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Adducts of Cobalt(II) complexes of cyclo(1,2)-dibigu-anidinyl bis[2-hydroxy-w-(benzoyl /4-chlorobenzoy1/3-nitrobenzoyl/3,5-dinitrobenzoyl) acetophenone] with pyridine, 2-methylpyridine and 4-methlpyridine

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Abstract

The conductance values (135-150 ohm^{-1} cm^{2}mol^{-1})elemental analysis and molecular weight determinationindicated the Gornetslon of ionic, 1:1 Co(II)complexes. The structure elucidation of the complexes wasdone on the basis of spectral and magnetic studies.

In the infrared spectra of the complexes a hypsochromie shift in (C=N) stretching mode of(>C=N-C) group from 1645-1615 to 1630-1595 cm^{-1} and adownward shift in the (C-N) from 1350-1320 and 1290-1260to 1325-1300 and 1275-1245 cm^{-1} depicted the participationof nitrogen of imine group (>C=N-C) in coordination.

The stretching vibrations' due to (N-H) modeand (C=N) mode of (>C=N-H) group remained unaltered in thespectra of the metal complexes. This strongly suggestedthat the nitrogen of (N-H) group was not involved incoordination.

Introduction

The chelate ring absorption frequencyobserved at 1240-1225 cm^{-1}suggesting the complex formation. The presence ofcoordinated water was confirmed by a new broad band in theregion 3450-3400 cm^{-1}due to (O-H) mode in the spectra ofcomplexes (Rana and Shah, 1986). These conclusions werefurther supported by the appearance of new bands at 500-490in the spectra of the complexes(Syamal, 1978) was absent in the spectra of ligandsand 455-430 cm^{-1} diagnostic of (M-O) and (M-N)vibrations, respectively in the spectra of complexes(Nakamoto, 1978) Ferraro, 1971).

(ii) Magnetic moment and electronic spectra

The magnetic moment values for octahedral complexesof cobalt(II) lie in the range of 4.8-5.2 B.M. whereas thosefor tetrahedral complexes vary from 4.4 to 4.8 B.M. at

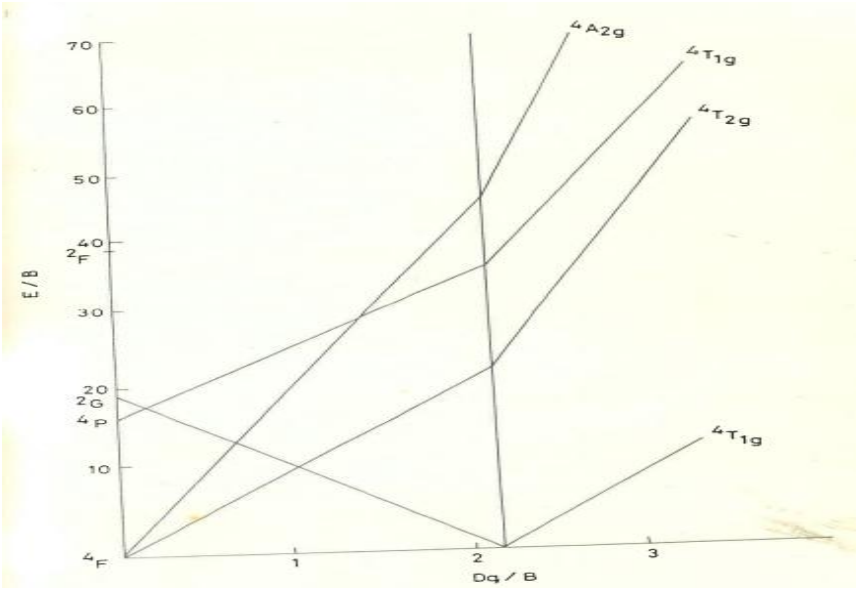
roomtemperature (Greenwood and Earnshaw, 1990). The magneticmoment values for spin-free octahedral and tetragonallydistorted octahedral cobalt(II) complexes are higher thanthe spin-only value for three unpaired electrons (3.87 B.M.)because of unquenched orbital contribution of both theground state and the first excited state(Figgis, 1976).

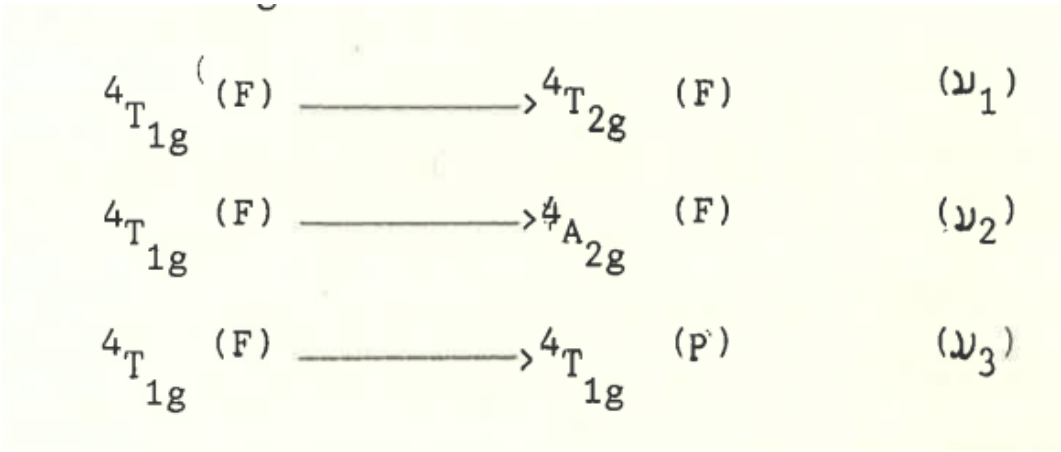
The exact excess magnitude, however,depends upon the ligand field strength. The magneticmoments of low spin cobalt (II) complexes correspond tosingle unpaired electron (1.73 B.M.) with slight orbitalcontribution and these complexes are formed with the ligandsof higher field strength only.

In the present investigationeffective magnetic moment values ranged from 4.84 to 4.89B.M. which-correspond to three unpairedelectrons with significant orbital contribution.

Cobalt(II) is the most important a' species and inan octahedral field three spin allowed d-d transitions areexpected due to the splitting of the free ion, ground 4pterm and the accompanying 4p term (Carlin, 1965).

Tanabe-Sugano diagram for cobalt(II) in an octahedral field is shown in Fig. The three electronic transitions generally observed in such complexes originate from the ground term $^4T_{1g}$ (F)





In the complexes under study the absorption frequenciesobserved in the region 9220-9700, 18100-18730 and 23100-23800 cm^{-1} were assigned to correspondingtransitions, respectively and were characteristic ofoctahedral geometry (Lever, 1968).

Adducts of Cobalt(II) complexes of cyclo(1,2)-dibigu-anidinyl bis[2-hydroxy-w-(benzoyl /4-chlorobenzoy1/3-nitrobenzoyl/3,5-dinitrobenzoyl) acetophenone] withpyridine, 2-methylpyridine and 4-methlpyridine

The adducts were characterized on the basis ofelemental analysis, molecular weight determination, magnetic moment and infrared and electronic spectralstudies. The molar conductance values in dry DMSO were inthe range 115-145 $ohm^{-1}cm^2mol^{-1}$ suggesting 1:2 electrolytic nature of these adducts.

(i) Infrared spectra

Anegative spectral shift of 25-20 cm^{-1}in the absorptionfrequency of the (>C=N-C) moiety in adducts occurred due tothe lowering of C=N bond order on coordination throughnitrogen (Roychowdhury et al., 1988).

Hypsochromic shiftingof (C-N) stretching frequency from 1350-1320 to 1325-1300and from 1290-1260 to 1240-1220 cm^{-1}, respectively furthersupported the participation of imine nitrogen in coordinationwith metal ion. The appearance of a new band at1240-1220 cm^{-1} ascribed to chelate ring stretching vibrationin the spectra of the adducts clearly indicated the metal-ligand bond formation (Syamal, 1978).

Theband due to (O-H) was absent in the spectra of the adductsindicating the replacement of coordinated water molecules inthe complexes by base molecules in the adducts. It

wasfurther confirmed by the disappearance of U(M-O) band at500-490 cm^{-1} in the spectra of the adducts.

(ii) Magnetic moment and electronic spectra

The absorption frequenciesobserved in the region 9680-9850 cm^{-1}, 18500-19200 and23000-24100 cm^{-1} in the electronic spectra of the adductswere assigned to the corresponding transitions respectively.

RESULTS

Table : Physical and analytical data of Cobalt(II) complexes of cyclo(1,2)-dibiguanidinyl bis[2-hydroxy-3-(benzoyl /4-chlorobenzoyl) acetophenone] (L_I and L_{II}) and their adducts.

Compound	Molecular formula	Yield (%)	Analytical data % observed (calculated) C	H	N	Cl	M	Molecular weight
$[Co(L_I)(H_2O)_2]Cl_2$	$C_{34}H_{34}Cl_2N_{10}O_4Co$	69	52.11 (52.65)	4.31 (4.38)	18.00 (18.06)	9.12 (9.16)	7.41 (7.60)	770.0 (774.9)
$[Co(L_I)(Py)_2]Cl_2$	$C_{44}H_{40}Cl_2N_{12}O_2Co$	64	58.17 (58.86)	4.07 (4.45)	18.17 (18.73)	7.84 (7.91)	6.52 (6.56)	884.0 (896.9)
$[Co(L_I)(2\text{-Me-Py})_2]Cl_2$	$C_{46}H_{44}Cl_2N_{12}O_2Co$	61	59.40 (59.68)	4.21 (4.75)	18.05 (18.16)	7.63 (7.67)	6.13 (6.36)	907.0 (924.9)
$[Co(L_I)(4\text{-Me-Py})_2]Cl_2$	$C_{46}H_{44}Cl_2N_{12}O_2Co$	67	59.53 (59.68)	4.13 (4.75)	18.01 (18.16)	7.60 (7.67)	6.18 (6.36)	913.0 (924.9)
$[Co(L_{II})(H_2O)_2]Cl_2$	$C_{34}H_{32}Cl_4N_{10}O_4Co$	79	48.11 (48.40)	3.71 (3.79)	16.19 (16.60)	16.81 (16.84)	6.81 (6.98)	834.0 (842.9)
$[Co(L_{II})(Py)_2]Cl_2$	$C_{44}H_{38}Cl_4N_{12}O_2Co$	81	54.07 (54.72)	3.40 (3.93)	17.21 (17.41)	14.53 (14.71)	6.00 (6.10)	961.0 (964.9)
$[Co(L_{II})(2\text{-Me-Py})_2]Cl_2$	$C_{46}H_{42}Cl_4N_{12}O_2Co$	67	55.16 (55.59)	4.09 (4.23)	16.13 (16.92)	14.03 (14.30)	5.17 (5.93)	985.0 (992.9)
$[Co(L_{II})(4\text{-Me-Py})_2]Cl_2$	$C_{46}H_{42}Cl_4N_{12}O_2Co$	82	55.41 (55.59)	4.17 (4.23)	16.18 (16.92)	14.17 (14.30)	5.39 (5.93)	984.0 (992.9)

Table : Physical and analytical data of cobalt(II) complexes of cyclo(1,2)-dibiguanidinyl bis[2-hydroxy-3-(3-nitrobenzoyl/3,5-dinitrobenzoyl) acetophenone](L_{III} and L_{IV}) and their adducts.

Compound	Molecular formula	Yield (%)	Analytical data % observed (calculated) C	H	N	Cl	M	Molecular weight
$[Co(L_{III})(H_2O)_2]Cl_2$	$C_{34}H_{32}Cl_2N_{12}O_8Co$	71	46.86 (47.11)	3.60 (3.69)	19.17 (19.40)	8.14 (8.19)	6.14 (6.80)	860.0 (865.9)
$[Co(L_{III})(Py)_2]Cl_2$	$C_{44}H_{38}Cl_2N_{14}O_6Co$	67	53.31 (53.39)	3.81 (3.84)	19.49 (19.82)	7.07 (7.17)	5.21 (5.95)	975.0 (988.9)
$[Co(L_{III})(2\text{-Me-Py})_2Cl_2$	$C_{46}H_{42}Cl_2N_{14}O_6Co$	66	54.14 (54.28)	4.07 (4.13)	19.13 (19.27)	6.91 (6.98)	5.44 (5.79)	1000.0 (1016.9)
$[Co(L_{III})(4\text{-Me-Py})_2]Cl_2$	$C_{46}H_{42}Cl_2N_{14}O_6Co$	82	54.07 (54.28)	4.09 (4.13)	19.16 (19.27)	6.88 (6.98)	5.38 (5.79)	1008.0 (1016.9)
$[Co(L_{IV})(H_2O)_2]Cl_2$	$C_{34}H_{30}Cl_2N_{14}O_{12}Co$	72	42.51 (42.68)	3.07 (3.13)	20.16 (20.50)	7.09 (7.42)	6.00 (6.16)	942.0 (955.9)
$[Co(L_{IV})(Py)_2]Cl_2$	$C_{44}H_{36}Cl_2N_{16}O_{10}Co$	67	48.11 (48.98)	3.13 (3.33)	20.32 (20.78)	6.47 (6.58)	5.19 (5.46)	1064.0 (1077.9)
$[Co(L_{IV})(2\text{-Me-Py})_2]Cl_2$	$C_{46}H_{40}Cl_2N_{16}O_{10}Co$	66.5	49.09 (49.91)	3.26 (3.61)	20.08 (20.25)	6.37 (6.42)	5.13 (5.32)	1091.0 (1195.9)
$[Co(L_{IV})(4\text{-Me-Py})_2]Cl_2$	$C_{46}H_{40}Cl_2N_{16}O_{10}Co$	67.5	49.87 (49.91)	3.41 (3.61)	20.19 (20.25)	6.29 (6.42)	5.21 (5.32)	1098.0 (1105.9)

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

Compound	Assignment (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)
$[Co(L_I)(H_2O)_2]Cl_2$	3320,3190	1680	1605	1325,1260	1225	500	455
$[Co(L_I)(Py)_2]Cl_2$	3320,3190	1680	1615	1315,1260	1240	-	450
$[Co(L_I)(2\text{-Me-Py})_2]Cl_2$	3320,3190	1680	1605	1320,1265	1230	-	455
$[Co(L_I)(4\text{-Me-Py})_2]Cl_2$	3320,3190	1680	1615	1315,1255	1225	-	440
$[Co(L_{II})(H_2O)_2]Cl_2$	3340,3260	1665	1595	1300,1260	1225	490	445
$[Co(L_{II})(Py)_2]Cl_2$	3340,3260	1665	1590	1320,1265	1235	-	435
$[Co(L_{II})(2\text{-Me-Py})_2]Cl_2$	3340,3260	1665	1600	1315,1255	1220	-	440
$[Co(L_{II})(4\text{-Me-Py})_2]Cl_2$	3340,3260	1665	1605	1325,1260	1230	-	435

Table : Infrared spectral characteristics of cobalt(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	Assignment (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)
$[Co(L_{III})(H_2O)_2]Cl_2$	3300,3210	1665	1600	1300,1245	1235	495	430
$[Co(L_{III})(Py)_2]Cl_2$	3300,3210	1665	1600	1305,1240	1225	-	435
$[Co(L_{III})(2\text{-Me-Py})_2]Cl_2$	3300,3210	1665	1605	1305,1240	1220	-	435
$[Co(L_{III})(4\text{-Me-Py})_2]Cl_2$	3300,3210	1665	1600	1300,1240	1220	-	425
$[Co(L_{IV})(H_2O)_2]Cl_2$	3280,3190	1670	1630	1320,1275	1240	490	450
$[Co(L_{IV})(Py)_2]Cl_2$	3280,3190	1670	1625	1320,1280	1240	-	435
$[Co(L_{IV})(2\text{-Me-Py})_2]Cl_2$	3280,3190	1670	1625	1315,1270	1235	-	440
$[Co(L_{IV})(4\text{-Me-Py})_2]Cl_2$	3280,3190	1670	1620	1320,1280	1230	-	440

CONCLUSION

Comparison of the IR spectral data of the ligands and the adducts revealed that absorption frequencies due to Y(C-N) mode of Y(>C=N-H) group and Y(N-H) modes observed at 1680-1665 and 3340-3280; 3260-3190 cm^{-1}, respectively in the spectra of the ligands were present at the same positions in the spectra of the adducts suggesting the non-involvement of nitrogen of N-H groups in coordination. The magnetic moment values for the adducts of cobalt (II) complexes were in the range 4.88 - 4.98 B.M. which corresponded to para-magnetism due to the presence of three unpaired electrons.

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