



Adducts of the Copper(II) complexes of cyclo(1,2)-dibiguanidinyll [bis 2-hydroxy-w(benzoyl/4-chloroben-zoyl/3-nitrobenzoyl/3,5-dinitrobenzoyl) acetophenone]with pyridine,2-methylpyridine and 4-methylpyridine

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Abstract

Copper(II) forms neutral, anionic and cationic complexes, both non-chelate and chelate. The d^9 configuration subjects Cu(II) to Jahn-Teller distortion if placed in an environment of cubic symmetry and this has a profound effect on its stereochemistry. The Jahn-Teller effect decreases the energy of the d_z^2 orbital which is, therefore, occupied by two electrons while the dx^2-y^2 orbital is occupied by two electrons only.

Consequently, the approach of a nucleo-philic ligand on the Z-axis is resisted which leads to greater Cu-L distances along the Z-axis as compared to the four Cu-L distances in the XY plane and causes severe distortion.

Introduction

The structural elucidation of the complexes has been done on the basis of elemental analysis, molecular weight determination, infrared and electronic spectra and magnetic data. The conductance values ($148-168 \text{ ohm}^{-1}\text{cm}^{-2}\text{mol}^{-1}$) were indicative of the ionic nature of the complexes.

A broad band centered at $3450-3400 \text{ cm}^{-1}$ was assigned to (O-H) stretching frequencies of coordinated water (Rana and Shah, 1986).

The participation of oxygen and nitrogen was further confirmed by the appearance of new bands in the far infrared region at 500-480 and 465-440 cm^{-1} in the spectra of the complexes and assigned to Y(M-O) and Y (M-N) modes ,respectively (Ferraro, 1971).

The spin only magnetic moment value for copper(II) complexes is expected to be 1.73 B.M. In the present investigation the observed effective magnetic moment values for $\text{CuL}_I\text{-CuL}_{IV}$, ranged from 1.94-1.98 B.M. confirming the presence of single unpaired electron with significant orbital contribution to the spin-only magnetic moment value (Cotton and Wilkinson, 1988).

Since d^9 is equivalent of d^1 a simple spectra, analogous to that of Ti(III) should be expected for Cu(II).

Only one broad band is predicted for the octahedral complexes of d^1 or d^9 configuration and the energy of transition is 10 Dq. However, Copper (II) complexes are subject to considerable distortion which renders their absorption spectra quite complex. This distortion alongwith high spin orbit coupling coefficient of Cu(II) (-830 cm^{-1}) causes the broadening of the absorption band observed in the visible region near 16000 cm^{-1} (Lever, 1968).

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In the present investigation, the copper(II) complexes exhibited a single broad absorption band in the region $13300\text{-}14800 \text{ cm}^{-1}$ which was assigned to corresponding electronic transition and is a characteristic distorted octahedral stereochemistry (Hathaway, 1971).

The 10 Dq values ($13300\text{-}14800 \text{ cm}^{-1}$) and ligand field stabilization energies (95.45 - 106.22 KJ mol) further supported distorted octahedral geometry around Cu(II) for the complexes $\text{CuL}_I\text{-CuL}_{IV}$ - (Ravinder et al., 1984 and Rao et al., 1985).

Based on the above discussion, the copper(II) complexes were assigned distorted octahedral geometry with a 1:1 stoichiometric ratio in which the ligands acted as tetradentate, coordinating through the nitrogen atoms of imine groups.

The adducts were ionic in nature as evidenced by molar conductance values ($140-160 \text{ ohm}^{-1} \text{cm}^{-2} \text{mol}^{-1}$).

(i) Infrared spectra

A perusal of the infra-red spectra of the adducts of Cu(II) complexes revealed the disappearance of (O-H) band which was present at $3450-3400 \text{ cm}^{-1}$ in the spectra of the complexes suggesting thereby the replacement of coordinated water molecules by base molecules, which was further supported by the absence of U(M-O) vibration in the IR spectra of the adducts.

The new bands observed in the region $1240-1215$ and $460-440 \text{ cm}^{-1}$ were assigned to chelate ring and (M-N) stretching, respectively.

(ii) Magnetic moment and electronic spectra

The magnetic moment values for the adducts of copper(II) complexes of L_I-L_{IV} were in the range $1.80-2.13 \text{ B.M.}$ indicating significant degree of orbital contribution to the spin-only value for a single unpaired electron (Cotton and Wilkinson, 1988).

The electronic spectra of these adducts exhibited a single broad absorption band in the region $13500-15900 \text{ cm}^{-1}$ which was due to transition suggesting distorted octahedral geometry for these adducts (Hathaway, 1971).

The values for $10 Dq$ ($13500-15900 \text{ cm}^{-1}$) and LFSE ($96.88 -114.11 \text{ KJ mol}^{-1}$) were also consistent with the proposed geometry (Ravinder et al., 1984).

On the basis of above discussion, a distorted octahedral geometry was assigned to the ionic adducts in which ligand behaved as tetradentate.

RESULTS

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

Compound	Molecular formula	Yield (%)	Analytical data % observed (calculated)					Molecular weight
			C	H	N	Cl	M	
$[Cu(L_I)(H_2O)_2]Cl_2$	$C_{34}H_{34}Cl_2N_{10}O_4Cu$	69	52.20 (52.27)	4.33 (4.36)	17.66 (17.97)	8.96 (9.10)	8.12 (8.15)	770.0 (780.5)
$[Cu(L_I)(Py)_2]Cl_2$	$C_{44}H_{40}Cl_2N_{12}O_2Cu$	64	58.53 (58.60)	4.21 (4.43)	18.60 (18.64)	7.80 (7.87)	7.00 (7.04)	894.0 (902.5)
$[Cu(L_I)(2-Me-Py)_2]Cl_2$	$C_{46}H_{44}Cl_2N_{12}O_2Cu$	62	59.00 (59.41)	4.37 (4.73)	18.00 (18.08)	7.51 (7.63)	6.54 (6.83)	914.0 (929.5)
$[Cu(L_I)(4-Me-Py)_2]Cl_2$	$C_{46}H_{44}Cl_2N_{12}O_2Cu$	59	59.11 (59.41)	4.58 (4.73)	17.81 (18.08)	7.49 (7.63)	6.66 (6.83)	921.0 (929.5)
$[Cu(L_{II})(H_2O)_2]Cl_2$	$C_{34}H_{32}Cl_4N_{10}O_4Cu$	65	48.08 (48.17)	3.21 (3.77)	16.32 (16.52)	16.60 (16.75)	7.41 (7.48)	840.0 (847.5)
$[Cu(L_{II})(Py)_2]Cl_2$	$C_{44}H_{38}Cl_4N_{12}O_2Cu$	63	54.33 (54.48)	3.72 (3.91)	17.01 (17.33)	14.53 (14.64)	6.32 (6.54)	960.0 (969.5)
$[Cu(L_{II})(2-Me-Py)_2]Cl_2$	$C_{46}H_{42}Cl_4N_{12}O_2Cu$	61	55.09 (55.36)	4.12 (4.21)	16.44 (16.85)	14.07 (14.23)	6.16 (6.36)	985.0 (997.5)
$[Cu(L_{II})(4-Me-Py)_2]Cl_2$	$C_{46}H_{42}Cl_4N_{12}O_2Cu$	62	55.02 (55.36)	4.09 (4.21)	16.24 (16.85)	14.18 (14.23)	6.13 (6.36)	987.0 (997.5)

Table : Physical and analytical data of copper(II) complexes of cyclo(1,2)-dibiguanidinyl bis[2-hydroxy-*o*-(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	
$[Cu(L_{III})(H_2O)_2]Cl_2$	$C_{34}H_{32}Cl_2N_{12}O_8Cu$	69	46.80 (46.86)	3.60 (3.67)	19.11 (19.29)	8.10 (8.15)	7.13 (7.29)	865.0 (870.5)
$[Cu(L_{III})(Py)_2]Cl_2$	$C_{44}H_{38}Cl_2N_{14}O_6Cu$	55	53.00 (53.14)	3.71 (3.82)	19.21 (19.73)	7.07 (7.14)	6.21 (6.39)	982.0 (993.5)
$[Cu(L_{III})(2-Me-Py)_2]Cl_2$	$C_{46}H_{42}Cl_2N_{14}O_6Cu$	67	54.00 (54.03)	4.07 (4.11)	19.00 (19.19)	6.80 (6.95)	6.00 (6.21)	1017.0 (1021.5)
$[Cu(L_{III})(4-Me-Py)_2]Cl_2$	$C_{46}H_{42}Cl_2N_{14}O_6Cu$	83	53.70 (54.03)	4.01 (4.11)	19.14 (19.19)	6.93 (6.95)	6.15 (6.21)	1013.0 (1021.5)
$[Cu(L_{IV})(H_2O)_2]Cl_2$	$C_{34}H_{30}Cl_2N_{14}O_{12}Cu$	76	42.13 (42.50)	3.10 (3.12)	20.35 (20.41)	7.31 (7.39)	6.16 (6.61)	948.0 (960.5)
$[Cu(L_{IV})(Py)_2]Cl_2$	$C_{44}H_{36}Cl_2N_{16}O_{10}Cu$	78	48.37 (48.79)	3.19 (3.32)	20.15 (20.70)	6.48 (6.55)	5.18 (5.86)	1072.0 (1082.5)
$[Cu(L_{IV})(2-Me-Py)_2]Cl_2$	$C_{46}H_{40}Cl_2N_{16}O_{10}Cu$	74	49.42 (49.72)	3.41 (3.60)	20.00 (20.18)	6.29 (6.39)	5.29 (5.71)	1098.0 (1110.5)
$[Cu(L_{IV})(4-Me-Py)_2]Cl_2$	$C_{46}H_{40}Cl_2N_{16}O_{10}Cu$	66	49.31 (49.72)	3.54 (3.60)	20.04 (20.18)	6.17 (6.39)	5.36 (5.71)	1095.0 (1110.5)

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

Compound	Assignments (cm^{-1})						
	$\nu(\text{N-H})$	$\nu(\text{C=N})$ of ($>\text{C=N-H}$)	$\nu(\text{C=N})$ of ($>\text{C=N-C}$)	$\nu(\text{C-N})$	Chelate ring Vibration	$\nu(\text{M-O})$	$\nu(\text{M-N})$
$[\text{Cu}(L_I)(\text{H}_2\text{O})_2]\text{Cl}_2$	3320,3190	1680	1615	1320,1245	1225	480	460
$[\text{Cu}(L_I)(\text{Py})_2]\text{Cl}_2$	3320,3190	1680	1610	1325,1250	1215	-	445
$[\text{Cu}(L_I)(2\text{-Me-Py})_2]\text{Cl}_2$	3320,3190	1680	1615	1315,1245	1230	-	440
$[\text{Cu}(L_I)(4\text{-Me-Py})_2]\text{Cl}_2$	3320,3190	1680	1605	1315,1260	1220	-	450
$[\text{Cu}(L_{II})(\text{H}_2\text{O})_2]\text{Cl}_2$	3340,3260	1665	1595	1305,1260	1225	500	445
$[\text{Cu}(L_{II})(\text{Py})_2]\text{Cl}_2$	3340,3260	1665	1590	1300,1250	1225	-	460
$[\text{Cu}(L_{II})(2\text{-Me-Py})_2]\text{Cl}_2$	3340,3260	1665	1605	1300,1255	1235	-	455
$[\text{Cu}(L_{II})(4\text{-Me-Py})_2]\text{Cl}_2$	3340,3260	1665	1600	1300,1250	1220	-	450

Table : Infrared spectral characteristics of copper(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})						
	$\nu(\text{N-H})$	$\nu(\text{C=N})$ of ($>\text{C=N-H}$)	$\nu(\text{C=N})$ of ($>\text{C=N-C}$)	$\nu(\text{C-N})$	Chelate ring vibration	$\nu(\text{M-O})$	$\nu(\text{M-N})$
$[\text{Cu}(L_{III})(\text{H}_2\text{O})_2]\text{Cl}_2$	3300,3210	1665	1615	1300,1245	1230	500	440
$[\text{Cu}(L_{III})(\text{Py})_2]\text{Cl}_2$	3300,3210	1665	1605	1305,1250	1230	-	445
$[\text{Cu}(L_{III})(2\text{-Me-Py})_2]\text{Cl}_2$	3300,3210	1665	1610	1310,1235	1225	-	440
$[\text{Cu}(L_{III})(4\text{-Me-Py})_2]\text{Cl}_2$	3300,3210	1665	1605	1305,1240	1220	-	460
$[\text{Cu}(L_{IV})(\text{H}_2\text{O})_2]\text{Cl}_2$	3280,3190	1670	1630	1320,1275	1240	500	465
$[\text{Cu}(L_{IV})(\text{Py})_2]\text{Cl}_2$	3280,3190	1670	1630	1315,1275	1235	-	455
$[\text{Cu}(L_{IV})(2\text{-Me-Py})_2]\text{Cl}_2$	3280,3190	1670	1625	1315,1265	1232	-	450
$[\text{Cu}(L_{IV})(4\text{-Me-Py})_2]\text{Cl}_2$	3280,3190	1670	1620	1325,1270	1240	-	455

Table : Magnetic moment, electronic spectral and molar conductance data of copper(II) complexes of cyclo(1,2)-dibiguanidinyl bis[2-hydroxy- ω -(benzoyl/4-chlorobenzoyl) acetophenone] (L_I and L_{II}) and their adducts.

Compound	${}^2E_g \rightarrow {}^2T_{2g}$ (cm^{-1})	10Dq (cm^{-1})	LFSE ($KJ mol^{-1}$)	μ_{eff} (B.M.)	Molar conductance ($ohm^{-1}cm^2mol^{-1}$)
$[Cu(L_I)(H_2O)_2]Cl_2$	14800	14800	106.22	1.98	152
$[Cu(L_I)(Py)_2]Cl_2$	15100	15100	108.37	1.93	145
$[Cu(L_I)(2-Me-Py)_2]Cl_2$	15900	15900	114.11	1.89	158
$[Cu(L_I)(4-Me-Py)_2]Cl_2$	15000	15000	107.65	2.00	148
$[Cu(L_{II})(H_2O)_2]Cl_2$	14200	14200	101.91	1.95	168
$[Cu(L_{II})(Py)_2]Cl_2$	14400	14400	103.34	1.97	160
$[Cu(L_{II})(2-Me-Py)_2]Cl_2$	14100	14100	101.19	2.10	145
$[Cu(L_{II})(4-Me-Py)_2]Cl_2$	14800	14800	106.22	2.13	158

Table : Magnetic moment electronic spectral and molar conductance data of copper(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	${}^2E_g \rightarrow {}^2T_{2g}$ (cm^{-1})	10 Dq (cm^{-1})	LFSE ($KJ mol^{-1}$)	μ_{eff} (B.M.)	Molar conductance ($ohm^{-1}cm^2mol^{-1}$)
$[Cu(L_{III})(H_2O)_2]Cl_2$	13300	13300	95.45	1.94	148
$[Cu(L_{III})(Py)_2]Cl_2$	13500	13500	96.88	1.95	145
$[Cu(L_{III})(2-Me-Py)_2]Cl_2$	14000	14000	100.47	1.92	142
$[Cu(L_{III})(4-Me-Py)_2]Cl_2$	14200	14200	101.91	1.98	158
$[Cu(L_{IV})(H_2O)_2]Cl_2$	14500	14500	104.06	1.98	148
$[Cu(L_{IV})(Py)_2]Cl_2$	14100	14100	101.19	1.89	151
$[Cu(L_{IV})(2-Me-Py)_2]Cl_2$	14300	14300	102.63	1.80	146
$[Cu(L_{IV})(4-Me-Py)_2]Cl_2$	14150	14150	101.55	1.92	140

CONCLUSION

The spectra of free Ligands L_I-L_{IV} exhibited 'strong absorption bands in the region 1680-1665 and 3340-3280, 3260-3190 cm⁻¹ which are assigned to (C=N) mode of (>C=N-H) group and D (N-H) vibrations, respectively. These bands remained unaltered in the spectra of the complexes suggesting thereby the non-involvement of nitrogen atom of (N-H) group in coordination.

The lowering (35-25 cm⁻¹) of the (>C=N) stretching frequency of (>C=N-C) group and V(C-N) (30-20 cm⁻¹) in the spectra of the metal complexes was due to the participation of nitrogen atom of (>C=N-C) group in coordination. The appearance of a 'new band at 1240-1225 cm⁻¹ was attributed to chelate ring formation.

REFERENCES

1. Merianos, J.J. (1990). Preparation of bis(pyrrolidonyl) alkylene biguanides as antimicrobial agents. U.S. "US 4, 952, 704 (CL. 548-519: C010207/27), 28 Aug. 1990, Appl. 350, 882, 12 May, 1989; 4 pp. [Chem. Abstr. 144 (1991) 42568 u).
2. Mitchinson, C., Pain, R.H., Vinson, J.R. and Walker, T. (1983). The relative effectiveness of guanidinium and some biguanide salts as denaturants. Assessment against penicillinase. *Biochem. Biophys. Acta.* 743(1): 31-6.
3. Molina, P., Alajarin, Ms, Lopez-leonardo, C-; Foces-Foces, M.C. Cano, I.H., Claramunt, R.M. and Elguero, J. (1989). Reactivity of 1,3-diaryl-2, 4-bis(heteroarylimino)-1, 4-diazetidines. Formation of nickel, copper, nickel substituted biguanides. *J. Org. Chem.*, 54(6): 1264-8.
4. Mukhopadhyay, C.C. and De, G.S- (1993). Kinetics and mechanistic studies on substitution reactions of aqua ligands from cis-diaquobis (biguanide) cobalt(II) with pyridine 2-aldoxime in various ethanol water mixtures. *Indian J. Chem.* 32A: 802-804.
5. Murthy, G.R., Rao, A.B.; Reddy, V.M. and Sisodia, P. (1986). New hypoglycemic agents: part I. Synthesis and hypoglycemic activity of some new nickel-(5-aryl-1; 3-4-oxadiazol-1-yl)-N^o-(arylsulfonyl) biguanides. *Indian Drugs.* 23(6): 354-7.

6. Nakamoto, K. (1978). "Infrared and Raman Spectra of Inorganic and Coordination Compounds", Wiley Interscience, New York.
7. Oeckl, S., Radt, W., Genth, H. and Paulus, W. (1984). Polymeric biguanides, and their use in microbicidal agents.
8. Ostrogovich, A- (1910). Bull. Soc, Stiinte Bucharesti 19-64.
9. Parashar R.K. and Sharma, R.C. (1987). Synthesis and biocidal activity of zinc(II) complexes of some 2,2'-substituted diphenylamines. J. Inorg. Biochem. , 29:225.
10. Piceinini, F., "berti, E.M. and Lucattelli, I. (1960). Hypo-glycemic activity of some biguanides and their corresponding copper complexes. Farmaco (Pavia), Ed, Sci. 15: 521-9.