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Synthesis and characterization of copper(II) complex of 3-methyl-2,6-diphenylpiperidin-4-one oxime

G. Thirunarayanan^{1,*}, K. Lakshmanan²

¹Department of Chemistry, Annamalai University, Annamalainagar - 608002, India

²Department of Chemistry, National College, Tiruchirappalli - 620001, India

*E-mail address: drgtnarayanan@gmail.com,
thirunarayanan.g.10313@annamalaiuniversity.ac.in

ABSTRACT

A novel six membered heterocyclic oxime namely 3-methyl-2,6-diphenylpiperidin-4-oneoxime was prepared from the condensation of 3-methyl-2,6-diphenylpiperidin-4-one and hydroxylamine hydrochloride. The obtained oxime was characterized by their physical, analytical and spectroscopic data. This oxime was utilized as ligand for preparation of the copper complex. The oxime belongs to bidentate ligand nature. The copper complex of this oxime was prepared by the conventional heating of ethanolic solution of this oxime and copper chloride pentahydrate. The obtained copper complex was analyzed by their physical constants, analytical, pH measurements, UV and IR spectral data. These physicochemical analysis results confirmed, the structure of the complex was octahedral.

Keywords: Piperidine-4-one, Piperidine-4-oneoxime, Complexation, Copper chloride, UV and IR spectra

1. INTRODUCTION

Coordination compounds are those molecular compounds formulated as consisting of a central atom or ion surrounded by a set of ions or small molecules, the later called ligands. The resulting compounds is often called a complex or, if it is charged, a complex ion. The set of ligands need not consist of several small, independent of atoms (or single atom) but may

involve fairly elaborate arrangements of atoms connecting those few that are directly bound to or coordinated to the central atom. Coordination compounds have always been a challenge to the inorganic chemists. In the early days of chemistry seemed unusual (hence the same "complex" ions) and seemed to defy the usual rules of valence. Today they comprise a large body of current inorganic research. A survey of articles in recent issues of the journal inorganic chemistry indicates that perhaps 70% could be considered to deal with coordination compounds [1-5]. Although the usual bonding theories can be extended to accommodate these compounds, they still provide stimulating problems to be resolved by the excellent physical techniques such as various spectroscopic, thermodynamical and magnetism.

Further the ligand field and molecular theories could explain all the experimental facts. Coordination compounds are very important for animal and plant kingdom. Blue copper proteins such as, stellacyanin, plastocyanin, azurin, chlorophyll and hemin the red colouring matters of blood etc., are all coordination compounds. Coordinating agents are often used in winning of metals from their ores, in electroplating catalyzing reactions and obtaining the effects of considerable catalysis in precipitation of metallic ions [1-5]. The reagents which form metal chelates are used extensively in both qualitative and quantitative analysis. Dimethylglyoxime, 8-hydroxyquinoline, Cupferron, Ferrouin etc., are substances which are indispensable in analytical separations and precipitations. In physiological chemistry the biuret reactions, the amino acid salts of heavy metals and medicinals of the pyrocatechol series are illustrated of useful chelate compounds. Copper in 2+ state forms a number of complexes in which the coordination number is generally 4 and 6. Ammonia a typical ligand of monodentate, forms a ammines of the type $\text{CuX}_2 \cdot n\text{NH}_3$ usually n having the values of 2, 4, 5 and 6. The diamines are polymeric in the solid state, the anion X forming a bridge between the metal atom as in $\alpha\text{-CuBr}_2 \cdot 2\text{NH}_3$, $\text{Cu}(\text{N}_3)_2 \cdot 2\text{NH}_3$, $\text{Cu}(\text{NCS})_2 \cdot 2\text{NH}_3$ and $\text{Cu}(\text{NH}_3)_2\text{Ag}(\text{SCN})_3$.

The complex $\text{Cu}(\text{NH}_3)_5(\text{ClO}_4)_2 \cdot \text{NH}_4\text{ClO}_4$ is one of the few cupric compounds which contains planar four coordinated copper [1-5]. Although a maximum of five ammonia molecules will coordinate to copper in aqueous solution, treatment of either the anhydrous chloride and bromide or the tetrammines of CuI_2 , $\text{Cu}(\text{ClO}_4)_2$, $\text{Cu}(\text{BF}_4)_2$ with liquid ammonia will give the hexammine $\text{Cu}(\text{NH}_3)_6\text{X}_2$, which are so unstable that they have stable at room temperature in an atmosphere of ammonia gas. But this is undergone distortion have the static tetragonally-distorted octahedral environment. Pyridine and substituted pyridine are similar to ammonia in forming strong complexes except that under circumstances a maximum of four pyridine molecules are able to complex with copper (II), even pure pyridine, cupric chloride gives only $\text{Cu}(\text{Py})_2\text{Cl}_2$. The compound $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{Py}$ loses two molecules of pyridine very readily and is thought to be $\text{Cu}(\text{Py})_4(\text{NO}_3)_2 \cdot 2\text{Py}$ because coordinated nitrate groups and both coordinated and uncoordinated pyridine are indicated by the infrared spectrum [1-5].

Alkylamines and anilines form complexes with a variety of cupric salts the copper (II) ion in the amine complexes are reduction to the cuprous state. The ligands strength of amines towards copper (II) are in the order, $\text{NH}_3 > \text{RNH}_2 > \text{R}_2\text{NH} > \text{R}_3\text{N}$.

The imidazole system behaves a typical monodentate amine complexes of the type $\text{Cu}(\text{L})_4\text{X}_2$ ($\text{X} = \text{I}^-, \text{Cl}^-, \text{NO}_3^-$) the ligand occupies four planar around copper the anion making distorted octahedral arrangement, the complex has complete distorted coordination.

The complexes of copper(II) with bidentate ligands containing nitrogen type, the typical of the bis(1,2-diaminoethane) salts, $\text{Cu}(\text{en})_2(\text{NO}_3)_2$, $\text{Cu}(\text{en})_2\text{Hg}(\text{SCN})_4$, $\text{Cu}(\text{en})_2(\text{ClO}_4)_2$ and $\text{Cu}(\text{en})_2(\text{SCN})_2$ and $\text{Cu}(\text{en})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ have been shown to have the nitrogen atoms of the two chelate molecule in a plane around the copper [1-5].

This chelate system is stable. The thermal stability of the chelate complexes was in the ligand order decreases by 1,2-diamino propane > 1,3-diamino propane. The electron spin resonance spectrum of the biuret ion $\text{Cu}(\text{C}_2\text{O}_2\text{N}_3\text{H}_4)_2^{2-}$ shows hyperfine coupling of the unpaired electron with the four nitrogen atoms in the plane around copper.

The 2,2-bipyridyl (bip = 2-pyridyl pyridine) is a powerful bidentate ligand but has different steric requirements to the diamine alkanes. Steric factors prevents the two bipyridyl ligands in $\text{Cu}(\text{bip})_2^{2+}$ from assuming square planar coordination around the metal and the most convenient way for the two ligands to coordinate with a cis configuration as found in the iodobis (2,2-dipyridyl) copper (II) ion. Schiff 's bases are those compounds containing azomethine group (R-C=N) are usually prepared by the condensation of a primary amine with an active carbonyl compound. Some of the Schiff 's bases are: 1. Salicylaldehyde based Schiff 's bases, 2. Vnalline based Schiff 's base and 3. The amine-guanine based Schiff 's base. The organic chelating ligands containing the oximes functional groups have been studied extensively, mainly its applications in analytical chemistry for the detection or separation of metal ions [1-5]. Tschugaeff first introduced dimethyl glyoxime as a gravimetric reagent for nickel and since then, analytical applications have been found for a variety of bidentate chelating oximes such as dioximes, acyloin oximes and aromatic-ortho hydroxyoximes. Numerous review have appeared [6-9] on various aspects of the chemical properties of metal oxime complexes including recent views on the structural chemistry transition of metal complexes [6,7-9].

Hydroximes are ambidentate with the potential of a variety of coordinate modes depending upon a number of stabilizing factors including steric hindrance, hydrogen bonding and electronic considerations. In a vast majority of the complexes reported the oximes function as bidentate chelating ligands bonding through the nitrogen and the oxygen of the phenolic group for the acyloin and aromatic ortho hydroxy oximes respectively.

The acyloin oximes also have been reported to act as neutral bidentate ligands with transition [10,11] metals in which [10,11] the hydroxime is coordinated through both the hydroxyl and oxime groups remaining as such without deprotonation. This coordination made usually occurs under acidic conditions. Electronic absorption spectroscopy has been used extensively for characterizing transition metal hydroximes complexed. The UV-Vis. Spectrum of nickel (II) complex with 2-hydroxy-4,5-methyl chalcone oxime resemble the spectra of other octahedral nickel (II) complexes [12].

Similarly, the electronic spectrum of the nickel (II) complexes with an aliphatic acyloin oxime has been reported to be typical of nickel square planar complexes [13] and the structure assigned accordingly. The infra-red spectra of transition metal hydroximes complexes have absorption in the $3600\text{-}2400\text{ cm}^{-1}$ region where hydroxyl stretching modes are found and the $1700\text{-}1500\text{ cm}^{-1}$ region were the C=N group generally absorbs. The shapes and position of the bands assigned to OH variations can be utilized to provided information on the nature of the bridging intramolecular hydrogen bond formed in the transition metal complexes.

Burger et. al. [14, 15] and Ramaswamy et al. [16] have examined the hydrogen bonding in a variety of substituted salicylaldoxime complexes and they have shown that strong hydrogen bridges are formed in all complexes and exists as trans /cis depending upon the metal. The exact frequency of the OH vibrations is often difficult to ascertain with any precision as a result of very broad bands which are often observed in the transition metal-hydroxime complexes. s with salicylaldoxime, salicylaldoxime acid complexes with transition metals were first prepared as a result of the use of the oxime as a gravimetric reagent for the detection and determination various ions in aqueous solution [17-19].

Cox [20] proposed a square planar structure of nickel salicylaldoxime in solid state by X-ray diffraction measurements. A similar structure was confirmed by Lingenfelter and co-workers [12, 22] for the copper salicylaldoxime derivative [23] in which the square planar units are linked through longer copper-oxygen bonds.

The studies on oximes themselves revealed the stabilization of C=N bond by [24-26] resonance with the nonbonding electron pair on the oxygen atom of the hydroxy imino group. Gurumurthy et al., [27] synthesized and characterized the titanium (IV) complexes of 2,6-diacetylpyridine dioxime. Infrared spectra, electronic spectra magnetic measurement and NMR spectral studies are indicated that the ligand as a bidentate chelating ligand as in the present complexes. Literature survey reveals that the oximes of piperidine-4-ones are subjected to kinetic and conformational investigations [27,28].

Harini et al. have studied the synthesis and antioxidant activities of some novel vanillin based piperidine-4-one oxime esters [29]. But the coordinating properties of the oxime of piperidine-4-one are not studied. The coordinating complexes of piperidine-4-ones are reported in literature [30,31].

2. EXPERIMENTAL

2. 1. Quantitative analysis

The cations and anions of the complex were estimated by standard methods³².

2. 1. 1. Estimation of chloride ion

The chloride ion was estimated by Volhard's method [32]. About 0.2g of complex was weighed accurately and transferred into a dry beaker. It is digested with AnalaR nitric acid. The solution was evaporated to dryness and residue is extracted with water. Thus the solution was made to 100 ml with distilled water. 20 ml of the solution was pipetted out into a beaker provided with a glass rod. 5ml of dilute nitric acid was added followed by 40 ml of the standard (0.01M) silver nitrate. The mixture was carefully warmed to coagulate the precipitate of silver chloride. It is cooled and filtered. The precipitate is washed with cold water till it is free from silver nitrate. About 1 ml of ferric alum indicator is added to the filtrate, and it is titrated against standardized (0.01M) ammonium thiosulphate solution taken in a burette. The red brown colour is the end point. From the values the volume of $\text{NH}_4\text{CNS}=\text{AgNO}_3$ reacted with the chloride solution is determined from which the amount of chloride in the solution is calculated.

2. 1. 2. Estimation of copper

Accurately 0.5g of the complex was taken in Jaldar flask, a pellet of potassium bromide and 5 ml of concentrated nitric acid were added and digested the content, to dryness the solid colourless mass was extracted with distilled water, to make 100 ml. Exactly 20 ml of the solution was pipetted out into a conical flask, 5ml of concentrated hydrochloric acid was added, followed by 20 ml of potassium iodide solution, the dark yellow solution was titrated against N/40 standardized thiosulphate solution taken in a burette. When a solution becomes pale yellow colour 1 ml of starch indicator was added to continue the titration, the end point was disappearance of blue colour. From the value of thiosulphate solution volume, the amount of copper was estimated.

2. 1. 3. Estimation of ligand

The ligand estimation was done by using C, H, N analysis.

2. 2. Electrical conductivity measurements [33]

The electrical conductivity measurement was done for the complex prepared to see whether anion of the metal salt in the complex was coordinated to the central metal or remained outside the coordination sphere. The conductance measurements is made in dimethylformamide solution at room temperature (35 °C) using Elico conductivity bridge model CM 82T with dip type cell. The cell constant of the conductivity cell is used 1.009. The concentration of the solution used for the measurements were the order of 10^{-3} M.

2. 3. Magnetic susceptibility measurement

The magnetic susceptibility of the complex at room temperature was measured by Guoy method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the calibrant. The magnetic susceptibility measurement of the complex is useful to determine the effective magnetic moment of metal atom in the complex. The effective magnetic moment of metal atoms was calculated from the equation [34].

$$\mu_{\text{eff}} = 2.84[\chi^{\text{m}}\text{T}]^{1/2} \text{ B.M.}$$

where: the χ^{m} is the molar magnetic susceptibility of the complex obtained after applying the diamagnetic correction using Pascal's constant.

2. 4. Infrared spectral Measurement

The Infrared spectral measurement is obtained using Perkin Elmer 783 spectrophotometer. The measurements for ligand and the complex were recorded in KBr pellets in the region $4000\text{-}400 \text{ cm}^{-1}$. The spectral measurements were done to the determine the site of attachment and strength of bonding. Shifts in various characteristic ligand vibrations such as (C-N-C), (N-H), (C=N) and (N-OH) stretching frequencies of complex in comparison to those of the free ligand enables us to determine the site of attachment of the metal complex.

2. 5. Electronic spectral measurements

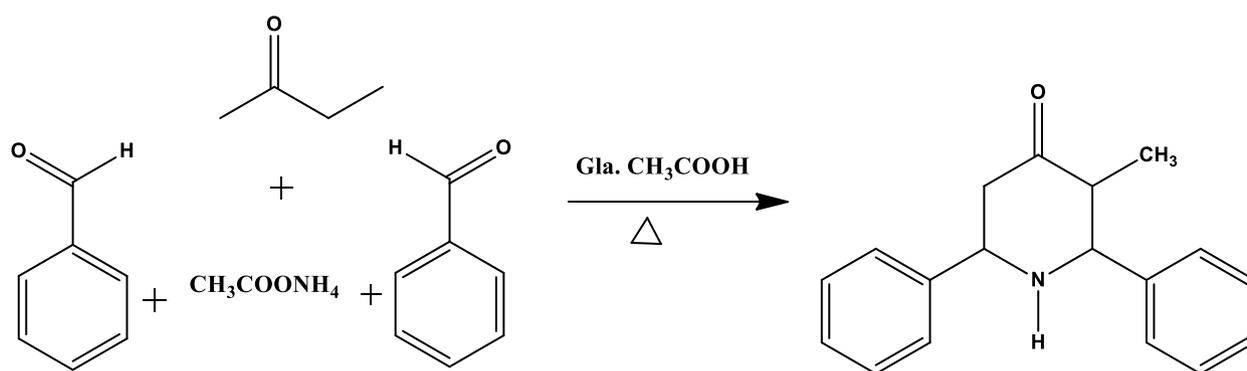
The electronic spectrum of the complex was measured in Ultraviolet – Visible region a HITACHI U – 3400 double beam UV-VIS-NIR spectrometer. The working range of the diffuse reflectance spectrophotometer is 200-900 nm. The UV range was not recorded due to failure of the UV source lamp. The electronic spectral measurement was used to assign the stereochemistry of metal ion in the complex based on the position and number of d-d transition peaks. In general, in the electronic spectra of transition metal complexes, the charge transfer band is found in the ultraviolet spectral region while much less intense band due to d-d transition appears in the visible region.

2. 6. Synthesis of ligand and complex

The synthesis of 3-methyl-2,6-diphenyl piperidin-4-one oxime was based on Mannich and related reactions reported in the earlier literature [35, 36].

2. 6. 1. Preparation of 3-methyl-2,6-diphenyl piperidin-4-one

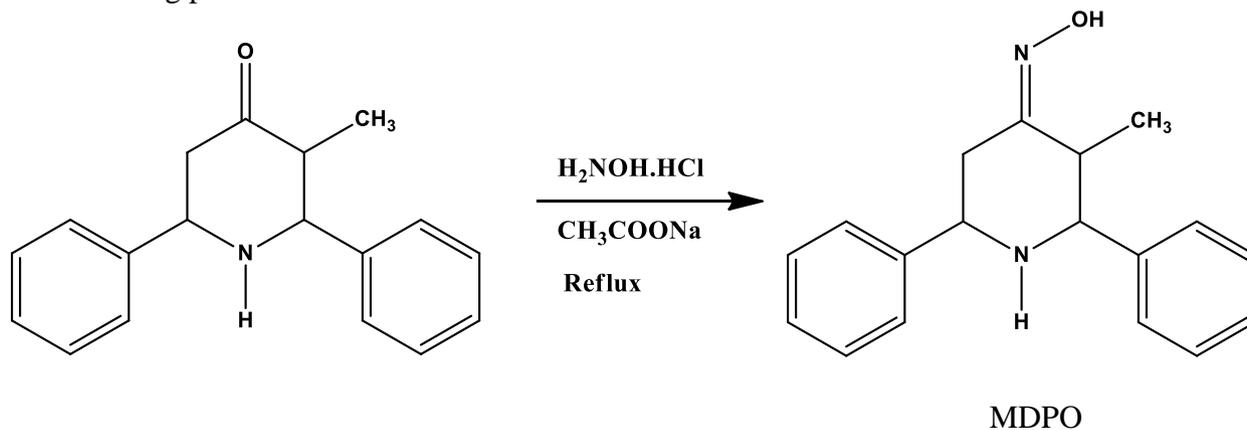
About 53g (0.5 mol) of freshly distilled benzaldehyde and 18g (0.25 mol) of freshly distilled ethyl methyl ketone and 19.5g (0.25 mol) of ammonium acetate were taken in 400 ml beaker. 20 ml of glacial acetic acid was added. Now the mixture was heated to 85 °C and then allowed to cool to room temperature, kept aside as such for 24h (**Scheme 1**). The product separated as a solid mass, then the free base was converted to hydrochloride and separated hydrochloric acid (slightly excess) into ether solution of base. The piperidone hydrochloride, the insoluble component in ether was filtered by suction and washed with ether in which the ether components can go into solution. The filtered hydrochloride was converted into free base by adding liquid was obtained then by dilution with water it formed a yellow solid. Then the solid was filtered, dried and weighed. It was recrystallized using 95% ethanol. The melting point of the piperidone was 88 °C in agreement with the value given in literature [36].



Scheme 1. Synthesis of 3-methyl-2,6-diphenyl piperidin-4-one

2. 6. 2. Preparation of 3-methyl-2,6-diphenyl piperidin-4-oneoxime (MDPO)

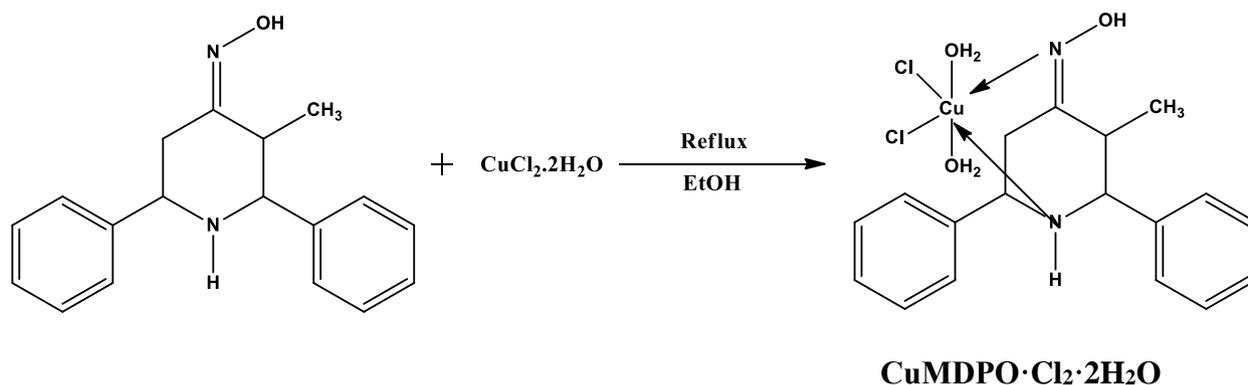
The piperidone (0.1 mol) was dissolved in ethanol (50 ml). Saturated solution of hydroxylamine hydrochloride and sodium acetate in water were added. The mixture was refluxed in a water bath for one hour (**Scheme 2**). Then it was cooled, poured into the water and the solid oxime obtained was filtered. The oxime was recrystallized from ethanol [36,37]. The melting point of the oxime was 188-189 °C.



Scheme 2. Synthesis of 3-methyl-2,6-diphenyl piperidin-4-oneoxime

2. 6. 3. Preparation of the complex [CuMDPO·Cl₂·2H₂O]

Complexing property of the ligand has not been reported in literature so far. So, we took up a study of the synthesis and structural characterization of the ligand with metal salt. The complex is prepared by mixing hot ethanolic solution of CuCl₂·2H₂O salt and hot ethanolic solution of ligand refluxing the mixture for 3h (**Scheme 3**). The resulting solid complex was washed with hot ethanol and dichloromethane or acetone and dried under reduced pressure [37].



Scheme 3. Synthesis of copper (II) complex of 3-methyl-2,6-diphenylpiperidin-4-oneoxime.

The colour and analytical data of the complex and the ligand of oxime was given in **Tables 1-3**.

Table 1. The colour and analytical data for the complex [CuMDPO·Cl₂·H₂O].

Colour	Metal ion		Anion		Ligand	
	Found	Cal.	Found	Cal.	Found	Cal.
Dark green	13.81	14.10	14.8	15.7	63.40	62.40

Table 2. The CHN analysis data of the ligand (3-methyl-2,6-diphenyl piperidin-4-one oxime).

Ligand	% of Carbon		% of Nitrogen		% of Hydrogen	
	Found	Cal.	Found	Cal.	Found	Cal.
MDPO	76.89	77.14	7.0	7.14	9.94	10.00

Table 3. The CHN analysis data for the complex [CuMDPO·Cl₂·H₂O].

Complex	% of Carbon		% of Nitrogen		% of Hydrogen	
	Found	Cal.	Found	Cal.	Found	Cal.
CuMDPO·Cl ₂ ·2H ₂ O	47.07	47.98	5.67	4.43	7.17	6.21

3. RESULTSL AND DISCUSSION

The results of chemical analysis of the copper complex and ligand are given in experimental section. The chemical analysis shows the following composition for the complex is



where: MDPO = 3-methyl-2,6-diphenyl piperidin-4-one oxime

3. 1. Molar conductance and magnetic moment

The molar conductance measured in 10⁻³ M solution of the complex shows the anion of the metal salt in the complex are coordinated to the central metal ion. The magnetic moment, colour and the conductance are presented in the Table 4.

Table 4. The magnetic moment, colour and the conductance of the complex.

Complex	[Cu.MDPO·Cl ₂ ·2H ₂ O]
Colour	Dark green
Magnetic moment (B.M.)	1.82
Conductance 10 ⁻³ M	7.0
Nature of the complex	Non-electrolyte

The magnetic moment value (1.82 B.M) of the complex is equal to the spin only moment and it indicates the presence of one unpaired electron [38]. The magnetic moment value and the electronic spectral data suggested a distorted octahedral geometry for the complex tentatively it is supported by the conductance data and presence of peaks of H₂O in the infrared spectrum of the complex. The tentative assigned structure for the complex is octahedral.

3. 2. UV spectral study

The electronic spectrum of the complex shows a broad band around at 819 nm and a shoulder at 703.8 nm 12210 cm^{-1} and 142085 cm^{-1} which can be assigned to (${}^2E_g \rightarrow {}^2T_{2g}$) transition is characteristic of a distorted octahedral geometry [38]. The UV spectra of the complex was illustrated in Figure 1.

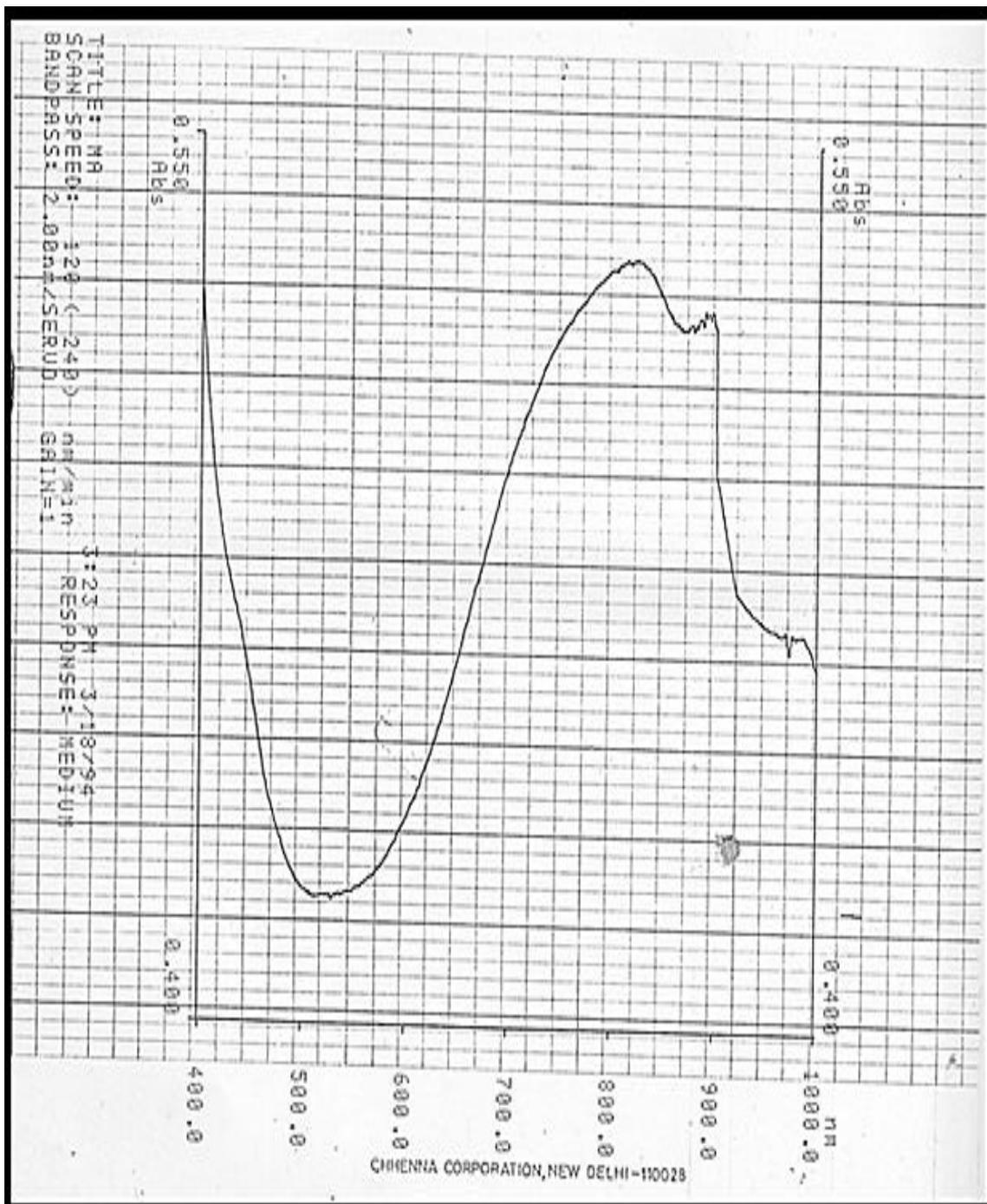


Figure 1. The UV spectra of the complex $[\text{Cu.MDPO}\cdot\text{Cl}_2\cdot 2\text{H}_2\text{O}]$

3. 3. IR spectra of ligand and complex

The IR spectrum of the complex and the IR spectrum of the ligand are shown in Figures 2 and 3. The ligand MDPO shows absorptions at 3350 – 3300, 1620, 1470 – 1450 and 3000 – 2850 cm^{-1} which are assigned to $\nu_{\text{N-H}}$, $\nu_{\text{C=N}}$, $\nu_{\text{C-N-C}}$ and $\nu_{\text{N-OH}}$ respectively [39].

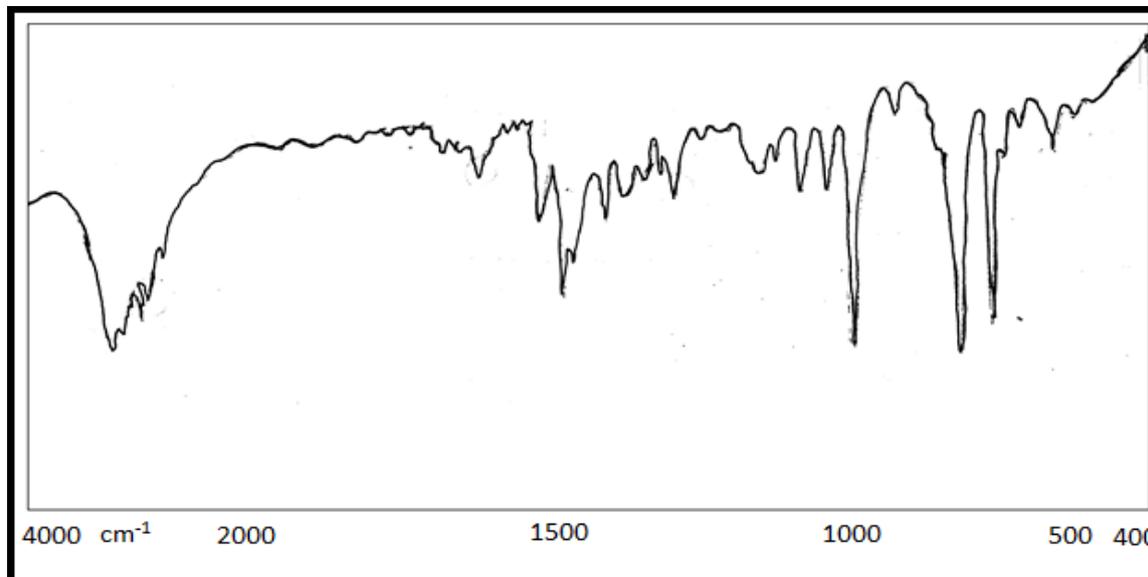


Figure 2. The IR spectrum of 3-methyl-2,6-diphenylpiperidin-4-one oxime ligand [MDPO].

In the copper complex, the absorption band due to oxime OH observed in the range 3000-2850 cm^{-1} in the infrared spectrum of ligand appeared more or less at the same position in the complex indicating that the OH of the oxime is not involved in the coordination. Very weak band found at 1620-1600 cm^{-1} in the spectrum of the oxime, attributable to $\nu_{\text{C=N}}$, is shifted to lower wave number and appears in the region 1575 cm^{-1} in the infrared spectrum of the complex. It indicates that the nitrogen atom of the oxime group is coordinated to the metal ion [40].

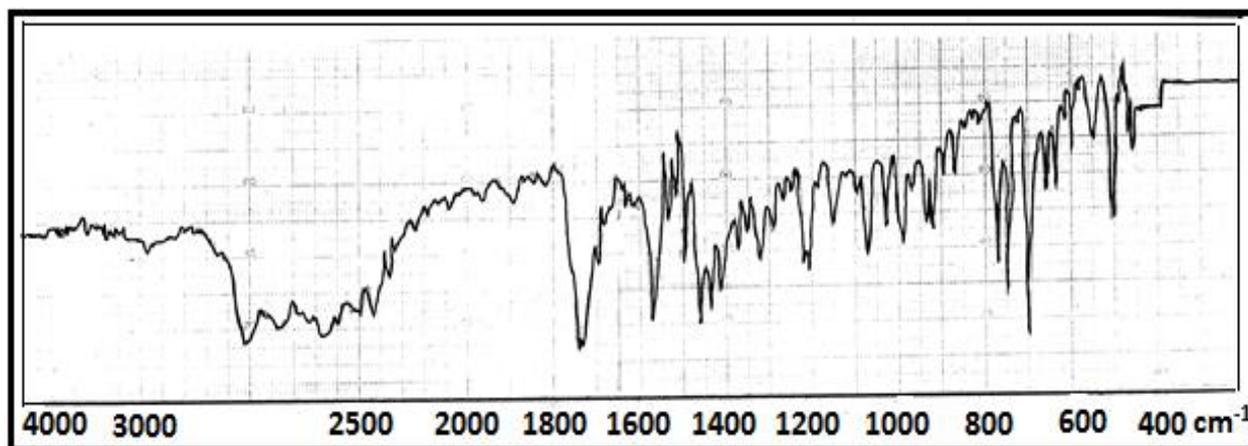


Figure 3. IR spectrum of copper (II) complex of 3-methyl-2,6-diphenylpiperidin-4-one oxime [Cu.MDPO·Cl₂·2H₂O].

The absorption band due to ν_{C-N-C} observed in the range $1470-1450\text{ cm}^{-1}$ in the infrared spectrum of the ligand appeared with three peaks more or less at the same position in the spectrum of the complex showed the involvement of the N-H group coordination with the metal ion and the broad band in the region $3350-3300\text{ cm}^{-1}$ in the spectrum of the ligand, attributable to ν_{N-H} , is not appeared and a very weak peak appeared in the 3450 cm^{-1} region indicated the coordination of the secondary amino nitrogen³¹ in the ring with the central metal ion. The chelating structure proposed for the complex demands boat conformation in the complex.

The presence of vibrational bands at ≈ 3500 , ≈ 3400 , ≈ 1600 and $920-650\text{ cm}^{-1}$ in the complex are a characteristic of coordination of water [41]. Based on the above observation the structure of the complex was assigned as shown in **Figure 4**.

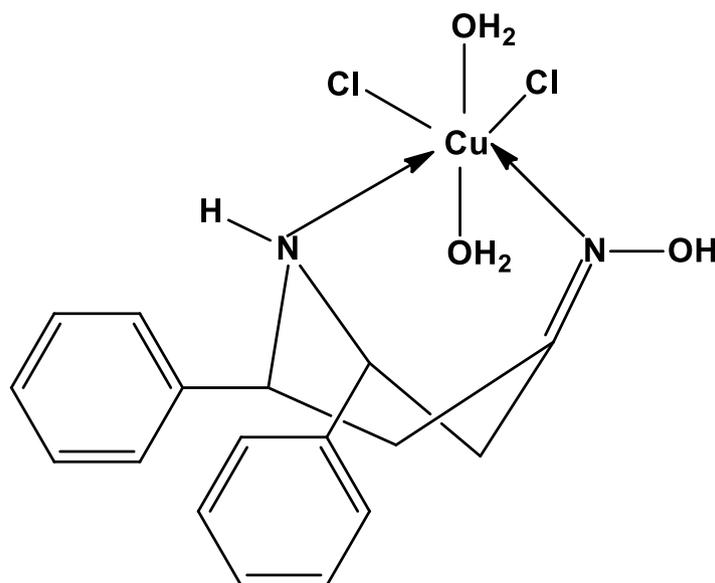


Figure 4. The assigned distorted octahedral structure of copper (II) complex of 3-methyl-2,6-diphenyl piperidin-4-one oxime [$\text{CuCl}_2 \cdot \text{MDPO} \cdot 2\text{H}_2\text{O}$].

4. CONCLUSIONS

In this investigation, the authors concluded with a general survey of the earlier work on metal complexes with oximes ligand highlighting the infrared, electronic spectral and magnetic moment studies. Various physico-chemical techniques are employed such as electrical conductance measurements, infrared, electronic spectral studies and magnetic susceptibility measurements and the preparation of 3-methyl-2,6-diphenyl piperidin-4-one oxime ligand and its metal complex have been described. The stereochemistry of the complex and the bonding sites of the ligand are discussed using the magnetic moment value, infrared electronic spectral data and conductivity measurements. From infrared studies it is found that the ligand coordinates through oxime nitrogen and piperidin ring nitrogen. It also provides evidences for the coordination of water molecule. The metal complex was tentatively assigned as distorted octahedral structure.

References

- [1] L. Tschugaeff, *Chem. Ber.* 38, 2520, (1905).
- [2] F. Feigl, *Chem. Ber.* 56, 2083, (1923).
- [3] E. Ephraim, *Chem. Ber.* 63, 1928, (1930).
- [4] F. J. Welcher, *Organic Analytical Reagents*, Van Nostrand, New York, (1947).
- [5] K. Burger, "Organic Reagents in metal Analysis" Pergmon Oxford (1973).
- [6] B. Egneus, *Talanta*, 19, 1387, (1972).
- [7] A. Chakavorty, *Coor. Chem. Rev.* 13, 1, (1974).
- [8] R.B. Singh, B.S. Gray and R.P. Singh, *Talanta*, 26, 425, (1979).
- [9] R.C. Mechrota, A.K. Rai, A. Singh and R. Bohra, *Inorg. Chem. Acta* 13, 91, (1975).
- [10] M.E. Keeny and K. Osseo-Asare, *Polyhedron* 29,448, (1984).
- [11] J.S. Jennings, E. Sharratt and W. Wardlaov, *J. Chem. Soc.* 81, 818, (1993).
- [12] N.S. Bhave and R.B. Kharat., *J. Indian Chem. Soc.* 56, 224, (1979).
- [13] Flett, D.S., Cox, M., Heels, J.D. Proc. ISEC '74; Jeffreys, G.V. Ed.; Soc. Chem. Ind., London, 1974; Vol 3, 2560-2575.
- [14] K. Burger and I. Egyed, *J. Inorg. Nucl. Chem.* 27, 2361, (1965).
- [15] K. Burger, F. Ruff, I. Ruff and I. Dgyed, *Acta Chim.* 46, 1, (1965).
- [16] K. Ramaswamy, C.I. Jose and D.N. Sen, *Indian J. Chem.* 5, 156, (1956).
- [17] C. Musante, *Gazz. Chim. Ital.* 78, 536, (1948).
- [18] A.S. Bhauri and P. Ray, *Fresenius Z. Anal. Chem.* 151, 109, (1956).
- [19] A.S. Bhauri and P. Ray, *Fresenius Z. Anal. Chem.* 154, 103, (1957).
- [20] P. Cox, *J. Chem. Soc.* 459, (1935).
- [21] M.A. Janski and E.C. Lingafelter, *Acta Crystallogr.* 17, 1109, (1964).
- [22] P.L. Orioli, E.C. Lingafelter and B.W. Brown, *Acta Crystallogr.* 17, 1113, (1964).
- [23] F. Ephraim, *Chem Ber.* 63B, 1928, (1930).
- [24] R.A. Krause, N.B. Colthup and B.H. Busch, *J. Physics. Chem.* 65, 2216, (1961).
- [25] F.G. Bordwell, "Organic Chemistry", McMillan, New York (1962).
- [26] R.C. Fuson, "Reactions of Organic Compounds", Wiley, New York, (1962).
- [27] R. Gurumurthy, G. Mangalam and K. Sathiyarayanan, *J. Hetrocyl. Chem.* 2(2), 81, (1992).
- [28] (a). V. Baliah and R. Jeyaraman, *Indian J. Chem.* 9, 1020, (1971).
(b). R. Jeyaraman, L. Chandrasekaran, K. Ganapathy and V. Gopalakrishnan, *Indian J. Chem.* 27A, 695, (1988).

- [29] S. T. Harini, H. V. Kumar, J. Rangaswamy and N. Naik, *Bioorg. Med. Chem. Lett.* 22, 7588, (2012).
- [30] B.N. Cockburn, D.V. Howe, T. Keating, B.F.G. Jhonson and J. Lewis, *J. Chem. Soc. (Dalton Trans)* 404, (1973).
- [31] Janaki Arunan and V. Meenakshi, *J. Indian Chem. Soc.* 68, 607, (1991).
- [32] A. I. Vogel, "A Text book of Quantitative Inorganic Analysis", Longmann ELBS, 4th Edition (1986).
- [33] W. J. Geary, *Coord. Chem. Rev.* 7, 81, (1971).
- [34] B.N. Figgs and Lewis, "Modern Coordination Chemistry", Interscience, New York, (1960).
- [35] C.R. Neller and V. Baliah, *J. Am. Chem. Soc.* 70, 3853, (1948).
- [36] S. Rajam, M.Phil. Thesis, Annamalai University, India, (1989).
- [37] K. Lakshmanan and G. Thirunarayanan, "Synthesis, characterization and geometry of Cu (II) complex of 3-methyl-2,6-diphenylpiperidin-4-one oxime", OSA-9, pp.12, National Level Seminar of Recent Advances in Physical Organic Chemistry, 11-12th, February (2008), National College, Tiruchirappalli.
- [38] A.B. P. Lever, "Inorganic Spectroscopy", 2nd Ed., Elsevier, New Delhi, (1984).
- [39] L.J. Bellamy, "The Infrared spectra of complex Molecules", John Wiley, New York, (1958).
- [40] K.P. Kariya and N.S. Bhavani, *Indian J. Chem.* 26A, 972, (1972).
- [41] K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", Interscience John Wiley, New York (1970).