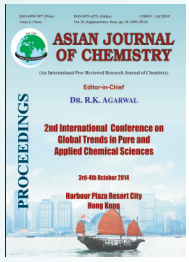
Asian Journal of Chemistry; Vol. 26, Supplementary Issue (2014), S163-S166

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.19037



Synthesis and Characterization of Metal Complexes of Schiff Base Ligand Derived from Isonitrosoacetophenone and Hydrazine

JYOTI V. PATIL* and N.B. LAXMESHWAR

Department of Chemistry, D.G. Ruparel College of Arts, Science and Commerce, Senapati Bapat Marg, Mahim, Mumbai-400 016, India

*Corresponding author: E-mail: patil_jyotiv@yahoo.co.in

Published online: 24 December 2014; AJC-16462

The complexes of Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with Schiff base ligand, namely 1-phenyl-1-hydrazonyl 2-oximino 1,2-ethanedione (HPHOED) have been synthesized *in situ* by the reaction of isonitrosoacetophenone (phenyl glyoxaldoxime *i.e.*, Hpgaldox) with hydrazine sulphate and metal chloride. The complexes have been characterized by various physico-chemical methods. The analytical data corresponds to the general formula $ML_2 \cdot xH_2O$ where L is deprotonated ligand HPHOED, M is a divalent metal ion and x = nil or 2 while the Cr(III) complex of the Schiff base ligand can be formulated as $CrL_2Cl \cdot H_2O$. The analytical and infrared spectral data also indicates that the ligand HPHOED act as monobasic bidentate ligand. The electrical conductance in nitrobenzene solution indicates their non-electrolytic nature. The room temperature magnetic susceptibility measurements suggest an octahedral geometry for the complexes, which is further supported by their diffuse reflectance spectra. The infrared spectra of the complexes of Cr(III), Cu(II), Zn(II) and Cd(II) with HPHOED indicate bonding through imino nitrogen and oximino oxygen in case of symmetrical structure involving six membered chelate rings while the infrared spectra of the Mn(II), Co(II), Ni(II) complexes of HPHOED indicate bonding through imino and oximino nitrogen in case of an asymmetrical structure involving five and six membered chelate rings.

Keywords: Schiff base, Isonitrosoacetophenone, Metal complexes, Diffuse reflectance spectra.

INTRODUCTION

In view of potential interesting structural features and properties, we considered it worthwhile to attempt synthesis of some transition and non-transition metal complexes of Schiff base ligand derived from phenyl glyoxaldoxime and hydrazine. The complexes have been characterized by various physico-chemical methods.

EXPERIMENTAL

All the chemicals used were of AR grade. Solvents were purified and doubly distilled before use. Isonitrosoacetophenone was prepared by the procedure described by Welcher[1]. Schiff base ligands derived by the reactions of isonitrosoacetophenone, an oximino ketone with organic compound containing amino group like hydrazine. The Schiff base derivatives could not be isolated in the free state. Hence their metal complexes were prepared *in situ* by the following procedure.

The alcoholic solutions of isonitrosoacetophenone, hydrazine sulphate and metal chloride were mixed in stoichiometric proportions [(2:2:1) for divalent metal ions; (3:3:1) for trivalent metal ion]. Little water was required to be added to ensure complete dissolution of hydrazine sulphate. The solution was refluxed for 4 h [30 min for Cu (II), Zn(II) and Cd(II)]. The pH of the mixture was then raised to about 8 with dilute NaOH solution (0.1 N) when solid metal complexes were obtained. These were digested on hot water bath for 0.5 h, filtered, washed repeatedly with hot water and 20 % alcohol and dried at 110 °C. Metal contents in the complexes were estimated by standard methods. Conductance values were measured in nitrobenzene at 10^{-3} M concentration. The infrared spectra were recorded in KBr disc on Perkin-Elmer FTIR spectrophotometer. The reflectance spectra of the complexes in the visible range were taken on Carl-Zeiss VACU 2P Jena spectrophotometer. The magnetic susceptibility measurement were carried out by Gouy method using $Hg[Co(SCN)_4]$ as a calibrant. The ESR spectra of Cu(II) complexes were recorded on a varian-eline, E-112 Eletron Spin Resonance spectrometer using TCNE as standard.

Thermogravimetric studies of the complexes were also made to investigate the thermal properties. Complexes were screened against the standard strains of *Escherichia coli* and *Staphylococcus aureus* by Agar plate method.

RESULTS AND DISCUSSION

The transition metal complexes are colored while the non-transition metal complexes of Zn(II) and Cd(II) are either off-white or very faintly colored. The complexes are in general non-hygroscopic and thermally stable (at least up to 180 °C) indicating a relatively strong metal-ligand bonding. The analytical data of the metal complexes (Table-1) of divalent metal is consistent with their general formulation $ML_2 \cdot xH_2O$. Where L is deprotonated ligand 1-phenyl-1-hydrazonyl 2-oximino 1,2-ethanedione (HPHOED), M is divalent metal ion and x = 0 or 2. The Cr(III) complexes of the Schiff base ligand can be formulated as $CrL_2Cl \cdot H_2O$.

The analytical data also indicates that the ligand HPHOED and acts as monobasic bidentate ligand. The molar conductance values for the complexes in nitrobenzene solution at 10^{-3} M concentrations are in the range of 0.012-0.692 mho cm^2mol^{-1} indicating their non electrolytic nature[2].

Magnetic moments: The magnetic moments are consistent with the proposed octahedral configuration for transition metal complexes, except Cu complex. The experimentally observed magnetic moment for Cu(II) complex is slightly higher than spin-only value of 1.73 B.M. expected for d^9 system with one unpaired electron and is in the range normally found for Cu(II) complexes[3] (Table-1).

TABLE-2
MAGNETIC SUSCEPTIBILITY DATA OF METAL COMPLEXES OF 1-PHENYL 1-HYDRAZONYL 2-OXIMINO 1,2-ETHANEDIONE

Compound	μ_{eff} (BM)	Geometry
$Cr(PHOED)_2Cl \cdot H_2O$	3.82	Octahedral
$Mn(PHOED)_2$	5.95	Octahedral
$Co(PHOED)_2$	4.77	Octahedral
$Ni(PHOED)_2$	3.00	Octahedral
$Cu(PHOED)_2$	1.87	Square planar

At room temperature

FTIR spectra: The FTIR spectra of the metal complexes of HPHOED are quite complex as they in general contain large number of bands of varying intensities. The task of assigning these bands without ambiguity is rendered difficult as the spectrum of Schiff base ligand HPHOED is not available for comparision since the complexes have been prepared *in situ* by reaction of constituent ligand with appropriate metal salts. However several structurally significant bands have been evaluated on the basis of the reported positions of these bands in the spectra of related compounds like imino complexes of some carbonyl oxime, Hpgaldox[4] and hydrazine (Table-2).

Some common features of infra red spectra are noteworthy: (i) The spectra of all the metal complexes do not show strong band due to C=O stretching frequency observed at 1675 cm^{-1} in the spectrum of Hpgaldox. This indicates successful Schiff base formation by the reaction of carbonyl oxygen of Hpgaldox with the amino group of hydrazine prior to the complex formation; (ii) Since two types of C=N linkages due to presence of azomethine and oxi imine groups in proposed ligand HPHOED, two absorption bands attributable to ν(C=N) (azomethine) and $\nu_{C=N}$ (oximino) frequencies are expected to be present in the spectra of their metal complexes. But the spectra of these metal complexes show two bands in the regions 1615-1506 cm^{-1}. The bands around 1615-1575 cm^{-1} are assigned to azomethine group, where as those around 1595-1506 cm^{-1} are attributed to oximino C=N vibrations; (iii) Metal complexes of HPHOED show two bands in the range of 3558-3200 cm^{-1} which are attributed to symmetric and asymmetric ν(N-H) stretching vibrations of $-NH_2$ group; (iv) An oxime group is known to co-ordinate through either its nitrogen or oxygen donar atoms. In the metal complexes with ligand, in which oxime group co-ordinates through nitrogen atom, the formation of N → O linkage is an essential feature which is observed[4,5-11] as a medium strong intensity band around 1300-1200 cm^{-1}. On the other hand bonding through oximino oxygen atom entails a band due to N-O stretching vibrations at around 1100-1000 cm^{-1}. Presence of only one band ν(N→O) around 1300-1200 cm^{-1} would mean bonding essentially through oximino nitrogen. Conversely a single band around 1100-1000 cm^{-1} would mean bonding only through oxygen atom of the oxime group.

In case of bidentate imino-oximes of the type under present investigation, the appearance of only one ν_{N-O} band in the region around 1100-1000 cm^{-1} in complexes of divalent metal ions of the type $ML_2 \cdot n \cdot H_2O$ (n = nil or 2) would mean a $M\text{-}N_2O_2$ chromophore with a symmetrical six membered ring structure involving bonding only through oximino oxygen donor. A $M\text{-}N_3O$ type of chromophore with an unsymmetrical structure containing five and six membered chelate rings shows a band in both the regions around 1300-1200 and 1100-1000 cm^{-1}; (v) The I.R. spectra of Cr(III), Zn(II) and Cd(II) complexes reveal a broad band in the region 3600-3200 cm^{-1}. The position and shape of this band indicate that they are not due to ν(O-H) stretching vibrations of =NOH group, it may be attributed to presence of coordinated water molecules. Presence of water molecules is further supported by thermal studies (Table-3).

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF METAL COMPLEXES OF 1-PHENYL-1 HYDRAZONYL 2-OXIMINO 1,2-ETHANEDIONE

Compound	Colour (formula weight)	Decomposition temp. (°C)	Elemental analysis (%) found/(calculated)				Molar conductance* mho cm^2 mol^{-1} at10^{-3} M
			M	C	N	H	
$Cr(PHOED)_2Cl \cdot H_2O$	Blue black (429.5)	> 260	12.50 (12.11)	44.10 (44.70)	19.25 (19.56)	4.5 (4.19)	0.167
$Mn(PHOED)_2$	Light brown (379.0)	180	14.36 (14.51)	50.71 (50.66)	21.75 (22.16)	5.0 (4.22)	0.054
$Co(PHOED)_2$	Dark brown (382.9)	220	15.56 (15.40)	49.80 (50.13)	22.30 (21.93)	4.4 (4.18)	0.383
$Ni(PHOED)_2$	Green (382.7)	220	15.05 (15.34)	50.86 (50.16)	21.60 (21.95)	3.6 (4.18)	0.434
$Cu(PHOED)_2$	Brownish green (387.6)	260	16.15 (16.40)	49.92 (49.54)	21.45 (21.67)	3.21 (4.13)	0.692
$Zn(PHOED)_2 \cdot 2H_2O$	Brown (425.38)	>255	15.90 (15.37)	45.96 (45.14)	20.18 (19.75)	4.8 (4.7)	0.012
$Cd(PHOED)_2 \cdot 2H_2O$	Offwhite (472.4)	>300	24.10 (23.80)	40.05 (40.64)	17.65 (17.78)	4.4 (4.23)	0.114

* in nitrobenzene

TABLE-3
SOME IMPORTANT FTIR BANDS FOR METAL COMPLEXES OF 1-PHENYL-1 HYDRAZONYL 2-OXIMINO 1,2-ETHANEDIONE AND THEIR ASSIGNMENTS

Compound	ν(O-H) (H_2O) (cm^{-1})	ν(N-H) (cm^{-1})	ν(C=N) (Azomethine) (cm^{-1})	ν(C=N) (Oximino) (cm^{-1})	ν(C=C) (Phenyl) (cm^{-1})	ν(N →O) (cm^{-1})	ν(N-O) (cm^{-1})	ν(N-N) (cm^{-1})	ν(M-N) (cm^{-1})	ν(M-O) (cm^{-1})
$Cr(PHOED)_2Cl·H_2O$	3280	3382	1615	1595	1444	-	1045	865	612	524
$Mn(PHOED)_2$	-	3558, 3474	1595	1580	1455	1191	1039	885	590	492
$Co(PHOED)_2$	-	3500, 3292	1596	1562	1454	1229	1070	890	612	375
$Ni(PHOED)_2$	-	3450, 3309	1598	1562	1459	1198	1038	888	615	508, 411
$Cu(PHOED)_2$	-	3500, 3221	1593	1559	1460	-	1062, 974	889	617	500
$Zn(PHOED)_2·2H_2O$	3360	3360	1575	1506	1440	-	1030	830	600	450
$Cd(PHOED)_2·2H_2O$	3274	3274, 3200	1575	1509	1435	-	1004	-	606	523, 477

Eletronic spectra: The σ and π-electron system of the Schiff base ligand HPHOED is expected to undergo substantial change on co-ordination with the metal ion. Effect of perturbation due to metal ion can be examined by electronic spectra of the ligand and its metal complexes. It gives wealth of information on geometry and electronic structure of the metal complexes. All the metal complexes show intra-ligand transitions in the ultra-violet region. The band observed at 47620 cm^{-1} is assigned to σ-σ* intra ligand transitions while the bands in the range 39370-30120 cm^{-1} may be ascribed to π-π* transitions.

In case of Zn(II)and Cd(II) complexes the charge transfer transitions seem to be tailing into visible region and appear to be responsible for observed colour of the complexes (Table-4).

ESR spectrum: The ESR spectrum of $Cu(PHOED)_2$ was recorded at room temperature as well as at liquid nitrogen temperature (LNT) in chloroform solution. The two g values obtained from spectrum, g‖ and g⊥ follows the trend g‖ > g⊥ > 2.0023 characteristically indicating tetragonally distorted octahedral geometry. The g‖ value is less than 2.3 which indicate covalent charcter of complex, further the value is consistent with the mixed Cu-N and Cu-O bonded copper complex. The g⊥ value is less than 2.1 which indicates tetragonal distortion and presence of an unpaired electron in dx^2-y^2 ground state in an elongated axial symmetry. G factor[12] is higher than 4 indicating that Cu-Cu exchange interactions are largely absent. The hyperfine splitting parameters A‖ and $A\perp_{values}$ obtainted from the spectrum are in the range of co-valent Cu(II) complex[13]. The A‖ value could be used to obtain a factor $\alpha^2 = 0.505$ indicate appreciable co-valent character of complex (Table-5).

TABLE-4
ELECTRONIC SPECTRAL DATA OF METAL COMPLEXES OF 1-PHENYL1- HYDRAZONYL

Sr. no.	Compound	Observed band position λ_{nm} (ν cm^{-1})	Assignment (transition)
1	$Cr(PHOED)_2Cl·H_2O$	210 (47,620)	Intra-ligand
		280 (35,715)	Intra-ligand
		540 (18,518)	$^4A_{2g}\rightarrow{}^4T_{2g}$
2	$Mn(PHOED)_2$	210 (47,620)	Intra-ligand
		278 (35,971)	Intra-ligand
		*395 (25,316)	Charge transfer
		*450 (22,222)	$^6A_{1g}\rightarrow{}^4T_{1g}(G)$
		*600 (16,666)	$^6A^{1g}\rightarrow{}^4T_{2g}(G)$
3	$Co(PHOED)_2$	210(47,620)	Intra-ligand
		289(34,602)	Intra-ligand
		350(28,571)	Charge transfer
		380(26,315)	Charge transfer
		*370(27,027)	Charge transfer
		*430(23,255)	Charge transfer
		*490(20,408)	$^4T_{1g(F)}\rightarrow{}^4T_{2gF})$
		*1150(08,695)	$^4A_{1g(F)}\rightarrow{}^4T_{1g(P)}$
4	$Ni(PHOED)_2$	210(47,620)	Intra-ligand
		254(39,370)	Intra-ligand
		*390(25,641)	Charge transfer
		*690(14,493)	$^3A_{2g}\rightarrow{}^3T_{1g(F)}$
		*1050(09,523)	$^3A_{2g}\rightarrow{}^3T_{2g}$

PMR Spectra: Attempts were made to record the PMR spectra of metal complexes of HPHOED to seek the information on mode of bonding in these metal complexes and also to derive a co-relation between the observed chemical shifts of various protons.

Limited solubility in suitable solvents and paramagnetic nature of complexes lead to noisy base line and broadening of signals, did not yield PMR spectra of satisfactory quality. Comparison of PMR spectra of metal complexes of HPHOED with that of HPgaldox indicate that oximino protons of the parent ligand HPHOED observed at -1.40τ in dioxane[14] or at 0.94τ in $CDCl_3$ is missing in the spectra of metal complexes. Complex formation takes place by replacement of hydrogen atom of the oxime functional group by the metal ion. The phenyl protons are observed as complex multiplets in most cases in the range 2.50-2.75τ. Amine protons are usually observed as a sharp peak in the range 8.45-8.75τ. A considerable shift is indicative of involvement of $–NH_2$ protons in co-ordination[14].

Thermal studies: Non transition metal complexes of the Schiff base ligand were subjected to thermo gravimetric (TG) and differential thermal analysis (DTA). The TG analysis shows that they are thermally stable, they show a very small gradual loss in weight in the temperature range 20-80/100 °C. This indicates the absence of any lattice or crystal water. Presence of water molecule in the complexes can be computed on the basis of percentage weight loss which is supported by IR studies of Zn(II) and Cd(II). The gradual loss of two water molecules

TABLE-5
ESR PARAMETERS* FOR CU(II) COMPLEX OF HPHOED

Compound	g‖	g⊥	g_{av}	A‖	A⊥	A_{av}	G	α^2
$Cu(PHOED)_2$	2.148	2.028	2.068	110	20.0	50.0	5.29	0.505

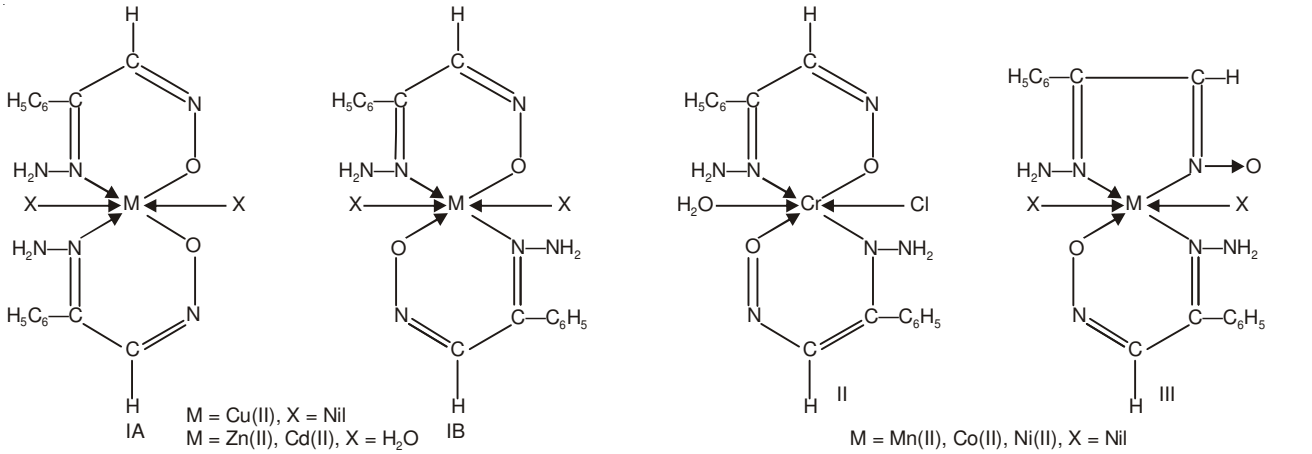


Fig. 1

is observed below 220 and 315 °C for Zn(II) and Cd(II), respectively.

The DTA curve for $Zn(PHOED)_2 \cdot 2H_2O$ reveals an endothermic drift during the loss of first water molecule and an endothermic peak on the loss of second water molecule. The DTA curve for $Cd(PHOED)_2 \cdot 2H_2O$ exhibits and endothermic drift followed by two endothermic peaks at 295 and 315 °C accompanying the loss of each water molecule. The temperature at which these losses are observed suggest that the two water molecules are co-ordinated to the metal ions. Thus confers octahedral geometry for these complexes.

Antimicrobial activity: Complexes were screened against the standard strains of Gram-positive bacteria *Staphylococcus aureus* and Gram-negative bacteria *Escherichia coli* by Agar plate method[15]. Results were evaluated by measuring zone inhibition diameters. Co(II) complexes show moderate activity against bacteria.

Conclusion

Ligand HPHOED acts as a monobasic bidentate ligand, which loses oximino proton during formation of Schiff base complexes which is supported by infrared spectra. Electronic spectra & magnetic susceptibility measurement reveals Octahedral geometry for Cr(III), Mn(II), Co(II), Ni(II), Zn(II) and Cd(II) complexes and square planar geometry for Cu(II) complexes (Fig. 1).

ACKNOWLEDGEMENTS

Thanks to Dr. N.V. Thakkar, Former Professor, The Institute of Science, Mumbai, for his help and constant encouragement.

REFERENCES

1. F.J. Welcher, Organic Analytical Reagents, Vol III, D. Van Nostrand (1955).
2. W.J. Geary, *Coord. Chem. Rev*., **7**, 81 (1971).
3. B.J. Hathaway and D.E. Billing, *Coord. Chem. Rev*., **5**, 143 (1970).
4. P.L. Pathak and B.C. Haldar, *J. Indian Chem. Soc*., **49**, 745 (1972).
5. S.S. Bodas, Ph. D. Thesis, University of Bombay (1983).
6. P.M. Dhadke and B.C. Haldar, *J. Indian Chem. Soc*., **56**, 461 (1979).
7. R.G. Deshmukh and N.V. Thakkar, *Indian J. Chem*., **24A**, 1066 (1985).
8. N.V. Thakkar and B.C. Haldar, *J. Inorg. Nucl. Chem*., **42**, 843 (1980).
9. N.J. Patel and B.C. Haldar, *J. Inorg. Nucl. Chem*., **29**, 1037 (1967).
10. A.R. Butler, A.M. Calsy and C. Glidewell, *Polyhedron*, **8**, 175 (1989).
11. U.B. Talwar and B.C. Haldar, *J. Inorg. Nucl. Chem*., **32**, 213 (1970).
12. I.M. Procter, B.J. Hathaway and P. Nicholls, *J. Chem. Soc. A*, 1678 (1968).
13. B.R. McGarvey, *J. Phys. Chem*., **60**, 71 (1956).
14. H.A. Szymansky and R.E. Yelin, NMR Handbook, FI/Plenum, N.Y., (1968).
15. S.S. Raphael, Lynch's Medical Laboratory, Saunders Co., edn 4, pp. 433-434 (1983).