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Complexes of Co(II), Ni(II) and Cu(II) with 3-Phenyl Quinazoline-4(3H)-One Carboxaldehyde Semicarbazone and Thiosemicarbazone

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Complexes of 3-phenyl quinazoline 4(3H) one carboxaldehyde semicarbazone (PQCASC) and 3-phenyl quinazolien 4(3H) one carboxaldehyde thiosemicarbazone (PQCATSC) with bivalent metal ion of composition $[M(PQCASC)_2]X_2$ and $[M(PQCATSC)_2]X_2$, M = Co(II), Ni(II) and Cu(II) and $X = Cl^-, Br^-$ or I^- have been prepared and characterised on the basis of elemental analysis, IR spectra, electronic spectra, magnetic susceptibility and conductivity measurements and are found to be octahedral in geometry. The complexes are found to be electrolytic in nature of 1 : 2 type.

INTRODUCTION

Semicarbazone and thiosemicarbazone are reported to be active as antilepral[1], antitubercular[2], antiviral[3], antimalarial[4], anticancer[5] and antibacterial[6–8] drugs. Metal complexes of semicarbazone and thiosemicarbazone have attracted special attention due to their activity against smallpox, viral diseases and certain kinds of tumor[9–11]. Considering the importance of such complexes, in the present paper, synthesis and characterisation of Co(II), Ni(II) and Cu(II) complexes with ligands 3-phenyl-quinazoline-4(3H)-one-carboxaldehyde semicarbazone(PQCASC) and 3-phenyl quinazoline 4(3H)-one-carboxaldehyde thiosemicarbazone (PQCATSC) are reported.

EXPERIMENTAL

All the chemicals used were BDH reagent except 3-phenyl quinazoline-4(3H)-one 2-carbaxaldehyde which was prepared by earlier reported method[12].

Preparation of the ligand PQCASC

3-Phenyl-quinazoline-4(3H)-one carboxaldehyde dissolved in freshly distilled pyridine (10 mL) was treated with semicarbazide hydrochloride dissolved in 10% ethanolic sodium acetate in the molar ratio 1 : 1. The resulting mixture was heated on water bath, then a crystalline colourless solid began to separate after 1 h. It

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was heated for further 30 min for complete precipitation. It was cooled, filtered, washed with aqueous ethanol, dried and crystallised with dimethyl formamide to furnish a colourless crystalline solid, m.p. 283°C, yield 70%.

Preparation of the ligand PQCATSC

3-Phenyl-quinazoline-4(3H)-one-2-carboxaldehyde dissolved in freshly distilled pyridine (10 mL) was treated with thiosemicarbazide hydrochloride dissolved in 10% ethanolic solution of sodium acetate in the molar ratio 1 : 1. The resulting reaction mixture was heated on water bath, then a crystalline colourless solid began to separate after 2 h. It was heated for a further 30 min for complete precipitation. It was cooled, filtered, washed with aqueous ethanol, dried and analysed. m.p. 293°C, yield 75%.

Preparation of the complexes

The complexes of Co(II), Ni(II) and Cu(II) were formed by reacting an ethanolic solution of corresponding metal salts with the solution of the ligands PQCASC and PQCATSC dissolved in tetrahydrofuran in the molar ratio 1 : 2.

The metal contents of the complexes were analysed using standard methods[13]; carbon, hydrogen and nitrogen by semimicro combustion methods at CDRI, Lucknow. The infrared spectra of the ligands and the complexes were recorded on Perkin-Elmer spectrophotometer, Magnetic susceptibilities were measured by Gouy method using mercury- tetraisothiocyanato cobalt(II) as the calibrant. The conductivity measurements are made on Systronics conductometer model 303 using dimethyl sulphoxide as a solvent. Analytical data, colour, magnetic moment, conductivity measurement and electronic spectral data have been given in Table-1 and salient features of IR spectral data are recorded in Table-2.

RESULTS AND DISCUSSION

It is known[14] that semicarbazone and thiosemicarbazone coordinate through oxygen or sulphur and N^1($>C{=}N^1{-}N^2H{-}(C{=}X){-}N^3<$).

The IR spectra of the ligands PQCASC and PQCATSC observed strong band in 3360–3330 cm^{-1} region which can be assigned to ν(N—H) vibrations[15]. This band remains undisturbed on complexation and suggests non-involvement of either terminal amino or secondary amino group in coordination. The IR spectra of both the ligands PQCASC and PQCATSC show broad band of medium intensity at 1600 cm^{-1} which can be assigned to ν(C=N) (azomethine) and ν(C=N) (aldimine)[16]. In the spectra of the complexes this band shows red shift appearing in the region 1540–1500 cm^{-1} clearly indicating coordination of the N atom, of aldimine group as well as azomethine group. The spectra of ligand PQCASC show a sharp and strong band at 1700 cm^{-1} which can be assigned[17] to ν(C=O). In the spectra of the complexes this band is shifted downward appearing in the region 1660–1620 cm^{-1} clearly indicating coordination to take place through oxygen atom of semicarbazone moiety.

TABLE-1
COLOUR, ANALYTICAL, MAGNETIC MOMENT, ELECTRONIC SPECTRA AND CONDUCTIVITY MEASUREMENT DATA FOR METAL COMPLEXES OF LIGANDS PQCASC AND PQCATSC

Compound/ Colour	% Analysis found (Calculated)				λ_{max} electronic cm^{-1}	μ_{eff} (B.M.)	Ω_{max} ohm^{-1} cm^2 mol^{-1}
	Metal	C	H	N			
$[Co(PQCASC)_2]Cl_2$ (Purple)	7.73 (7.93)	51.53 (51.75)	3.12 (3.23)	18.72 (18.86)	9100 16300	5.5	110.6
$[Co(PQCATSC)_2]Cl_2$ (Light grey)	7.54 (7.61)	49.45 (49.61)	2.93 (3.10)	17.93 (18.08)	9200 16400	5.1	114.1
$[Co(PQCASC)_2]Br_2$ (Greenish grey)	6.94 (7.09)	46.09 (46.22)	2.76 (2.88)	16.72 (16.85)	9110 16430	5.4	112.3
$[Co(PQCATSC)_2]Br_2$ (Grey)	6.74 (6.83)	44.31 (44.50)	2.69 (2.78)	16.10 (16.22)	9160 16230	5.3	117.5
$[Co(PQCASC)_2]I_2$ (Yellowish brown)	6.25 (6.37)	41.30 (41.52)	2.51 (2.59)	14.96 (15.13)	9130 16240	5.0	119.3
$[Co(PQCATSC)_2]I_2$ (Brown)	6.03 (6.15)	39.94 (40.13)	2.43 (2.50)	14.49 (14.63)	9140 16220	5.2	120.6
$[Co(PQCATSC)_2]Cl_2$ (Light blue)	7.77 (7.91)	51.58 (51.77)	3.17 (3.23)	18.69 (18.87)	11300 15300 23500	2.92	124.7
$[Ni(PQCATSC)_2]Cl_2$ (Light green)	7.49 (7.58)	49.51 (49.63)	2.92 (3.10)	17.92 (18.09)	11200 15400 23600	2.99	127.3
$[Ni(PQCASC)_2]Br_2$ (Green)	6.92 (7.06)	46.11 (46.23)	2.71 (2.88)	16.71 (16.85)	11000 15600 23800	3.10	131.3
$[Ni(PQCATSC)_2]Br_2$ (Light green)	6.71 (6.80)	44.30 (44.51)	2.65 (2.78)	16.08 (16.23)	11100 15700 23700	3.05	128.1
$[Ni(PQCASC)_2]I_2$ (Deep green)	6.26 (6.35)	41.35 (41.59)	2.51 (2.59)	14.89 (15.14)	11400 16200 23900	2.80	132.6
$[Ni(PQCATSC)_2]I_2$ (Green)	6.01 (6.13)	39.89 (40.14)	2.39 (2.50)	14.44 (14.63)	11300 16000 24000	2.85	134.1
$[Cu(PQCASC)_2]Cl_2$ (Green)	8.29 (8.51)	51.36 (51.43)	3.11 (3.21)	18.61 (18.75)	12800 17400	1.80	137.2
$[Cu(PQCATSC)_2]Cl_2$ (Green)	8.03 (8.16)	49.18 (49.32)	2.93 (3.08)	17.84 (17.98)	12900 17300	1.90	136.3
$[Cu(PQCASC)_2]Br_2$ (Marine grey)	7.51 (7.60)	45.73 (45.96)	2.79 (2.87)	16.63 (16.75)	13000 17600	1.75	138.7
$[Cu(PQCATSC)_2]Br_2$ (Grey)	7.19 (7.32)	41.09 (41.27)	2.64 (2.76)	15.91 (16.14)	13100 17700	1.86	141.3

TABLE-2
SALIENT FEATURES OF IR SPECTRAL BANDS OF LIGANDS PQCASC AND PQCATSC AND ITS COMPLEXES

Compounds	ν(C=N) (aldimine)	ν(C=N) (azomethine)	ν(C=O)	ν(C=S)	ν(M—N)	ν(M—O)	ν(M—S)
PQCASC	1600 m,b	1620 m,b	1700 s,s	—	—	—	—
PQCATSC	1620 m,b	1600 m,b	—	840 s,s	—	—	—
$[Co(PQCASC)_2]Cl_2$	1540 m,b	1530 m,b	1620 s,s	—	485 m	510 m	—
$[Co(PQCATSC)_2]Cl_2$	1530 m,b	1525 m,b	—	805 s,s	480 m	—	420 m
$[Co(PQCASC)_2]Br_2$	1520 m,b	1515 m,b	1635 s,s	—	490 m	495 m	—
$[Co(PQCATSC)_2]Br_2$	1530 m,b	1510 m,b	—	815 s,s	485 m	—	425 m
$[Co(PQCASC)_2]I_2$	1510 m,b	1535 m,b	1640 s,s	—	480 m	505 m	—
$[Co(PQCATSC)_2]I_2$	1520 m,b	1530 m,b	—	800 s,s	485 m	—	420 m
$[Ni(PQCASC)_2]Cl_2$	1500 m,b	1500 m,b	1655 s,s	—	490 m	510 m	—
$[Ni(PQCATSC)_2]Cl_2$	1510 m,b	1505 m,b	—	805 s,s	485 m	—	425 m
$[Ni(PQCASC)_2]Br_2$	1520 m,b	1540 m,b	1640 s,s	—	485 m	520 m	—
$[Ni(PQCATSC)_2]Br_2$	1510 m,b	1535 m,b	—	815 s,s	480 m	—	415 m
$[Ni(PQCASC)_2]I_2$	1540 m,b	1520 m,b	1625 s,s	—	485 m	520 m	—
$[Ni(PQCATSC)_2]I_2$	1435 m,b	1515 m,b	—	805 s,s	480 m	—	430 m
$[Cu(PQCASC)_2]Cl_2$	1525 m,b	1535 m,b	1645 s,s	—	490 m	505 m	—
$[Cu(PQCATSC)_2]Cl_2$	1515 m,b	1530 m,b	—	815 s,s	485 m	—	415 m
$[Cu(PQCASC)_2]Br_2$	1520 m,b	1525 m,b	1635 s,s	—	490 m	530 m	—
$[Cu(PQCATSC)_2]Br_2$	1515 m,b	1520 m,b	—	805 s,s	480 m	—	410 m

s = stron; b = broad; m = medium; s,s = sharp and strong

The spectra of the ligand PQCATSC show a sharp and strong band at 840 cm^{-1} which can be assigned[18] to ν(C=S). In the spectra of the complexes this band is shifted downward appearing in the region to 820–800 cm^{-1} clearly indicating coordination to take place through thione sulphur of thiosemicarbazone moiety. In the lower frequency region new bands at 530–460 cm^{-1}, 490–480 cm^{-1} and 435–410 cm^{-1} are assigned to ν(M—O)[19], ν(M—N)[20] and ν(M—S)[21] respectively. The above observations clearly indicate that the ligands PQCASC and PQCATSC are coordinated as a neutral tridentate molecule and bonded to the metal ions through oxygen/sulphur and nitrogen atoms.

Electronic spectra and magnetic moment data

The electronic spectra of Co(II) complexes of the type $[Co(L^{1-2})_2]X_2$ exhibit bands at 9300 and 16400 cm^{-1} corresponding to the transition ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(P)$ which correspond to that of octahedral[22] geometry of the Co(II) complexes. The magnetic moment values of the Co(II) complexes lie in the range 5.00–5.5 B.M. which corresponds to an octahedral streochemistry about the metal ion[23]. The electronic spectra of all the Ni complexes of the type $[Ni(L^{1-2})_2]X_2$ exhibits three bands, one in the region

11000–11500 cm^{-1}, the next one in the range of 15300–16200 cm^{-1} followed by a strong intense band in the vicinity of 24000 cm^{-1} which can be assigned to the transitions $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ respectively, which also support the octahedral[22] geometry of the Ni(II) complexes.

The magnetic moment of Ni(II) complexes of the type $[Ni(L^{1-2})_2]X_2$ lie in the range 2.85 to 3.10 B.M. at room temperature which suggests octahedral arrangement of the ligand atoms around the central Ni(II) ion[23].

The electronic spectra of all the complexes of Cu(II) exhibit two ligand field bands, one in the region 13600–12800 cm^{-1} and another in the region 17700–17200 cm^{-1} which explain the octahedral[22] nature of Cu(II) complexes. The magnetic moment values of Cu(II) complexes lie in the range 1.75–1.90 B.M. which also support the octahedral[23] geometry of the Cu(II) complexes.

Conductivities of the complexes of the type $[M(L^{1-2})_2]X_2$ were measured in the solvent dimethyl sulphoxide and all the complexes were found to be

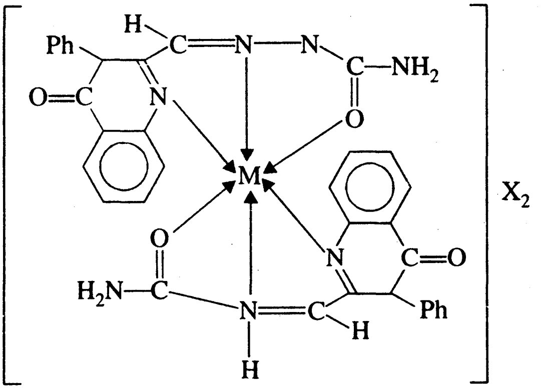

Fig. 1 $[M(PQCASC)_2]X_2$

M = Co(II), Ni(II) and Cu(II); X = Cl^-, Br^- or I^-

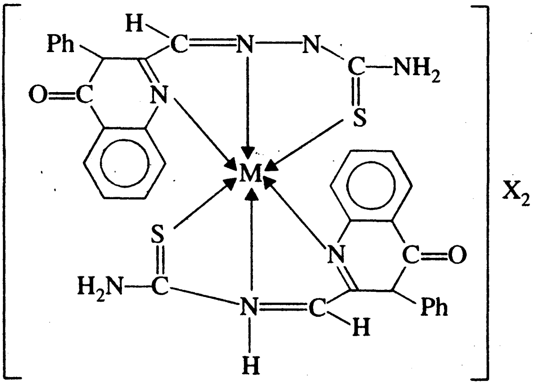

Fig. 2 $[M(PQCATSC)_2]X_2$

M = Co(II), Ni(II) and Cu(II); X = Cl^-, Br^- or I^-

electrolytic in nature of 1 : 2 type and conductivity values are in the range 110–150 ohm^{-1} cm^{2} mol^{-1}.

Hence on the basis of elemental analysis, IR spectra, electronic spectra, magnetic moment data and conductivity measurement the geometry of all the complexes of the Co(II), Ni(II) and Cu(II) of the type $[M(L^{1-2})_2]X_2$ can be presumed to have octahedral geometry as shown in Figs. 1 and 2.

REFERENCES

1. N.E. Morrison and F.M. Collins, *Inst. J. Leprosy*, **49**, 180 (1981).
2. W.H. Wagner and E. Winkelman, *Arzneim Forschi*, **22**, 1703 (1972).
3. D.H. Jones, R. Slack and S. Squires, *J. Med. Chem.*, **H-676** (1965).
4. D.L. Klayman and F. Joseph, *J. Med. Chem.*, **22**, 855 (1979).
5. J.P. Scovil and D. Klayman, *J. Med. Chem.*, **25**, 1261 (1982).
6. A.S. Dobeck and D. Klayman, *Antimicrobial Agents and Chemotherapy*, **18**, 27 (1980).
7. G. Domagk and W.L. Nobles, *J. Am. Pharm. Assoc. Sci. Ed.*, **45**, 729 (1956).
8. H.C. Caldwell and W.L. Nobles, *J. Am. Pharm. Assoc. Sci. Ed.*, **45**, 729 (1956).
9. N. Orlova, V.A. Aksensova, D.A. Selidovkin and G.N. Perkin, *Russ. Pharma. Toxicol.*, 348 (1968).
10. D.J. Bauer, L.S. Vincent, C.H. Kempe and A.W. Dowine, *Lancet*, **2**, 494 (1963).
11. H.G. Petering, H.H. Buskik and G.E. Underwood, *Cancer Res.*, **64**, 367 (1964).
12. B.D. Singh and D.N. Chaudhary, *J. Indian Chem. Soc.*, **45**, 313, 316 (1966).
13. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, Longmans, London (1982).
14. B.A. Gingras, R.L. Somarjai and C.S. Bayley, *Can. J. Chem.*, **39**, 974 (1961); K.A. Jensen and K.Z. Raneke-Madan, *Z. Anorg. Allg. Chem.*, **26**, 277 (1936); T.A. Prebrazhenskaya and Kazansk, *Univ. Estertv. Nauk. Kazam.*, 36 (1962); Mckenzie, Mellor, Mills and Short, *Proc. R. Soc., N.S.W.*, **78**, 70 (1944); Manch and Femelum, *J. Chem. Ed.*, **38**, 192 (1961).
15. K. Nakamato, Infrared Spectra of Inorganic and Co-ordination Compounds, Wiley Interscience, New York (1975).
16. Ratan Kumar Choudhary, R.N. Pathak and L.K. Mishra, *J. Indian Chem. Soc.*, **77**, 32 (2000).
17. A. Yamaguchi, R.B. Penland, S. Mizushima, T.S. Lane, T.J. Curran and J.V. Quaglianao, *J. Am. Chem. Soc.*, **80**, 527 (1958).
18. M. Goldstein and D. Unsworth, *Inorg. Chim. Acta*, **4**, 342 (1970).
19. N.K. Singh, S.C. Shrivastava and R.C. Agarwal, *Indian J. Chem.*, **22A**, 704 (1983).
20. S.N. Chaube, J.P. Srivastava and L.K. Mishra, *Inorg. Chim. Acta*, **23**, 1 (1977).
21. R.G. Gadag and M.R. Gajendragad, *Indian J. Chem.*, **16A**, 703 (1978).
22. A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsvier, Amsterdam (1986).
23. B.N. Figgis, Introduction to Ligand Field, Wiley Eastern Ltd., New Delhi, p. 279 (1978).

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