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Complexation of 3,4-Dialkyl Isoquinolones Semicarbazone and Thiosemicarbazone with Co(II), Ni(II) and Cu(II)

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A series of complexes of Co(II), Ni(II) and Cu(II) with 3-methyl-4-ethyl isoquinolone, semicarbazone and thiosemicarbazone [MEIQSC(HL^1) and MEIQTSC(HL^2)] 3-methyl-4-propyl isoquinolone semicarbazone and thiosemicarbazone [MPIQSC(HL^3) and MPIQTSC(HL^4)] 3-ethyl-4-propyl isoquinolone semicarbazone and thiosemicarbazone [EPIQSC(HL^5) and EPIQTSC(HL^6)] has been synthesized and characterized on the basis of elemental analysis, IR spectra, electronic spectra, magnetic moment data and conductivity measurements. The analytical data of all the complexes indicates, 1 : 2 metal : ligand stoichiometry of the type $[M(HL^{1-6})_2]$ where M = Co(II), Ni(II) and Cu(II). The ligands behaved as binegative tridentate ligands and can coordinate through amine and imine nitrogen and oxygen/sulphur donor atoms. The complexes were proposed to be octahedral in geometry and the low value of conductivity indicates their non-electrolytic nature.

Key Words: Cobalt, Nickel, Copper, 3,4-Dialkyl isoquinolones, Semicarbazone, Thiosemicarbazone.

INTRODUCTION

Semicarbazone and thiosemicarbazone and their derivatives are reported to be having antilepral[1], antitubercular[2], antimalarial[3], anticancer[4], antibacterial[5], antiviral[6] and chemotherapeutic properties[7] and metal complexes with semicarbazones and thiosemicarbazones has been found to be useful as potential drugs[8–9]. Considering the above facts in mind and in continuation of our earlier research work[10–13] on transition metal complexes with semicarbazone and thiosemicarbazone derivatives, in the present paper, synthesis and characterisation of Co(II), Ni(II) and Cu(II) complexes with ligands 3-methyl-4-methyl isoquinolone semicarbazone (MEIQSC), 3-methyl-4-ethyl isoquinolone thiosemicarbazone (MEIQTSC), 3-methyl-4-propyl isoquinolone semicarbazone (MPIQSC), 3-methyl-4-propyl isoquinolone thiosemicarbazone (MPIQTSC) 3-ethyl-4-propyl isoquinolone semicarbazone (EPIQSC) and 3-ethyl-4-propyl isoquinolone thiosemicarbazone (EPIQTSC) are reported.

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EXPERIMENTAL

All the reagents used were of BDH reagents. Metal, carbon, nitrogen and hydrogen contents of the complexes were determined by the standard methods[14]. The infrared spectra of the ligands as well as the metal complexes were recorded on Perkin-Elmer spectrophotometer, model-398 in the range 4000–200 cm^{-1} employing KBr pellets and data are given in Table-2. The electronic spectra were recorded on a Cary-2390 spectrophotometer. Magnetic moments were measured by Gouy method using mercury tetraisothiocyanato cobaltate as the calibrant. The conductivity measurements were made on Systronics conductometer model 303 using acetonitrile as a solvent. Analytical data, colour, electronic spectral data, magnetic moment and conductivity value are recorded in Table-1.

TABLE-1
COLOUR, ANALYTICAL, MAGNETIC MOMENT, ELECTRONIC SPECTRA AND CONDUCTIVITY MEASUREMENT DATA OF Co(II), Ni(II) AND Cu(II) COMPLEXES WITH HL^1 to HL^6

Compound/ Colour	% Analysis, found (calculated)				Ω_{max} (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (B.M.)	λ_{max} electronic (cm^{-1})
	M	C	H	N			
HL^1 (Yellow)	—	63.81 (63.93)	10.33 (10.25)	22.83 (22.95)	—	—	—
HL^2 (Yellow)	—	59.84 (60.00)	6.01 (6.15)	21.67 (21.53)	—	—	—
HL^3 (Yellow)	—	65.27 (65.11)	6.84 (6.97)	21.59 (21.70)	—	—	—
HL^4 (Yellow)	—	61.20 (61.31)	6.49 (6.56)	20.27 (20.43)	—	—	—
HL^5 (Yellow)	—	67.29 (67.13)	7.61 (7.69)	19.46 (19.58)	—	—	—
HL^6 (Yellow)	—	63.42 (63.57)	7.33 (7.28)	18.69 (18.54)	—	—	—
$[Co(HL^1)_2]$ (Red Brown)	10.59 (10.77)	57.17 (57.04)	5.48 (5.85)	20.54 (20.47)	6.9	4.78	9200, 13500, 20400, 26300
$[Co(HL^2)_2]$ (Brown)	10.23 (10.17)	53.73 (53.89)	5.67 (5.52)	19.47 (19.34)	7.1	5.03	9400, 13550 20500, 26900
$[Co(HL^3)_2]$ (Green)	10.33 (10.25)	58.61 (58.44)	6.12 (6.26)	19.31 (19.48)	7.4	4.81	9300, 13090 20440, 26310
$[Co(HL^4)_2]$ (Yellowish green)	9.83 (9.70)	55.40 (55.36)	6.03 (5.93)	18.59 (18.45)	7.2	5.07	9400, 13520 20410, 26320
$[Co(HL^5)_2]$ (Dark brown)	9.47 (9.34)	66.69 (66.86)	7.56 (7.68)	17.63 (17.75)	7.8	4.86	9500, 13600 20500, 20600
$[Co(HL^6)_2]$ (Dark green)	8.72 (8.88)	57.63 (57.92)	6.51 (6.63)	16.72 (16.89)	7.3	5.12	9550, 13570 20640, 26540
$[Ni(HL^1)_2]$ (Violet)	10.61 (10.73)	56.94 (57.06)	5.79 (5.85)	20.56 (20.48)	8.6	3.43	10300, 16500 22910
$[Ni(HL^2)_2]$ (Reddish brown)	10.22 (10.14)	53.78 (53.91)	5.63 (5.52)	19.26 (19.35)	8.1	3.33	10380, 16600 22900

Compound/ Colour	% Analysis, found (calculated)				Ω_{max} (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (B.M.)	λ_{max} electronic (cm^{-1})
	M	C	H	N			
[Ni(HL^3)$_2$] (Light green)	10.32 (10.21)	58.57 (58.46)	6.14 (6.26)	6.33 (6.26)	8.5	3.41	10340, 16620 22940
[Ni(HL^4)$_2$] (Green)	9.79 (9.67)	55.48 (55.36)	6.05 (5.93)	18.31 (18.46)	8.2	3.36	10330, 16660 22910
[Ni(HL^5)$_2$] (Deep red)	9.23 (9.30)	60.79 (60.88)	6.83 (6.97)	17.84 (17.75)	8.7	3.42	10400, 16640 22960
[Ni(HL^6)$_2$] (Dark blue)	8.74 (8.85)	57.83 (57.94)	6.51 (6.63)	16.78 (16.90)	8.9	3.31	10420, 16700 22980
[Cu(HL^1)$_2$] (Light green)	11.41 (11.52)	56.69 (56.56)	5.67 (5.80)	20.19 (20.30)	12.3	1.83	17420 2800
[Cu(HL^2)$_2$] (Greenish black)	10.71 (10.88)	53.29 (53.46)	5.36 (5.48)	19.27 (19.19)	13.4	1.92	17400 28600
[Cu(HL^3)$_2$] (Brownish black)	10.83 (10.96)	57.81 (57.97)	6.12 (6.20)	19.20 (19.32)	14.3	1.86	17440 28630
[Cu(HL^4)$_2$] (Steel gray)	11.17 (11.03)	54.78 (54.94)	5.71 (5.88)	18.19 (18.31)	14.8	1.90	17460 28630
[Cu(HL^5)$_2$] (Black)	10.08 (9.99)	60.29 (60.42)	6.81 (6.92)	17.35 (17.62)	15.1	1.87	17430 28660
[Cu(HL^6)$_2$] (Grey)	9.43 (9.51)	57.64 (57.52)	6.51 (6.59)	16.84 (16.77)	16.3	1.89	17410 28640

TABLE-2
SALIENT FEATURES OF IR SPECTRAL BANDS (cm^{-1}) OF LIGANDS HL$^{1-6}$ AND ITS METAL COMPLEXES

Compounds	ν(N—H)	ν(C=N)	ν(C=O)	ν(C=S)	ν(M—O)	ν(M—S)	ν(M—N)
HL^1	3220 s,b	1630 s, b	1760 s, b	—	—	—	—
HL^2	3280 s, b	1620 s, b	—	845 s, b	—	—	—
HL^3	3230 s, b	1635 s, b	1760 s, b	—	—	—	—
HL^4	3285 s, b	1625 s, b	—	840 s, b	—	—	—
HL^5	3235 s, b	1630 s, b	1765	—	—	—	—
HL^6	3290 s, b	1620 s, b	—	840 s, b	—	—	—
[Co(HL^1)$_2$]	3190 s, b	1595 s, b	1730 s, b	—	580 m	—	380 m
[Co(HL^2)$_2$]	3255 s, b	1585 s, b	—	800 s, b	—	460 m	385 m
[Co(HL^3)$_2$]	3185 s, b	1590 s, b	1725 s, b	—	570 m	—	390 m
[Co(HL^4)$_2$]	3250 s, b	1585 s, b	—	805 s, b	—	455 m	385 m
[Co(HL^5)$_2$]	3180 s, b	1595 s, b	1720 s, b	—	550 m	—	380 m
[Co(HL^6)$_2$]	3245 s, b	1600 s, b	—	815 s, b	—	465 m	385 m
[Ni(HL^1)$_2$]	3185 s, b	1580 s, b	1715 s, b	—	520 m	—	405 m
[Ni(HL^2)$_2$]	3240 s, b	1585 s, b	—	810 s, b	—	450 m	410 m
[Ni(HL^3)$_2$]	3190 s, b	1580 s, b	1735 s, b	—	535 m	—	400 m
[Ni(HL^4)$_2$]	3250 s, b	1590 s, b	—	800 s, b	—	455 m	405 m

Compounds	ν(N—H)	ν(C=N)	ν(C=O)	ν(C=S)	ν(M—O)	ν(M—S)	ν(M—N)
$[Ni(HL^5)_2]$	3195 s, b	1595 s, b	1720 s, b	—	540 m	—	405 m
$[Ni(HL^6)_2]$	3245 s, b	1600 s, b	—	805 s, b	—	440 m	410 m
$[Cu(HL^1)_2]$	3185 s, b	1598 s, b	1725 s, b	—	525 m	—	395 m
$[Cu(HL^2)_2]$	3255 s, b	1595 s, b	—	810 s, b	—	460 m	390 m
$[Cu(HL^3)_2]$	3180 s, b	1590 s, b	1715 s, b	—	532 m	—	390 m
$[Cu(HL^4)_2]$	3245 s, b	1580 s, b	—	805 s, b	—	470 m	385 m
$[Cu(HL^5)_2]$	3195 s, b	1580 s, b	1725 s, b	—	535 m	—	380 m
$[Cu(HL^6)_2]$	3240 s, b	1595 s, b	—	810 s, b		465 m	395 m

s = strong, b = broad, m = medium

EXPERIMENTAL

Preparation of the ligand: Ethanolic solutions of 3-methyl-4-ethyl isoquinolone/3-methyl-4-propyl isoquinolone/3-ethyl-4-propyl isoquinolone were treated with semicarbazide hydrochloride or thiosemicarbazide hydrochloride in the molar ratio 1 : 1 dissolved in 10% alcoholic solution of sodium acetate. The resulting mixture was refluxed on water bath for 3–4 h, then a crystalline yellow solid began to separate. It was heated for a further 30 min for complete precipitation. It was cooled, filtered washed with aquous ethanol, dried and crystallised from dimethyl formamide. Yields in all cases were in the range 60–65%.

Preparation of the complexes: The complexes of Co(II), Ni(II) and Cu(II) have been prepared by reacting an alcoholic solution of metal halide with the ethanolic solution of the respective ligand from HL^1 to HL^6, in the molar ratio 1 : 2. The solid coloured complexes which were separated and cooled are filtered, washed with ethanol, dried and recrystallised with dimethyl formamide. Yields in all cases were in the range 65–70%.

RESULTS AND DISCUSSION

In the light of previous assignments[15] it is established that semicarbazone or thiosemicarbazone can coordinate through oxygen or sulphur and N^1 (>C=N^1—N^2H—(C=X)—N^3<) of either semicarbazone or thiosemicarbazone moiety. The infrared spectra of all the six ligands observed strong and broad bands in 3280–3220 cm^{-1} region which can be assigned to ν(N—H)[16] of secondary amino group of isoquinolone ring. In the spectra of the complexes this band is present with much reduced intensity indicating cordination takes place through N atom of secondary amino group. The IR spectra of the ligand HL^1, HL^3 and HL^5 exibit two more bands at 1760 cm^{-1} and another at 1630 cm^{-1} which can be assigned to ν(C=O)[17] and ν(C=N)[18] respectively. In the spectra of the complexes these bands show red shift indicating coordination takes place through carbonyl oxygen as well as imine nitrogen of semicarbazone moiety.

The IR spectra of the ligands HL^2, HL^4 and HL^6 show strong and broad band at 1620 cm^{-1} and another at 840 cm^{-1} which can be assigned to ν(C=N) and ν(C=S)[18] respectively. In the spectra of the complexes these bands show red shift indicating coordination takes place through thione S as well as the imine N of the thiosemicarbazone moiety. The coordination through amine and imine nitrogen and oxygen/sulphur atoms is further confirmed by the occurrence of

three bands in the far infrared regions at 580–520 cm^{-1}, 470–440 cm^{-1} and 410–380 cm^{-1} which are assigned to ν(M—O)[19], ν(M—S)[20] and ν(M—N)[21] bands respectively.

Electronic spectra and magnetic moment of the complexes

The Co(II) complexes exhibiting bands at 9500, 13500 and 20600 cm^{-1} may be assigned to the transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, which indicate an octahedral[22] arrangement around Co(II) metal ion. The high frequency band observed at 26500 cm^{-1} may be due to charge transfer. The proposed geometry is further confirmed[23] by high μ_{eff} value in the range 4.78–5.12 B.M., for all the Co(II) complexes. The Ni(II) complexes exhibiting bands at 10400, 16600 and 22900 cm^{-1} may be assigned to the transitions from, $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ levels respectively which indicate an octahedral[24] geometry. The proposed geometries of all Ni(II) complexes are further confirmed by μ_{eff} value in the range 3.31–3.43 B.M. The Cu(II) complexes exhibit bands at 17900–17400 cm^{-1} and 28600–28000 cm^{-1} which may be assigned to the transitions, $^2E_g \rightarrow {}^2T_{2g}$ and charge transfer band. The electronic spectra of all the Cu(II) complexes suggest an octahedral[25] geometry of the complex. The proposed geometries of all the Cu(II) complexes are further confirmed[23] by the μ_{eff} value in the range of 1.83–1.92 B.M.

The molar conductance of the complexes of the type $[M(H^{1-6})_2]$ were measured by the solvent acetonitrile at the concentration 10^{-3} M and all the complexes were found to be non-electrolytic in nature[26] giving conductivity values in the range 6.8–16.3 $ohm^{-1}\ cm^2\ mol^{-1}$.

The above observations clearly indicate that all the six ligands HL^{1-6} are coordinated as binegative tridentate molecule and bonded to the metal ions through amine and imine nitrogen and oxygen/sulphur atoms. The structure of the complexes can be presumed to have octahedral structure as shown in Fig. 1.

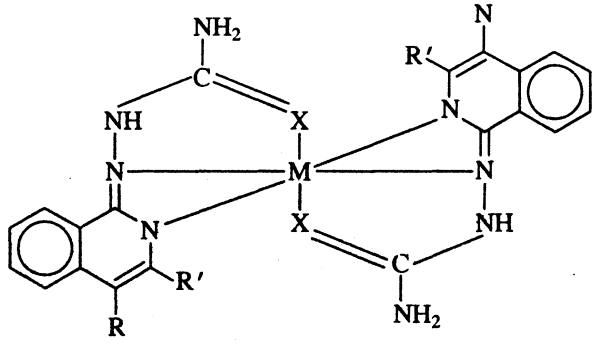

Fig. 1
$[M(HL^{1-6})_2]$
M = Co(II), Ni(II) and Cu(II); X = O or S
(1) R = methyl; R′ = ethyl
(2) R = methyl; R′ = propyl
(3) R = ethyl; R′ = propyl

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