of these compounds are used as ligand in complexometry topic [8]. For a long time tetradentate Schiff base complexes have attracted many interests in the field of coordination chemistry [9-12]. Also tetradentate Schiff bases with a N₂O₂ donor atom set are well known to coordinate with various metal ions [13,14]. Schiff base of 4-aminoantipyrine and its complexes have a variety of applications in biological, clinical, analytical and pharmacological areas [15-17]. The coordinating property of 4-aminoantipyrine ligand has been modified to give a flexible ligand system, formed by condensation with a variety of reagents like aldehydes, ketons and carbazides [18,19]. Literature search reveals that no work has been done on the condensation process of 4-aminoantipyrine, o-hydroxyacetophenone and 2-amino-2-methyl-1-propanol. In this paper, the synthesis and characterization of metal complexes containing Schiff base derived from 4-aminoantipyrine, o-hydroxyacetophenone and 2-amino-2-methyl-1-propanol have been reported.

Experimental

Materials and methods :

All the chemical used throughout these investigations were of Merck, B.D.H., Aldrich or Fluka, used as supplied without further purification.

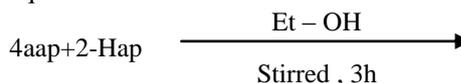
Analysis and physical measurements

The metal contents were determined following standard procedures (gravimetric methods) after decomposition with conc. HNO₃ [20]. Melting points measurements were measured using Richerk-Jung Heizbank apparatus. Molar conductance measurements were carried out using a 10⁻³M solution in dimethylformamide (DMF) on a LF-42 conductivity meter at room temperature. Infrared spectra were recorded on a Bruker (tensor 27) spectrophotometer in the 4000-400 cm⁻¹ range using KBr disc. Electronic spectra were recorded on a Shimadzu

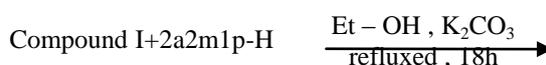
160 spectrophotometer at 25C⁰ for 10⁻³ M solution in DMF using a 1 cm quartz cell. Magnetic susceptibility measurements of the complexes in the solid state were determined by the Fraday method at room temperature using a Bruker BM6 apparatus.

Synthesis of the ligand (H₂L)

The ligand was prepared according to the following equations :



4[N-(2-hydroxyacetophenone)imino]antipyrine (Compound I).



(H₂L) (Schiff Base Ligand).

4-Aminoantipyrine (4aap) (0.01 mol) in ethanol was stirred with o-hydroxyacetophenone (2-Hap) (0.01 mol) for ~3h. The solid product was filtered and recrystallized from ethanol. This solid (0.01 mol) was refluxed in ethanol with 2-amino-2-methyl-1-propanol (2a2m1p-H) (0.01 mol) for ~18 h in presence of anhydrous potassium carbonate. The potassium carbonate was filtered off from the reaction mixture and solvent was evaporated. The brown solid separated was filtered and recrystallized from ethanol.

Synthesis of the complexes

All the complexes were prepared by the same general method : A solution of metal (II) chloride in ethanol (0.01 mol) was refluxed with an ethanolic solution of the ligand (0.01 mol) for ~7 h. The solution was then reduced to one-third of its volume on a water bath and was kept at a refrigerator for ~20 h. The solid product formed was separated by filtration, washed with ethanol and then air dried.

Results and discussion

All the prepared complexes are air stable. Their analytical data together with some physical properties are summarized in Table1. The data from complexes correspond well with the general formula [ML]. The monomeric nature of the complexes was evidenced from their magnetic susceptibility values (Table3). Study of magnetic and electronic spectral data is quite informative in characterizing the geometry of the complexes. These complexes were non-electrolytic [21] due to the low conductivity values (Table1).

Table (1) : Physical and analytical properties of the ligand and its complexes

Compound	Colour	m.p c ⁰	Yield %	% Metal		$\Lambda_M(\text{DMF})$ cm ² ohm ⁻¹ mol ⁻¹
				Calcd.	Found	
H ₂ L	Brown	152	62	-----	-----	-----
CoL	Red	207	50	13.11	12.72	6
NiL	Reddish brown	234	71	13.06	12.87	9
CuL	Dark brown	193	62	13.99	14.23	17
ZnL	Dark yellow	245	68	14.33	14.08	12
CdL	Milk brown	251	59	22.27	21.93	15

IR spectra

The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. The IR spectrum of the ligand showed a broad band in the region 3446 cm⁻¹, assignable to intramolecular hydrogen bonded -OH groups. The absence of this band, noted in the spectra of the complexes, indicates the deprotonation of the OH groups on complexation. A strong ligand band at 1250 cm⁻¹ has no corresponding bands in the metal complexes spectra, and is assigned to O-H bending vibration. This assignment is supported by the disappearance of the band when the hydroxyl hydrogen is replaced by a metal [22]. The spectrum of the ligand shows a C=N band in the region 1610 cm⁻¹, which

is shifted to lower frequencies in the spectra of all the prepared complexes (Table 2) indicating the involvement of -C=N nitrogen in coordination to the metal ion [23]. The C-O stretching vibrations appeared at 1303 cm⁻¹ in the Schiff base under a shift towards lower frequencies (13-32 cm⁻¹) in the complexes (Table 2). This shift confirms the participation of oxygen in the C-O-M bond [24]. Assignment of the proposed coordination sites is further supported by the appearance of new bands in the region 452-478 and 419-438 cm⁻¹ which could be attributed to the formation of M-O and M-N bonds respectively (Table 2).

Table (2) : Important I.R spectral bands (cm⁻¹)

Compound	ν (C=N)	ν (OH)/ δ (OH)	ν (C-O)	ν (M-O)	ν (M-N)
L	1610	3446/1250	1303	-----	-----
CoL	1574	-----	1290	469	419
NiL	1597	-----	1273	457	420
CuL	1579	-----	1282	452	425
ZnL	1580	-----	1271	478	431
CdL	1582	-----	1288	472	438

Electronic spectra and magnetic moments

The electronic spectral bands and magnetic moment values are given in Table 3. Although the square planar complexes of Co(II) are not very common, the electronic spectrum of Co(II) complex exhibit two bands at 16233 and 19531 cm⁻¹ in DMF solution. This is attributable to ²A_{1g} → ²B_{1g} and ²A_{1g} → ²E_g transitions, respectively, in square planar geometry. The magnetic moment of Co(II) complex was found to be 2.19 B.M. This may be to the mixing of the higher ligand field term ²A_{2g} with ²A_{1g} ground term on account of spin-orbit coupling whereby the magnetic moment of the cobalt complex goes above the spin value of 1.73 B.M [25-27] and also suggests a low spin square planar geometry. The Ni(II) complex shows two absorption bands at 16501 and 21459 cm⁻¹ due to ¹A_{1g} → ¹A_{2g} and ¹A_{1g} → ¹B_{1g} d-d transition

respectively, supporting the square planar structure of nickel complex. Also the nickel complex is diamagnetic suggesting square planar geometry for the metal ion [28, 29]. The Cu(II) complex shows two d-d absorption bands at 17421 and 21097 cm⁻¹ corresponding to ²B_{1g} → ²A_{1g} and ²B_{1g} → ²E_g transitions, respectively. These transitions apparently all occur under a broad envelop (Table 3).

A value of 1.81 B.M. for Cu(II) ion has been observed, which is well within the expected region found for square planar copper(II) complex [29,30]. The absorption spectra of Zn(II) and Cd(II) complexes shows no bands due to d-d transition. This phenomenon is natural as there is no possibility of transition due to non availability of empty d-orbital. These complexes are also found to be diamagnetic as expected for d¹⁰ configuration.

Table (3) : The electronic spectra and magnetic moments of the compounds

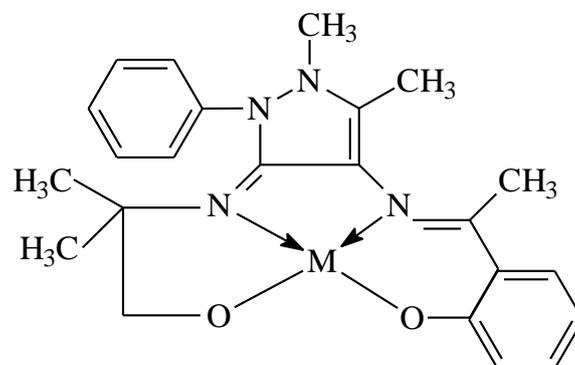
Compound	Solvent	Absorption region (cm ⁻¹)	Possible assignments	Magnetic moment (B.M)	Geometry
L	EtOH	42735	INCT*	-----	-----
CoL	DMF	16233	² A _{1g} → ² B _{1g}	2.19	Square planar
		19531	² A _{1g} → ² E _g		
		34722	INCT		
NiL	DMF	16501	¹ A _{1g} → ¹ A _{2g}	Diamagnetic	Square planar
		21459	¹ A _{1g} → ¹ B _{1g}		
		41493	INCT		
CuL	DMF	17421	² B _{1g} → ² A _{1g}	1.81	Square planar
		21097	² B _{1g} → ² E _g		
		40485	INCT		

*INCT = intraligand charge transfer band

Conclusions

In this paper, coordination chemistry of a Schiff base ligand, obtained from the reaction of 4 – aminoantipyrine, o-hydroxyacetophenone and 2-amino-2-methyl-1-propanol, is described. It acts as a tetradentate ligand and forms stable complexes with transition metal(II) ions

such as cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) in ethanol. The ligand and its complexes were characterized by spectral and analytical data. Based on these data, a square planar geometry has been assigned for the monomeric metal complexes as shown in the following figure:



M = Co(II) , Ni (II) , Cu(II) , Zn (II) or Cd(II)

Figure (1) : The proposed structure of the complexes

References

1. K.Y. Lau, A. Mayr and K.K. Cheung, *Inorg. Chim. Acta*, 285 (1999) 223.
2. A.S. Shawali, N.M.S. Harb and K. O. Badahdah, *J. Hetero. Chem.*, 22 (1985) 1397.
3. J. Wagler and G. Roewer, *Inorg. Chim. Acta*, 360 (2007) 1717.
4. S. Chattopadhyay, M.G.B. Drew and A. Ghosh, *Polyhedron*, 26 (2007) 3513.
5. J.J.V. Eynde and D. Fromont, *Bull. Soc. Chim. Belg.*, 106 (1997) 393.
6. A. Mukhopadhyay and S. Pal, *Polyhedron*, 23 (2004) 1997.
7. A.E. Taggi, A.M. Hafez, H. Wack, B. Young, D. Ferraris and T. Lectka, *Am. Chem. Soc.*, 124 (2002) 6626.
8. M.C.R. Arguelles, M.F. Belicchi, F. Bisceglie, C. Pelizzi, G. Pelosi, S. Pinelli and M. Sassi, *J. Inorg. Biochem.*, 98 (2004) 313.
9. A. Berkessel, M. Frauenkon, T. Schwenkreis and Steinmetz, *J. Mol. Catal. A., Chem.*, 117 (1997) 339.
10. L.A. Kovbasyuk, I.O. Fritzy, V. N. Kokozay and T.S. Iskenderov, *Tetrahedron*, 16 (1997) 1723.
11. A. Nishinaga, T. Tsutsui and H. Moriyama, *J. Mol. Catal.*, 83 (1993) 117.

12. M. Amirnasr, R. Vafazadeh and A.H. Mahmoudkhani, 21. W.J. Geary, Coord. Chem. Rev., 7 (1971) 81.
 Can. J. Chem., 80 (2002) 1196. 22. N.K. Jha and D.M. Joshi, Synth. Inorg. Met. -Org. Chem.
 13. H. Koksai, M. Dolaz, M. Tumer and S. Serin, Synth., 14(1984) 455.
 Inorg. Met.-Org. Chem., 31 (2001) 1141. 23. M. Thankamony and K. Mohanan, Indian J. Chem., A46
 14. A. Ghames, T. Douadi, D. Haffar, S. Chafaa, M. Allain,(2007) 249.
 M.A. Khan and G.M. Bouet, Polyhedron, 25 (2006) 3201. 24. G.Wang and J.C. Chang, Synth. Inorg. Met. -Org.
 15. T. Titoshi, N. Tamao, A. Hideyuki, F. Manabu and M.Chem., 24 (1994) 1091.
 Takayuki, Polyhedron, 16 (1997) 3787. 25. C. Natarajan and M. Palaniandavar, J. Indian Chem. Soc.,
 16. T. Punniyamurthy, S.J.S. Kalra and J. Iqbal, Tetrahedron60 (1983) 1.
 Lett., 36 (1995) 8497. 26. K.C. Satpathy, H.P. Mishra and B. N. Patel, Indian J.
 17. G.S. Trivedi and N.C. Desai, Indian J. Chem., B31 (1992) Chem., 22A (1983) 338.
 366. 27. R.L. Carlin, "Transition Metal Chemistry", Merce
 18. A. Kriza, A. Reiss, S. Florea and Caproiu, J. IndianDekker, Vol. I, (1995).
 Chem. Soc., 77 (2000) 207. 28. R. Dingle, Inorg. Chem., 10 (1968) 1141.
 19. N. Dharmaraj, P. Viswanathamurthi and K. Natarajan,29. R.L. Duta and A. Syamal, "Elements of Magneto-
 Trans. Met. Chem., 26 (2001) 105. Chemistry", Elsevier, 2nd Ed., New Delhi (1992).
 20. A.I. Vogel, "A Textbook of Quantitative Inorganic30. A.B.P. Lever, "Inorganic Electronic Spectroscopy",
 Chemistry", 3rd ed., John Wiely, (1971). Elsevier, Amsterdam (1984).

تحضير ودراسة خصائص طيفية لمعقدات فلزية لقاعدة شيف نوع N_2O_2

أكرم عبد القادر محمد

قسم الكيمياء، كلية التربية، جامعة الموصل، الموصل، العراق

(تاريخ الاستلام: ٥ / ١١ / ٢٠٠٧، تاريخ القبول: ٣١ / ١٢ / ٢٠٠٧)

الملخص

تم تحضير عدد من معقدات فلزية لايونات الكوبلت (II)، النيكل (II)، النحاس (II)، الخارصين (II) والكادميوم (II) مع قاعدة شيف نوع N_2O_2 (H₂L)،
 ٤ إن (٢-هيدروكسي اسيتوفينون) ايمينو [انتيبايرينيل -٢-امينو -٢-مثيل -١-بروبانول المشتقة من ٤-امينو انتيبايرين، اورثوهيدروكسي اسيتوفينون و ٢-
 امينو -٢-مثيل -١-بروبانول. شخصت المعقدات بالطرق الفيزيائية، الكيميائية والطيفية المعروفة.
 اوضحت النتائج المستحصلة للمعقدات بانها تمتلك الصيغة العامة [ML]. اظهر طيف الاشعة تحت الحمراء عمل الليكاند بشكل رباعي السن. اثبتت
 قياسات المغناطيسية والاطياف الالكترونية بنية المربع المستوي لجميع المعقدات. دلت قياسات التوصيلية الكهربائية لهذه المعقدات بانها غير الكتروليتية.