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Synthesis and characterization of co(iii), Ni(ii) and cu(ii) complexes of 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione Dioxime

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ABSTRACT

The ligand 3,8-Dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime was synthesized by the condensation of o-phneylenediamine with diacety monoxime in a 1:2 mole ratio. It has been isolated in the solid state and characterized by CHN, IR, and NMR spectra. The ligand is a neutral compound and on complexation with metal ions loses one of the oxime protons with the concomitant formation of the intramolecular hydrogen bond. Six coordinate Co(III) complex, four coordinate square planar Ni(II) complex and five coordinate square pyramidal Cu(II) complex are synthesized by the reaction of the respective metal chlorides. All these complexes are characterized by infrared, electronic spectroscopy and conductivity measurements. Indirect evidence for the formation of intra-molecular hydrogen bond in these complexes is obtained by replacing the hydrogen bonded proton by the BF_2 group by treating the complex [Cu (DO)(DOH) bzo) Cl] with BF_3OEt_2.

Introduction

It has been well documented that metal ions play an important role as catalyst, for many biological reactions in living systems. The activity of such metal ions depends on their confinement within approximately planar, tetra dentate, totally enclosed macrocyclic ligands, which are themselves highly conjugated species [1-4]. Quadridentate tetraaza macrocyclic ligands fulfil the above requirements and hence serve as effective models for biological systems [5-7].

The study of transition metal complexes of macrocyclic ligands as model for biological system stems mainly from the difficulties encountered in isolating the biological systems which is due to their high molecular weights, extreme molecular complexity, limited solubility and their instability in aerobic conditions. The macrocylic complexes of transition metal ions cannot serve as the biological mimics of the primary bioinorganic systems but can act as simple and an efficient model to extract the essential details of the biological systems.

A macrocyclic ligand is a cyclic compound with nine or more members having three or more donor atoms. They are usually obtained by the condensation of diammines with diketones or dihalo derivatives through Schiff's base condensation [8-10]. Curtis was the first to obtain a cyclic compound by condensing a mono carbonyl compound with the diamine, thus the ligand synthesized by the reaction of ethylene diamine with acetone in the presence of nickel perchlorate was named after him as the Curtis ligand. This was immediately followed by Thompson and Schrauzer respectively Macrocyclic ligands have been prepared both by direct conventional organic synthesis and "*in situ*" synthesis. In the case of condensation reactions, polymerization sometimes competes with cyclization and in such cases the cyclization is favoured over polymerization by conducting the synthesis by "high dilution" method [11-14].

Macrocycles were effectively synthesized by the condensation of primary amines with carbonyl compounds. The reaction is favoured due to the 'carbionalimine' intermediate formed as a result of nucleophilic attack of hydrogen donor on the carbonyl carbon. These reactions are mostly catalyzed by acids [15-17].

The first example of a pseudo-macrocyclic ligand synthesized by this method was obtained by the condensation of salicylaldehyde with ethylenediamine, similarly the condensation of salicylaldehyde with o-phenylenediamine is also prepared [18-21]. A large number of macrocylic ligands synthesized are highly conjugated and yield complexes that exhibit extensive electron delocalization [22-25]. The extensive conjugation dictates co-planarity of the ligand. The complexes of such chelates are therefore used to study the ligand bonding and the electronic transmission induced by the ligand to the metal ion. In an attempt to study the effect of conjugation on the Co-C bond, Ramanujam and Alexander have reported the tetraaza quadridentate ligand and its alkyl and (non-alkyl) cobalt (III) complexes which serves as vitamin B_{12} and coenzyme B_{12} model. The tetraaza quadridentate ligand, 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime reported recently by Ramanujam and Alexander seems to be convenient a vehicle to explore the variation in electronic properties of metal ions with respect to the effect of conjugation [26].

Experimental

All the chemicals used were of Anala R grade and were procured from Aldrich. Metal salts were purchased from Merck and used as received. All solvents used were of standard/spectroscopic grade.

Reagents

Cobalt (II) chloride (AR, BDH), Copper (II) chloride (AR, BDH), Nickel(II) chloride (AR, BDH) were used as such for the syntheses of the complexes. o-phenylenediammine (LOBA)

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anhydrous calcium chloride (SDS) and diacetyl monoxime were used. o-phenylenediamine was recrystallized from hot water using activated charcoal prior to use.

Solvents

Commercial grade ethyl alcohol was refluxed for 7 hr over lime and the fraction boiling at 78-79 ^{o}C was collected and used. Double distilled water was obtained by distilling water over alkaline $KMnO_4$ in an all glass apparatus.

Synthesis of the ligand

To a solution of o-phenylenediamine (10.8g, 0.1mol) in 100 mL of warm distilled water was added diacetylmonoxime (20.2g, 0.2mol) and refluxed for 1 hr when yellow crystals separated out. The reaction mixture was cooled to 5 ^{o}C and filtered. The yellow crystals (yield:80% and m.p.–176 ^{o}C) were recrystallized in dry ethanol.

Synthesis of Complexes

[Co (DO)(DOH)bzo)Cl_2] complex

To a solution of ((DOH)$_2$ bzo) (0.409 g, 5 mmol) of ethanol is added to a hot ethanol solution of Co(II) chloride (1.4g, 5 mmol) and refluxed for 3 hours. It was cooled overnight and the pale green crystals which separated out (Yield 80%) were filtered through sintered crucible washed with cooled ethyl alcohol and dried over anhydrous $CaCl_2$.

[Ni (DO)(DOH)bzo)]Cl complex

To a solution of ((DOH)$_2$ bzo) (0.409 g, 5 mmol) of ethanol is added to a hot ethanol solution of Ni(II) chloride (0.95g, 5 mmol) and refluxed for 3 hours. It is cooled overnight and the pale rosy pink crystals which separated out (Yield 84%) were filtered through sintered crucible washed with cooled ethyl alcohol and dried over anhydrous $CaCl_2$.

[Cu (DO)(DOH)bzo)Cl] complex

To a solution of ((DOH)$_2$ bzo) (0.409 g, 5 mmol) of ethanol is added to a hot ethanol solution of Co(II) chloride (0.554g, 5 mmol) and refluxed for 2 hours. It is cooled overnight and the shiny dark green crystals which separated out (Yield 78%) were filtered through sintered crucible washed with cooled ethyl alcohol and dried over anhydrous $CaCl_2$.

Results and discussion

Synthesis of the ligand

3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime was synthesized by the condensation of o-phneylenediamine with diacety monoxime in a 1:2 mole ratio in distilled water by the procedure reported by Ramanujam and Alexander [26]. The free ligand separated out in the pure form from the reaction medium due to its insolubility. The yield was found to be 80%. The recrystallized pure ligand melts at 276 ^{0}C as reported in the literatures [27-32].

Characterization of the Ligand

IR Spectral study

The infrared spectrum of the recrystallized ligand clears that there is no characteristic absorptions assignable to either C=O or NH_2 function, which easily confirms the formation of the ligand. The sharp band of medium intensity occurring at 1575 cm^{-1} is attributed to –(C=N) while a similar band at 1630 cm^{-1} is assigned to –(C=C) the strong as well as sharp band at 1220 cm^{-1} due to the N-O stretching vibrations. The weak band at 3260 cm^{-1} is due to the CH stretching vibrations and the broad band around 2900 cm^{-1} is assigned to (OH). The very strong band of medium broadness at 1430 cm^{-1} and a weak band at 1430 cm^{-1} are assigned to the ring models of o-disubstituted benzenes. The sharp bands of medium intensity at 1375 and 1445 cm^{-1} are due to the symmetric and asymmetric deformation vibrations, respectively, of the methyl groups.

The strong bands appearing at 1260, 1180 and 1130 cm^{-1} are assignable to ν(C-C), ν(C-N) vibrations or to the coupled vibrations of these modes. The metal sensitive strong as well as sharp band at 765 cm^{-1} may be attributed to C=N-O deformation vibrations. The metal dependent strong vibration as well as sharp bands appearing at 990, 920, 910 cm^{-1} can be ascribed to the deformation vibrational modes of the ligand.

Characterization of complexes

The complexes reported here are synthesized by the reaction of the ligand with Co (II), Ni(II), and Cu(II) salts in ethanol (1:1 mole ratio). The complexes [Co(DO)(DOH)bzo)Cl_2], [Ni(DO)(DOH)bzo)]Cl, [Cu(DO)(DOH)bzo)Cl] were synthesized by the direct reaction between the free ligand and the respective metal halides in 1:1 mole ratio. All this complexes were obtained in the pure form and hence they were not further purified by recrystallization. The results of the percentages of metal present in the complexes determined by gravimetrically are given in Table 1. From the analytical data it is evident that the stoichiometries of all the complexes are same. The complexes have 1:6 stoichiometry ratios.

Molar conductance

The observed molar conductances of the complex in DMF are in range of 10-20 ohm^{-1} cm^{2} mole^{-1} at room temperature. So from conductivity measurement, it is concluded that the chloride ions are covalently bonded to Metal ions. Based on the metal-ligand ratio calculated by the analytical data and the nature of the electrolytes given by the conductance measurements, compositions were assigned for the prepared complexes. Molar conductivity results of the [Co(DO)(DOH)bzo)Cl_2], complex is DMF was found to be 27 ohm^{-1}cm^{2}mol^{-1}. The molar conductance of [Cu(DO)(DOH)bzo)Cl] is 32 ohm^{-1}cm^{2}mol^{-1} indicating that it is a neutral complex. This shows that the chloride acts as ligands and not as simple ions. The conductance is very low characteristic of a neutral complex.

The molar conductance of [Ni(DO)(DOH)bzo)]Cl, is 82 ohm^{-1}cm^{2}mol^{-1} indicating that it is a 1:1 electrolyte. The conductivity value fall within the range of molar conductance of neutral and 1:1 electrolytes in DMF confirming the formation of the proposed cationic complexes in solution. The molar conductivity data is provided in Table 2.

Infrared spectra

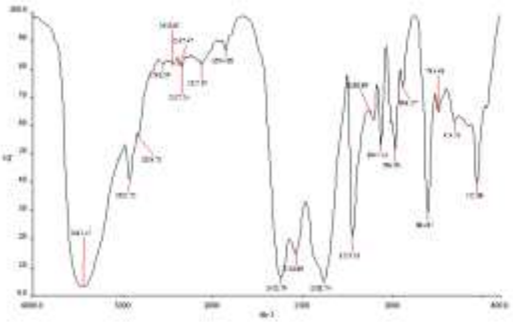
The IR spectra of ligand (L) with its octahedral complexes have been studied in order to characterise their structures. The IR spectra of the free ligand and its metal complexes were carried out in the 4000–400 cm^{-1} range. The IR spectra of all metal complexes were interpreted by comparing the spectra with those of the free ligand. On comparison the band positions of various vibrations were ascertained with good evidence. In the infrared spectrum of the ligand, the band at 1385 - 1400cm^{-1} is due to asymmetric C=N stretching vibration.

The presence of δ(C=N—C) asymmetric stretching vibration is confirmed by the band at 1520cm$^{—1}$ In the infrared spectrum of metal complexes, the ν C=N stretching vibrations were observed at ~1480 cm^{-1} and the results due to coordination of the nitrogen from C=N to the metal, stretching vibration for L reduced at the complex. The free ligand showed a strong peak at 1520 cm^{-1} for L, which is characteristic of the imine ν (C=N) group. The ν (C—C) stretching vibrations are affected upon complexation and are situated at a frequency significantly different than the free ligands. Coordination of the ligands to the metal centre through the nitrogen atom are expected to reduce the electron density in the methine and imine link and hence lower the ν(C—C) and ν(C=N) absorption frequencies. The peak due to ν(C—C) are slightly shifted to lower frequencies and appears between 1576–1579 cm^{-1}, indicates the coordination of the imine nitrogen to the metal. Hence, the shifts in the –C=N and C—C stretches of the metal complex provide support for ML_6-type coordination.

The characteristic infrared absorption bands of the ligand are shifted and lowered in intensity on the formation of complex, and the new vibrational bands characteristic of the complex appears. The broad band of medium intensity occurring at 2900 cm^{-1} in the free ligand is shifted to 3120 cm^{-1} in [Cu(DO)(DOH)bzo)Cl] attributed to the ν·(OH) of the hydrogen bonding.

The ν(OH) of the complex is observed at 1196 cm^{-1}. The bands observed at 1330 and 1400 cm^{-1} are the symmetric and asymmetric deformation vibrations of the methyl groups. A unique feature is the occurrence of a new strong and sharp band at 1090 cm^{-1} in the complex, which is not observed in the ligand. The band is assigned to ν (NO) band. The Infrared spectrum of the Cu complex was shown in Fig. 1.

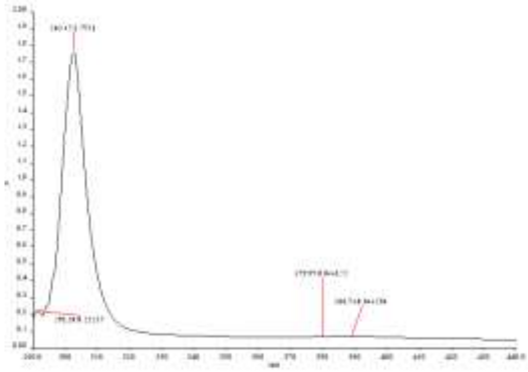
Fig 1. Infrared spectrum of the Cu complexes



Electronic spectral study

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The electronic spectral measurements were used for assigning the stereochemistry of metal ions in the complexes based on the positions and number of d–d transition peaks. The electronic absorption spectra of the Schiff base and its Co(III), Ni(II) and Cu(II) complexes were recorded at room temperature using acetone as solvent were shown in Fig. 2.

Fig 2. Electronic spectra of Nickel Complex



Only one broad band is observed at 16,638 cm^{-1} in the electronic spectrum of the Cu(II) complex assigned to ^{2}Eg □□$^2T_2$g transition which is in conformity with octahedral geometry. Though three transitions are expected in this case, since they are very close in energy they often appear in the form of one broad band envelope. The electronic spectra of Co(III) complex showed two spin-allowed transitions at 17856 and 21734 cm^{-1} assignable to $^4T_1$g(F) □□$^4A_2$g(F) and $^4T_1$g(F)□□$^4T_1$g(P) transitions respectively, are in conformity with octahedral arrangements for Co(III) ion. The appearance of a band at 19240 cm^{-1} due to $^3A_2$g(F) □□$^3T_1$g(P) transition favours an octahedral geometry for the Ni(II) complex. The absence of any band below 10,000 cm^{-1} eliminates the possibility of a tetrahedral environment in this complex.

Magnetic susceptibility measurements

The magnetic moment value of Cu(II) complex is 1□90 BM which suggests a distorted octahedral geometry, around the metal ion. The magnetic moment of Co(III) complex is 4.81 BM which suggests the high spin six-coordinated octahedral arrangement of ligand molecules around the metal ion. The Ni (II) complex has magnetic moment value of 2.8 BM indicating a spin-free octahedral configuration. The results obtained from magnetic moment measurements were shown in Table 3.

ESR spectra

The ESR spectra of copper complex provide information of importance in studying the metal ion environment. The X-band ESR spectra of the Cu(II) complex, recorded in DMSO at liquid nitrogen temperature and at room temperature (300 K), are shown in Fig. 3 and Fig. 4.

Fig 3. ESR spectra of Cu(II) complex at 77 K in DMSO solution.

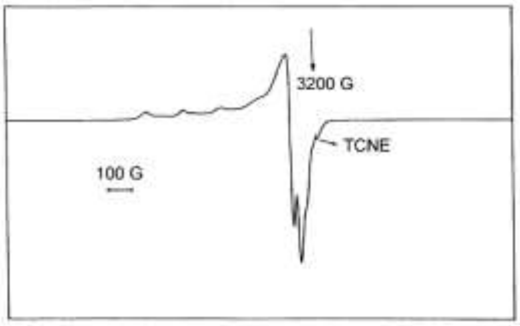
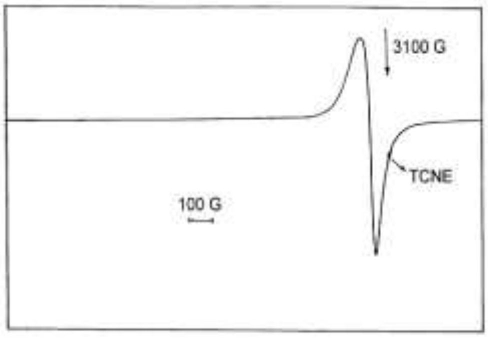


Fig 4. ESR spectra of Cu(II) complex at 300 K in DMSO solution



The spectrum of the copper complex at room temperature shows one intense absorption band in the high field and is isotropic due to the tumbling motion of the molecules. However, this complex in the frozen state shows four well resolved peaks with low field region. The copper complex exhibits the $g_{□□□}$ value of 2□31 and $g_{□}$□value of 2□16. These values indicate that the ground state of Cu(II) is predominantly dx^2–y^2. The spin-orbit coupling constant, l value (□ 486 cm^{-1}) calculated using the relations, $g$av = 1/3[g□□□+ 2g□] and $g$av = 2(1–2l/ 10Dq), is less than the free Cu(II) ion (–832 cm^{-1}) which also supports covalent character of M–L bond in the complex [24]. The G value of 3□82 indicates negligible exchange interaction of Cu–Cu in the complex. The covalency parameter $\square^2$ is calculated ($\square^2$ = 0□82) using the following equation:

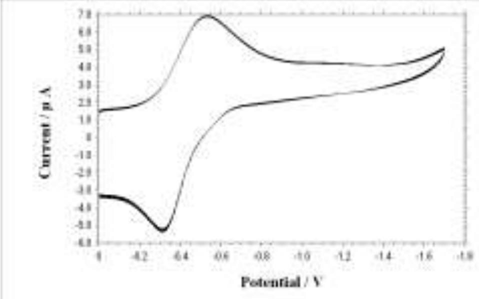
$\square^{\square 2}$Cu = –($A_{\square\square}$/0□036) + (g□□□– 2□0023) + 3/7(g□□– 2□0023) + 0□04.

If the value of □$\square^2$ = 0□5, then it indicates complete covalent bonding, while a value of $\square^2$= 1□0 suggests complete ionic bonding. The observed value of□$\square^2$ = 0□82, of the complex is less than unity, indicating that the complex has some covalent character in the ligand environment.

Cyclic voltammetric study

Cyclic voltammogram of Cu(II) complex was characterized in 1 mM Cu(II)-complex containing 0.1M MeCN on Pt electrode at the scan rate of 0.1 V S^{-1} were shown in Fig. 5. The cyclic voltammogram shows a well-defined redox process corresponding to the formation of the Cu(II)/Cu(III) couple at *Epa* = 0□22 V and the associated cathodic peak at Epc = 0□18 V. This couple is found to be reversible with □Ep □□0□04 V and the ratio of anodic to cathodic peak currents (Ipc/Ipa = 1) corresponding to a simple one-electron process. The complex also shows a quasi-reversible peak in the negative region, characteristic of the Cu(II) □□Cu(I) couple at Epc = –0□47 V, with associated anodic peak at Epa = –0□□4 V for Cu(I) □□Cu(II) oxidation.

Fig. 5. Cyclic voltammogram of 1 mM Cu(II)-complex in 0.1 M MeCN on Pt electrode, v=0.1 V S^{-1}, vs. Ag|Ag^+



Intramolecular hydrogen bonding

The free ligand is a neutral molecule which upon complexation loses one of the oxime protons with the concomitant formation of an intramolecular hydrogen bond. All these complexes exhibit two strong as well as sharp bands at 1220 and 1075 cm^{-1}, assignable to ν(NO) and ν'(NO). The appearance of only one band at 1220 cm^{-1}, assignable to ν(NO), in the free ligand shows that the two NO- linkages are identical while the appearance of two bands assignable to ν(NO) and ν'(NO) in the complexes indicate the presence of two unequal –NO linkages. Indeed, upon complexation, there are two-NO-linkages C=N-O-H and C=N-O···H due to the formation of hydrogen bonding.

Studies on Cobaloximes by Schruazer [33] and by Yamazaki and Honokabe [34] as also the work of Blinc and Hadzi [35] also confirm the presence of two unequal-NO-linkages due to hydrogen bonding. Disappearance of the ν (OH) band in the complexes is further evidence for O-H-O bond formation. Schrauzer replaced the two hydrogen bonded protons in bis(dimethyl glyoximato) Nickel(II) by the BF_2 group by treating with BF_3.OEt_2 for the first time. Later, Schrauzer and Windgassen replaced the hydrogen bonded proton in methyl (aquo) cobaloxime by the BF_2 group by the same method. Indirect evidence for the intra-molecular hydrogen bonding is obtained by replacing the hydrogen bonded proton in [Cu (DO)(DOH)bzo)Cl] by the BF_2 group by treating the complex with BF_3.OEt_2. This reagent readily reacts with the O–H–O bridge in the complex, affording the stable complex containing the O-BF_2-O bridge.

Conclusions

The quadridentate ligand employed in the present investigation coordinates readily with Co(III) in the equatorial position and readily affords the synthesis of six coordinate octahedral complexes. Ni(II) form stable square planar complex with the pseudo-macro cyclic ligand. Cu(II) forms square pyramidal five coordinate complexes in which the metal anion occupies one of the apical sites. The ligand readily affords synthesis of 6 coordinate complexes wherein the apical sites can be altered and it seems to be a convenient vehicle to explore the influence the ligand conjugation on the electronic properties of the metals. However detail EPR and electronic spectral investigation are needed to examine the influence of structure and conjugation on the geometry and reactivity of transition metals.

Recommendation for further investigation

The synthesis of octahedral complexes to the family of closely related monondendate ligands such as Lewis bases and detailed spectral investigations would enable the construction of spectrochemical series of the axial ligands. A detailed electro chemical investigation of such a series of complexes would throw more light on the influence of axial and equatorial ligands on the metal ion.

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Table 1. Analytical data of the complexes

Complex	Colour	Mol. Wt.	M.P. °C	Yield %
[Cu(DO)(DOH)bzo)Cl]	Pale Blue	1468	270	70
[Ni(DO)(DOH)bzo)]Cl	Green	758	295	70
[Co(DO)(DOH)bzo)Cl_2]	Pink	1480	280	65

Table 2. Molar conductance and nature of the complexes

Complex	Molar conductance ($\Omega^{-1}cm^2mol^{-1}$)	Nature
[Co(DO)(DOH)bzo)Cl_2]	27 ohm^{-1}cm^{2}mol^{-1}	Neutral
[Ni(DO)(DOH)bzo)] Cl	82 ohm^{-1}cm^{2}mol^{-1}	1:1
[Cu(DO)(DOH)bzo)Cl]	32 ohm^{-1}cm^{2}mol^{-1}	Neutral

Table 3. Elemental Analysis, Magnetic moment of the complexes

Complex	Elemental analysis Found (Calcd.)%					
	M	C	H	N	Cl	$\mu_{eff.}$ BM.
Cu(DO)(DOH)bzo)Cl]	7. 05 (7.45)	67.21 (67.32)	4.15 (4.55)	14.01 (14.00)	7.60 (7.05)	1.90
[Ni(DO)(DOH)bzo)]Cl	7.05 (7.00)	66.50 (66.51)	4.41 (4.77)	13.10 (13.08)	7.44 (7.41)	4.81
[Co(DO)(DOH)bzo)Cl_2]	7.56 (7.51)	64.84 (64.86)	3.42 (3.79)	13.17 (13.15)	7.54 (7.53)	2.8

Table 4. Characteristic Infrared Absorption Bands (cm^{-1}) of complexes

Complex	ν(CH)	ν(OH)	ν(C=N)	ν(NO)	ν’ (NO)
[[Cu(DO)(DOH)bzo)Cl]	3120 s	3250b	1484s	1196m	1090s
[Ni(DO)(DOH)bzo)]Cl	3150s	3250s	1484s	1200w	1090w
[Co(DO)(DOH)bzo)Cl_2]	3130s	3262b	1479s	1190m	1090s