International Journal of Engineering & Scientific Research (IJMRA Publications)
Vol. 6 Issue 2, February 2018,
ISSN: 2347-6532 Impact Factor: 6.660
Journal Homepage: http://www.ijmra.us Email: esrjeditor@gmail.com
Double-Blind Peer Reviewed Refereed Open Access International Journal - Included in the International Serial Directories Indexed & Listed at: Ulrich's Periodicals Directory ©, U.S.A., Open J-Gage as well as in Cabell's Directories of Publishing Opportunities, U.S.A

Adducts of Zinc(II) complexes of cyclol(1,2)dibiguan-idinyl bis[2-hydroxy-w (benzoy1/4-chlorobenzoyl/3nitrobenzoyl/3,5-dinitrobenzoyl) acetophenone] with pyridine, 2-methylpyridine and 4-methylpyridine

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Abstract

The complexes were ionic and diamagnetic as evidenced by molar conductance (132-149 ohm^{-1} cm^{2}mo1^{-1}) and magnetic susceptibility studies. The 1:1 stoichiometry of the complexes was confirmed by elemental analysis and molecular weight determination. This data coupled with infrared spectral characteristics suggested that Zn(II) was hexa-coordinated in these complexes.

The hypso chromic shifting of the stretching vibrations due to (C=N) of (>C=N-C) group from 1645-1615 cm^{-1} in the spectra of ligands to 1620-1600 cm^{-1} spectra of the complexes indicated coordination through the nitrogen atom of this group. This was further supported by a negative shift of the order of 20-15 cm^{-1} in V(C-N) mode in the spectra of complexes.

INTRODUCTION

A new band appearing at 1235-1220 cm^{-1} in the spectra of the complexes was assigned to chelate ring stretching vibrations (Syamal, 1978). The (N-H) and (>C=N-H) groups were not involved in bonding because the band frequencies of these groups in the spectra of the ligands did not undergo any change on complexation. Appearance of a new band at 3450-3400 cm^{-1} was assigned to Y (0-H) mode of coordinated water in the spectra of the complexes (Rana and Shah, 1986).

The participation of nitrogen and oxygen in coordination was evidenced by the appearance of new absorption bands in the far infrared region at 505-485 and 455-435 cm^{-1} attributed to the (M-0) and (M-N) stretching vibrations, respectively. (Ferraro,1971; Nakamoto, 1978).

On the basis of elemental analysis, molecular weight data and tetradentate behaviour of the ligands as evidenced by the infra-red spectral characteristics, an octahedral environment around Zn(II) has been suggested for the complexes [Zn (L_I-L_{IV}) (H_2O) 1C1$_2$.

Elemental analysis and molecular weight data suggested 1:1 stoichometry for the base adducts of (L_I-L_{IV}) complexes. Conductance values (130-155 ohm^{-1} cm^{2}mo1^{-1}) indicated 1:2 electrolytic natures of these compounds which were diamagnetic. A comparative study of the infra-red spectra of the ligands and corresponding adducts has been utilized to elucidate the structure of these compounds.

Review of Literature

Saha and Bagchi (1985) reported the synthesis of nickel(II) and copper(II) complexes of schiff base derived from the condensation of phenylbiguanide and benzil of type Ni. The Ni(II) complexes, Ni(HoL) and NiL were found to be diamagnetic suggesting square planar geometry.

The electronic spectral data further supported the square planar geometry while the Liege values suggested a partial tetragonal distortion for pyridine and picoline adducts of Ni(II) complexes. Square planar, square pyramidal and distorted octahedral geometries were proposed for Cu(HoL)Cl, Cu(HL)C1l and the adducts, respectively. In all these complexes the ligand behaved as tetradentate and acted as neutral, uninegative or binegative depending on pH.

Syamal and Mandal (1980) synthesized Co(III) mixed ligand complexes with the ligands biguanide, 2-picolylamine, trimethylenediamine and acetylacetone and characterized the same by elemental analysis, electronic and IR spectra, magnetic susceptibility, conductance and equivalent weight measurements.

The electronic spectra of the complexes exhibited one or ligand field bands around 20,000 and 29,000 en typical of octahedral Co(III) complexes.

The (C=N) frequency of the complex occurred at a lower frequency compared to that of free ligand and indicated participation of nitrogen of biguanide in coordination.

Ray (1989) studied the Copper(II) complexes of substituted biguanides by ‘ESR spectroscopy in water, in their polycrystalline form and in the corresponding nickel(II) complex matrix. In aqueous solution, nine nitrogen suferfine lines on the higher field 3/2 gx——3/2 copper hyperfine splitting component was indicative of four equivalent or nearly equivalent nitrogen atoms surrounding the copper(II) ion values suggested that like biguanide, substituted piguanides and their protonated forms were equally strong field ligands. The covalency parameter revealed that unpaired electron of copper(II) spends about 36 per cent of its time in the nitrogen donor sites of the ligands. The coordination properties of Nickel(II) and Copper(II) complexes with cyclo(1,2)-dibiguanidinyl dibenzil and of their adducts with pyridine and picoline were examined by Saha and Das (1993).

The conductance values were indicative of the non-electrolyte nature of the complexes. The Ni(II) complex was found to be diamagnetic and showed one broad absorption band 473.6 nm indicating square planar geometry for the complex. The Cu(II) complex was paramagnetic (Hoeee 1.78 BM) and square planar as evidenced by one absorption band 535 nm. The adducts of Cu(II) and Ni(II) were found to be paramagnetic with no change in spectra from that of the complexes. The TGA of adducts showed loss of two molecules of pyridine/picoline at two different temperatures.

Bera et al. (1989) studied the charge transfer adducts of Cu(II) and Ni(II) complexes of biguanide with iodine and tetra cyanoquinodimethane (TCNQ) which acted as acceptors. Appearance of new broad bands at 355 nm and 335 nm for Ip and TCNQ adducts, respectively and shifting ‘OE IR frequencies supported the formation of donor acceptor association. The elemental analysis established 1:1 stoichiometry of the adducts.

The absence of ESR signals suggested a dimer structure. The structure of chloro (biguanide) (pyridine-2-carboxylato) Copper (II) complex was studied by Kennard et al. (1986) using X-ray diffraction technique. The complex formed discrete pyramidal units with two biguanide atoms and with a N and an O from a picolinate ligand occupying positions about a square plane. The fifth position was occupied by Cl ion.

Saha and Bagchi (1984) reported the synthesis of 1:1 Cu(II) and 1:2 Ni(II) complexes of substituted biguanides containing ethyl acetate and acetic acid fragments. The complexes were characterized on the basis of analytical, spectral and magnetic data. Square planar geometry was assigned to 1:1 complexes and tetragonally distorted octahedral geometry to

1:2 complexes. The biguanide derivatives behaved as uninegative tridentate ligands coordinating through two N atoms and an atom of “the carbonyl group. Oxovanadium(IV) complexes of biguanide and dibiguanides were characterized by IR, electronic and ESR spectroscopy. The ESR parameters were similar in the oxovanadium(IV) complexes of biguanide and dibiguanide, indicating the similarity of bonding in these complexes.

Adducts of Zinc(II) complexes of cyclol(1,2)dibiguan-idinyl bis[2-hydroxy-w (benzoy1/4-chlorobenzoyl/3nitrobenzoyl/3,5-dinitrobenzoyl) acetophenone] with pyridine, 2-methylpyridine and 4-methylpyridine

The absorption bands diagnostic of (N-H) in the free ligand were present in the same region in the spectra of the adducts indicating the non-involvement of nitrogen of (N-H) group in coordination. A downward shift in (C=N) stretching mode of (>C=N-C) group from 1645-1615 cm^{-1} in the ligand to 1635-1595 cm^{-1} in the adducts suggested the coordination of the ligand through imine nitrogen atom of this group which was corroborated by a hypsochrowic shifting of the order of 20-15 cm^{-1} in the Y(C-N) mode (Das et al., 1990).

The band due to (0-H) mode observed at 3450-3400 cm^{-1} in the spectra of the complexes was absent in the spectra of the adducts, suggesting the replacement of coordinated water molecules by base molecules in adducts.

RESULTS

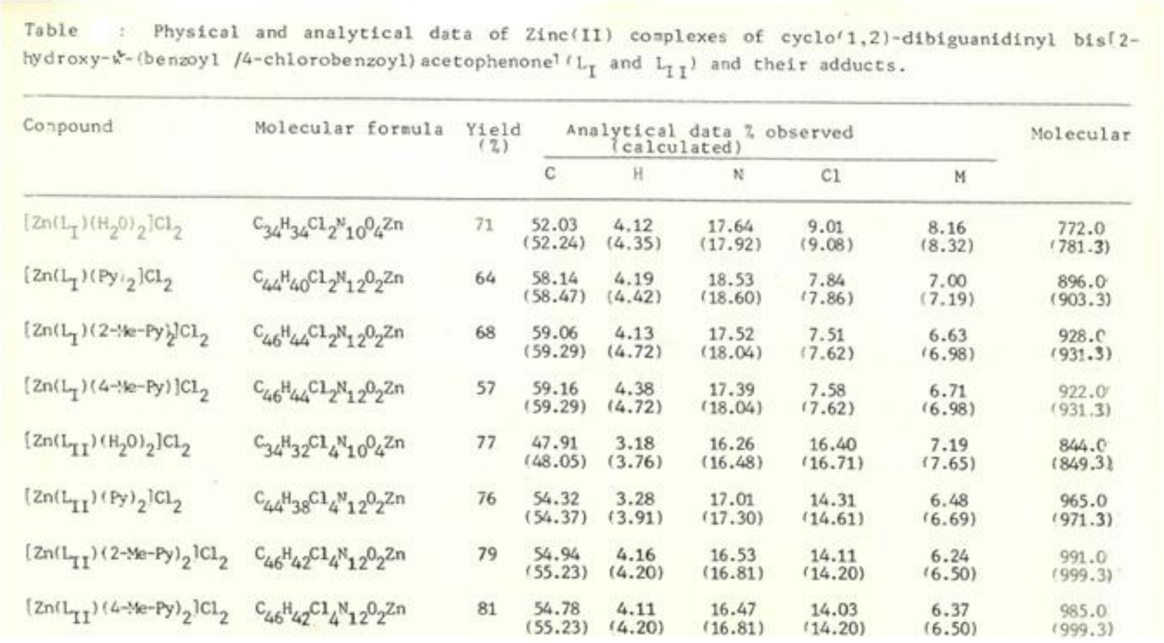

Table : Physical and analytical data of Zinc(II) complexes of cyclo(1,2)-dibiguanidinyl bis[2-hydroxy-ω-(benzoyl /4-chlorobenzoyl) acetophenone] (L_I and L_{II}) and their adducts.

Compound	Molecular formula	Yield (%)	Analytical data % observed (calculated)					Molecular
			C	H	N	Cl	M	
$[Zn(L_I)(H_2O)_2]Cl_2$	$C_{34}H_{34}Cl_2N_{10}O_4Zn$	71	52.03 (52.24)	4.12 (4.35)	17.64 (17.92)	9.01 (9.08)	8.16 (8.32)	772.0 (781.3)
$[Zn(L_I)(Py)_2]Cl_2$	$C_{44}H_{40}Cl_2N_{12}O_2Zn$	64	58.14 (58.47)	4.19 (4.42)	18.53 (18.60)	7.84 (7.86)	7.00 (7.19)	896.0 (903.3)
$[Zn(L_I)(2\text{-}Me\text{-}Py)_2]Cl_2$	$C_{46}H_{44}Cl_2N_{12}O_2Zn$	68	59.06 (59.29)	4.13 (4.72)	17.52 (18.04)	7.51 (7.62)	6.63 (6.98)	928.0 (931.3)
$[Zn(L_I)(4\text{-}Me\text{-}Py)]Cl_2$	$C_{46}H_{44}Cl_2N_{12}O_2Zn$	57	59.16 (59.29)	4.38 (4.72)	17.39 (18.04)	7.58 (7.62)	6.71 (6.98)	922.0 (931.3)
$[Zn(L_{II})(H_2O)_2]Cl_2$	$C_{34}H_{32}Cl_4N_{10}O_4Zn$	77	47.91 (48.05)	3.18 (3.76)	16.26 (16.48)	16.40 (16.71)	7.19 (7.65)	844.0 (849.3)
$[Zn(L_{II})(Py)_2]Cl_2$	$C_{44}H_{38}Cl_4N_{12}O_2Zn$	76	54.32 (54.37)	3.28 (3.91)	17.01 (17.30)	14.31 (14.61)	6.48 (6.69)	965.0 (971.3)
$[Zn(L_{II})(2\text{-}Me\text{-}Py)_2]Cl_2$	$C_{46}H_{42}Cl_4N_{12}O_2Zn$	79	54.94 (55.23)	4.16 (4.20)	16.53 (16.81)	14.11 (14.20)	6.24 (6.50)	991.0 (999.3)
$[Zn(L_{II})(4\text{-}Me\text{-}Py)_2]Cl_2$	$C_{46}H_{42}Cl_4N_{12}O_2Zn$	81	54.78 (55.23)	4.11 (4.20)	16.47 (16.81)	14.03 (14.20)	6.37 (6.50)	985.0 (999.3)

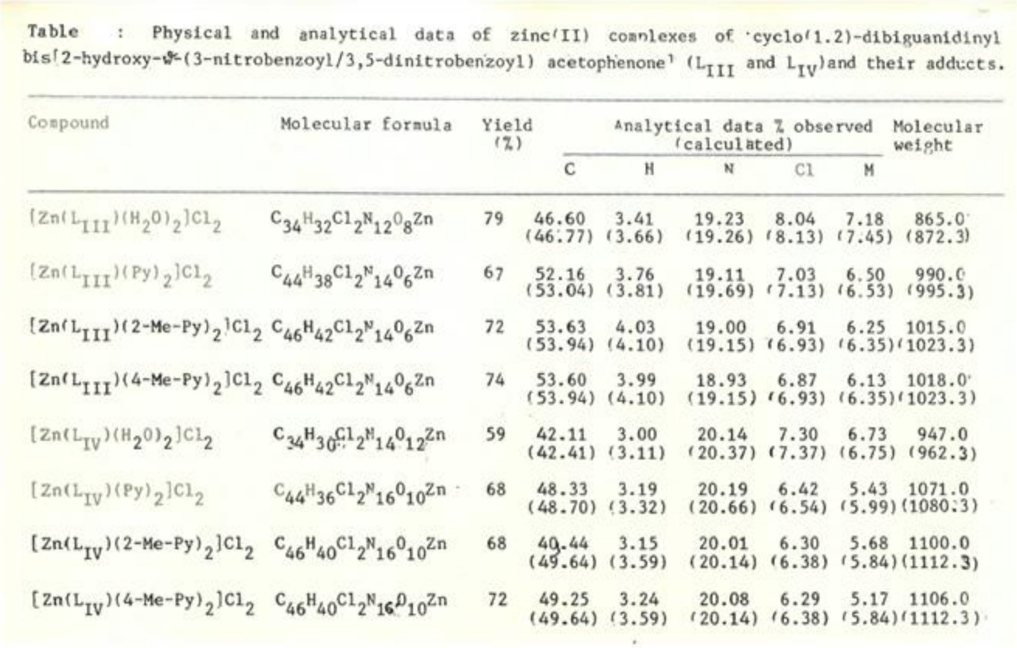

Table : Physical and analytical data of zinc(II) complexes of 'cyclo(1.2)-dibiguanidinyl bis[2-hydroxy-ω-(3-nitrobenzoyl/3,5-dinitrobenzoyl) acetophenone] (L_{III} and L_{IV})and their adducts.

Compound	Molecular formula	Yield (%)	Analytical data % observed (calculated)					Molecular weight
			C	H	N	Cl	M	
$[Zn(L_{III})(H_2O)_2]Cl_2$	$C_{34}H_{32}Cl_2N_{12}O_8Zn$	79	46.60 (46.77)	3.41 (3.66)	19.23 (19.26)	8.04 (8.13)	7.18 (7.45)	865.0 (872.3)
$[Zn(L_{III})(Py)_2]Cl_2$	$C_{44}H_{38}Cl_2N_{14}O_6Zn$	67	52.16 (53.04)	3.76 (3.81)	19.11 (19.69)	7.03 (7.13)	6.50 (6.53)	990.0 (995.3)
$[Zn(L_{III})(2\text{-}Me\text{-}Py)_2]Cl_2$	$C_{46}H_{42}Cl_2N_{14}O_6Zn$	72	53.63 (53.94)	4.03 (4.10)	19.00 (19.15)	6.91 (6.93)	6.25 (6.35)	1015.0 (1023.3)
$[Zn(L_{III})(4\text{-}Me\text{-}Py)_2]Cl_2$	$C_{46}H_{42}Cl_2N_{14}O_6Zn$	74	53.60 (53.94)	3.99 (4.10)	18.93 (19.15)	6.87 (6.93)	6.13 (6.35)	1018.0 (1023.3)
$[Zn(L_{IV})(H_2O)_2]Cl_2$	$C_{34}H_{30}Cl_2N_{14}O_{12}Zn$	59	42.11 (42.41)	3.00 (3.11)	20.14 (20.37)	7.30 (7.37)	6.73 (6.75)	947.0 (962.3)
$[Zn(L_{IV})(Py)_2]Cl_2$	$C_{44}H_{36}Cl_2N_{16}O_{10}Zn$	68	48.33 (48.70)	3.19 (3.32)	20.19 (20.66)	6.42 (6.54)	5.43 (5.99)	1071.0 (1080.3)
$[Zn(L_{IV})(2\text{-}Me\text{-}Py)_2]Cl_2$	$C_{46}H_{40}Cl_2N_{16}O_{10}Zn$	68	40.44 (49.64)	3.15 (3.59)	20.01 (20.14)	6.30 (6.38)	5.68 (5.84)	1100.0 (1112.3)
$[Zn(L_{IV})(4\text{-}Me\text{-}Py)_2]Cl_2$	$C_{46}H_{40}Cl_2N_{16}O_{10}Zn$	72	49.25 (49.64)	3.24 (3.59)	20.08 (20.14)	6.29 (6.38)	5.17 (5.84)	1106.0 (1112.3)

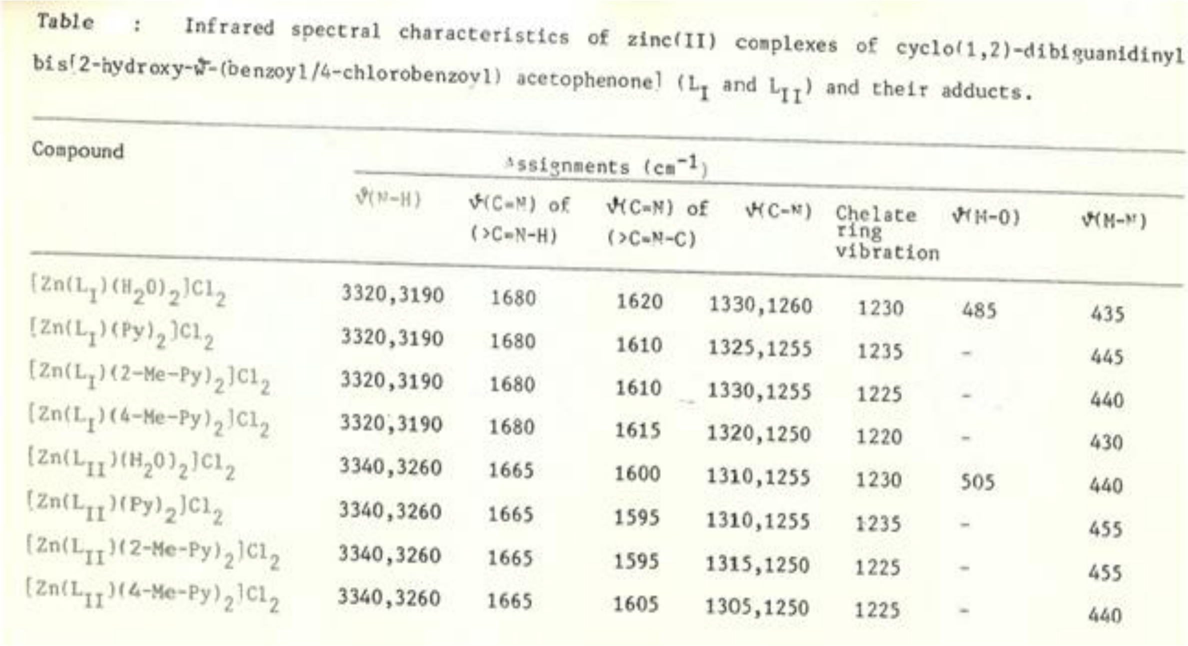

Table : Infrared spectral characteristics of zinc(II) complexes of cyclo(1,2)-dibiguanidinyl bis[2-hydroxy-ω-(benzoyl/4-chlorobenzoyl) acetophenone] (L_I and L_{II}) and their adducts.

Compound	Assignments (cm^{-1})						
	ϑ(N-H)	ϑ(C=N) of (>C=N-H)	ϑ(C=N) of (>C=N-C)	ϑ(C-N)	Chelate ring vibration	ϑ(M-O)	ϑ(M-N)
$[Zn(L_I)(H_2O)_2]Cl_2$	3320,3190	1680	1620	1330,1260	1230	485	435
$[Zn(L_I)(Py)_2]Cl_2$	3320,3190	1680	1610	1325,1255	1235	-	445
$[Zn(L_I)(2\text{-}Me\text{-}Py)_2]Cl_2$	3320,3190	1680	1610	1330,1255	1225	-	440
$[Zn(L_I)(4\text{-}Me\text{-}Py)_2]Cl_2$	3320,3190	1680	1615	1320,1250	1220	-	430
$[Zn(L_{II})(H_2O)_2]Cl_2$	3340,3260	1665	1600	1310,1255	1230	505	440
$[Zn(L_{II})(Py)_2]Cl_2$	3340,3260	1665	1595	1310,1255	1235	-	455
$[Zn(L_{II})(2\text{-}Me\text{-}Py)_2]Cl_2$	3340,3260	1665	1595	1315,1250	1225	-	455
$[Zn(L_{II})(4\text{-}Me\text{-}Py)_2]Cl_2$	3340,3260	1665	1605	1305,1250	1225	-	440

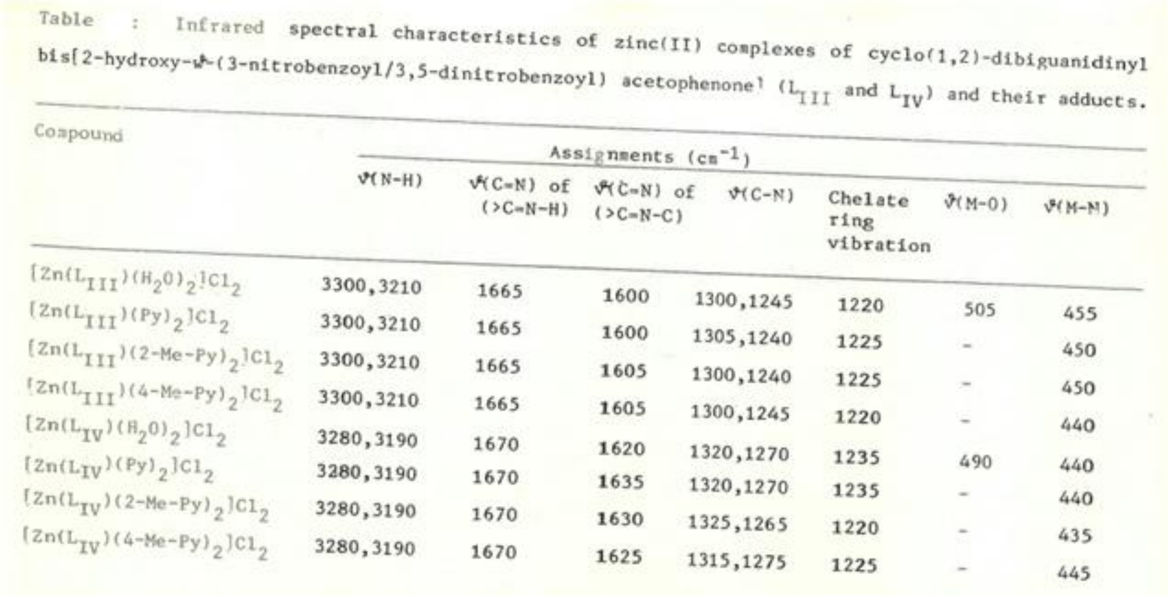

Table : Infrared spectral characteristics of zinc(II) complexes of cyclo(1,2)-dibiguanidinyl bis[2-hydroxy-ν-(3-nitrobenzoyl/3,5-dinitrobenzoyl) acetophenone] (L_{III} and L_{IV}) and their adducts.

Compound	Assignments (cm^{-1})						
	ν(N-H)	ν(C=N) of (>C=N-H)	ν(C=N) of (>C=N-C)	ν(C-N)	Chelate ring vibration	ν(M-O)	ν(M-N)
$[Zn(L_{III})(H_2O)_2]Cl_2$	3300,3210	1665	1600	1300,1245	1220	505	455
$[Zn(L_{III})(Py)_2]Cl_2$	3300,3210	1665	1600	1305,1240	1225	-	450
$[Zn(L_{III})(2\text{-}Me\text{-}Py)_2]Cl_2$	3300,3210	1665	1605	1300,1240	1225	-	450
$[Zn(L_{III})(4\text{-}Me\text{-}Py)_2]Cl_2$	3300,3210	1665	1605	1300,1245	1220	-	440
$[Zn(L_{IV})(H_2O)_2]Cl_2$	3280,3190	1670	1620	1320,1270	1235	490	440
$[Zn(L_{IV})(Py)_2]Cl_2$	3280,3190	1670	1635	1320,1270	1235	-	440
$[Zn(L_{IV})(2\text{-}Me\text{-}Py)_2]Cl_2$	3280,3190	1670	1630	1325,1265	1220	-	435
$[Zn(L_{IV})(4\text{-}Me\text{-}Py)_2]Cl_2$	3280,3190	1670	1625	1315,1275	1225	-	445

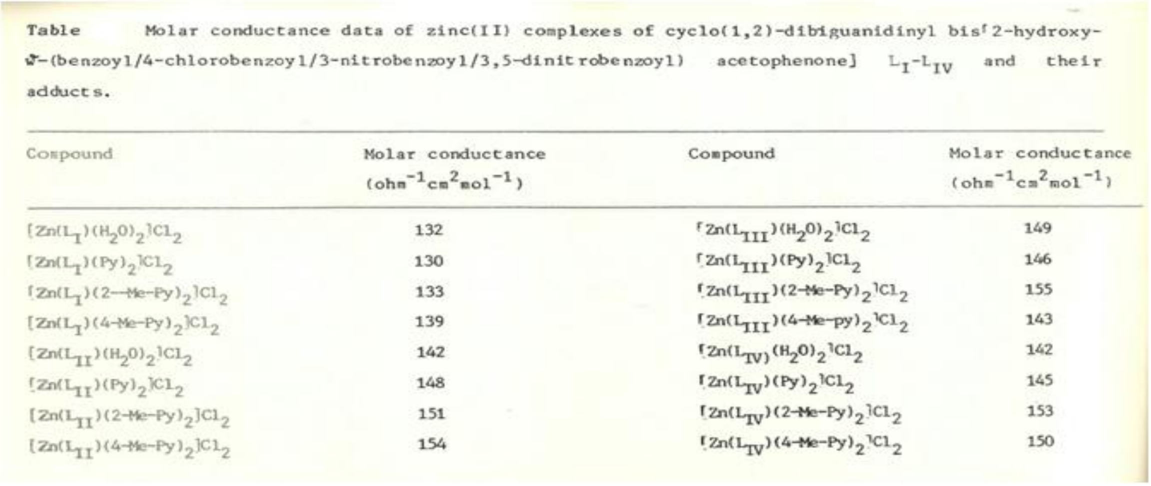

Table Molar conductance data of zinc(II) complexes of cyclo(1,2)-dibiguanidinyl bis[2-hydroxy-ν-(benzoyl/4-chlorobenzoyl/3-nitrobenzoyl/3,5-dinitrobenzoyl) acetophenone] L_I-L_{IV} and their adducts.

Compound	Molar conductance ($ohm^{-1}cm^2mol^{-1}$)	Compound	Molar conductance ($ohm^{-1}cm^2mol^{-1}$)
$[Zn(L_I)(H_2O)_2]Cl_2$	132	$[Zn(L_{III})(H_2O)_2]Cl_2$	149
$[Zn(L_I)(Py)_2]Cl_2$	130	$[Zn(L_{III})(Py)_2]Cl_2$	146
$[Zn(L_I)(2\text{-}Me\text{-}Py)_2]Cl_2$	133	$[Zn(L_{III})(2\text{-}Me\text{-}Py)_2]Cl_2$	155
$[Zn(L_I)(4\text{-}Me\text{-}Py)_2]Cl_2$	139	$[Zn(L_{III})(4\text{-}Me\text{-}py)_2]Cl_2$	143
$[Zn(L_{II})(H_2O)_2]Cl_2$	142	$[Zn(L_{IV})(H_2O)_2]Cl_2$	142
$[Zn(L_{II})(Py)_2]Cl_2$	148	$[Zn(L_{IV})(Py)_2]Cl_2$	145
$[Zn(L_{II})(2\text{-}Me\text{-}Py)_2]Cl_2$	151	$[Zn(L_{IV})(2\text{-}Me\text{-}Py)_2]Cl_2$	153
$[Zn(L_{II})(4\text{-}Me\text{-}Py)_2]Cl_2$	154	$[Zn(L_{IV})(4\text{-}Me\text{-}Py)_2]Cl_2$	150

CONCLUSION

The conclusion was supported by the disappearance of a band at 505-485 cm^{-1} due to Y (M-O) mode of vibration in the spectra of adducts. A new band at 455-430 cm^{-1} due to (M-N) mode was also observed in the adducts.

Based on the above studies, the ionic adducts of Zn(II) complexes having general formula $[Zn(L_I\text{-}L_{IV})B_2]CL_2$ were assigned octahedral geometry with the ligand exhibiting tetradentate behaviour, coordinating through imine nitrogen atoms of (>C=N-C) group as evidenced by infrared spectral data.

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