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Synthesis and Characterisation of Transition Metal Complexes of 2-(*p*-chlorophenyl)- 4,5-Dimethyl (8H) Pyrimido [4,5-d] Pyrimidine Semicarbazone and Thiosemicarbazone

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Complexes of 2-(*p*-chlorophenyl)-4,5-dimethyl(8H) pyrimido [4,5-d] pyrimidine semicarbazone [CPDPPS] and 2-(*p*-chlorophenyl)-4,5-dimethyl(8H)-pyrimido [4,5-d] pyrimidine thiosemicarbazone [CPDPPTS] with bivalent metal ion of composition $[M(CPDPPS)_2]X_2$ and $[M(CPDPPTS)_2]X_2$, M = Co(II),Ni(II) and Cu(II) and X = Cl^-, Br^- and I^- have been prepared and characterised physico-chemically and spectroscopically. The ligands were found to be neutral tridentate chelating agents for the metal ions and the complexes are found to be octahedral in geometry. The complexes were found to be electolytic in nature of 1 : 2 type.

Key words: Cobalt, nickel, copper, complexes 2-(*p*-chlorophenyl)-4,5-dimethyl (8H) pyrimido [4,5-d] pyrimidine, semicarbazone, thiosemicarbazone

INTRODUCTION

Metal complexes of semicarbazone and thiosemicarbazone have been known for their pharmacological properties including activity against tuberculosis[1], bacterial[2], viral functions[3] and certain kinds of tumours[4, 5]. Considering the importance of such complexes and in continuation of our earlier research work[6] an 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 2-(*p*-chlorophenyl)-4,5-dimethyl pyrimido-[4,5-d] pyrimidine semicarbazone (CPDPPS) and 2-(*p*-chlorophenyl)-4,5-dimethyl pyrimido-[4,5-d] pyrimidine thiosemicarbazone (CPDPPTS) are reported.

EXPERIMENTAL

All the reagents used were BDH except 2-(*p*-chlorophenyl-4,5-dimethyl) (8H) pyrimido [4,5-d] pyrimidine which was prepared by the treatment of 2-(4-chlorophenyl)-4-chloro-5-acetyl-6-methyl-pyrimidine with urea in equimolecular quantity in ethanol and then refluxed for 3 h on a water bath. The resulting solid was crystallised from ethanol as pale yellow crystals.

Preparation of the ligand CPDPPS: 2-(*p*-chlorophenyl-4,5-dimethyl) (8H)

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pyrimido [4,5-d] pyrimidine (0.01 M) dissolved in ethanol was added to semicarbazide hydrochloride (0.01 M) dissolved in 10% ethanolic solution of sodium acetate. The reaction mixture was stirred and refluxed on a water bath for 4 h. The resulting solid was crystallised from ethanol as pale yellow crystals.

Preparation of the ligand CPDPPTS: 2-(*p*-chlorophenyl-4,5-dimethyl) (8H) pyrimido [4,5-d] pyrimidine (0.01 M) dissolved in ethanol was added to thiosemicarbazide hydrochloride (0.01 M) dissolved in 10% ethanolic solution of sodium acetate. The reaction mixture was stirred and refluxed for about 4.5 h. The resulting solid was crystallised from ethanol as yellow crystals.

Preparation of the Complexes: Ethanolic solution of the ligands CPDPPS and CPDPPTS were added to the ethanolic solution of corresponding metal halides in the molar ratio 2 : 1 with constant stirring. The resulting solutions were refluxed on a water bath for 3–4 h. The coloured complexes were filtered, washed with ethanol and dried in an oven.

The complexes were analysed using standard procedures[7] and carbon, hydrogen and nitrogen were determined by semi-micro combustion methods. Analytical data, colour electronic spectral data, magnetic moment and conductivity value are recorded in Table-1. The elemental analysis shows that the complexes have 1 : 2 stoichiometry of the type $[M(CPDPPS)_2]X_2$ and $[M(CPDPPTS)_2]X_2$. ($M = Co^{2+}$, Ni^{2+}, or Cu^{2+}, $X = Cl^-$, Br^- or I^-).

The infrared spectra of the ligands as well as metal complexes were recorded on a Perkin-Elmer spectrophotometer (model 557) in the range 4000–300 cm^{-1} employing KBr pellets and the data have been given in Table-2. The conductivity measurements were carried out on 10^{-3} M solutions of the complexes in DMF at room temperature on a digital conductivity meter model 4070 (Jenway). The electronic spectra (DMF) were recorded on a Toshiniwal CL-54 spectrophotometer. Magnetic moments were measured by Gouy method using mercury tetraisothiocyanato cobaltate as the calibrant.

RESULTS AND DISCUSSION

Infrared spectra

In the light of previous assignments[8] it is established that semicarbazone and thiosemicarbazone ligands can coordinate metal ion through oxygen or sulphur and $\overset{1}{N}(\rangle C{=}\overset{1}{N}{-}\overset{2}{N}H{-}(C{=}X){-}\overset{3}{N}\langle)$ of either semicarbazone or thiosemicarbazone moiety. The IR spectra of the ligands CPDPPS and CPDPPTS observed strong and broad band in the 3300–3240 cm^{-1} region which can be assigned[9] to ν(N—H) of secondary amino group of pyrimidine ring. In all the complexes this band is shifted towards lower wave numbers by 40 cm^{-1}. This observation suggests coordination through the secondary amino group of pyrimidine ring. The IR spectrum of the ligand CPDPPS exhibits two more bands at 1780 cm^{-1} and 1620 cm^{-1} which can be assigned to ν(C=O)[10] and ν(C=N)[11] respectively. In the metal complexes, the intensities of these bands are considerably lowered. These observations are attributed to the fact that coordination takes place through carbonyl oxygen as well as azomethine nitrogen of semicarbazone moiety.

TABLE-1
COLOUR, ANALYTICAL, MAGNETIC MOMENT, ELECTRONIC SPECTRA AND CONDUCTIVITY MEASUREMENT DATA FOR $[M(CPDPPS)_2]X_2$ AND $[M(CPDPPTS)_2]X_2$

Compound/ Colour	% Analysis found (Calculated)				μ_{eff} (B.M.)	$^*\Omega_{max}$ (ohm^{-1} cm^{2}mol^{-1})	λ_{max} electronic (cm^{-1})
	M	N	H	C			
CPDPPS	—	28.49	3.67	52.39	—	—	—
Pale yellow		(28.61)	(3.79)	(52.55)			
CPDPPTS	—	27.41	3.54	50.31	—	—	—
Yellow		(27.36)	(3.62)	(50.20)			
$[Co(CPDPPS)_2]Cl_2$	8.14	26.21	3.28	48.51	5.16	122.2	8730, 17320
Brown	(7.92)	(26.34)	(3.49)	(48.39)			20310, 28930
$[Co(CPDPPS)_2]Br_2$	6.93	23.28	3.01	43.12	4.80	126.6	8740, 17330
Yellowish Green	(7.07)	(23.53)	(3.12)	(43.23)			20300, 28200
$[Co(CPDPPS)_2]I_2$	6.22	21.26	2.71	38.68	5.17	127.1	8725, 17310
Dark brown	(6.35)	(21.14)	(2.80)	(38.84)			20320, 28910
$[Co(CPDPPTS)_2]Cl_2$	7.43	25.41	3.43	46.53	5.07	122.8	8720, 17340
Bluish Green	(7.59)	(25.26)	(3.35)	(46.39)			20340, 28930
$[Co(CPDPPTS)_2]Br_2$	6.67	22.49	2.93	41.39	4.85	126.3	8715, 17335
Brown	(6.81)	(22.66)	(3.00)	(41.63)			20325, 28905
$[Co(CPDPPTS)_2]I_2$	6.21	20.27	2.83	37.37	5.20	127.7	8710, 17300
Yellowish brown	(6.14)	(20.44)	(2.71)	(37.54)			20330, 28915
$[Ni(CPDPPS)_2]Cl_2$	7.68	26.21	3.38	48.63	3.03	121.2	7900, 14000
Red	(7.89)	(26.35)	(3.49)	(48.40)			23000, 29700
$[Ni(CPDPPS)_2]Br_2$	7.14	23.76	3.04	43.43	2.89	123.4	8100, 14300
Light Green	(7.05)	(23.54)	(3.12)	(43.24)			25700, 29600
$[Ni(CPDPPS)_2]I_2$	6.21	21.03	2.91	38.93	2.85	124.3	7800, 14600
Violet	(6.33)	(21.15)	(2.80)	(38.85)			25000, 29700
$[Ni(CPDPPTS)_2]Cl_2$	4.71	25.43	3.21	46.28	3.08	131.9	8010, 14000
Blue	(4.86)	(25.26)	(3.35)	(46.40)			25500, 29040
$[Ni(CPDPPTS)_2]Br_2$	6.86	22.51	3.12	41.43	3.01	132.3	8040, 14700
Voilet	(6.79)	(22.67)	(3.03)	(41.64)			25800, 29800
$[Ni(CPDPPTS)_2]I_2$	6.04	20.59	2.63	37.69	2.95	135.1	7710, 14100
Light Green	(6.12)	(20.44)	(2.71)	(37.55)			25900, 29500
$[Cu(CPDPPS)_2]Cl_2$	8.32	26.30	3.32	48.21	1.91	135.2	13900, 27200
Green	(8.48)	(26.18)	(3.47)	(48.09)			
$[Cu(CPDPPS)_2]Br_2$	7.42	23.22	3.01	42.71	1.83	135.3	13600, 27700
Yellowish Green	(7.58)	(23.40)	(3.10)	(42.99)			
$[Cu(CPDPPTS)_2]Cl_2$	8.23	25.27	3.42	46.26	1.89	129.7	13650, 27600
Reddish Brown	(8.14)	(25.11)	(3.53)	(46.12)			
$[Cu(CPDPPTS)_2]Br_2$	7.21	22.66	2.83	41.53	1.87	128.3	13850, 27400
Dark Green	(7.30)	(22.54)	(2.99)	(41.40)			

TABLE-2
SALIENT FEATURES OF I.R. SPECTRAL BANDS OF LIGANDS CPDPPS AND CPDPPTS AND THEIR COMPLEXES

Compounds	ν(N—H)	ν(C=O)	ν(C=N)	ν(C=S)	ν(M—O)	ν(M—N)	ν(M—S)
CPDPPS	3240 s, b	1780 s, b	1620 s, b	—	—	—	—
CPDPPTS	3300 s, b	—	1680 s, b	780 s, b	—	—	—
$[Co(CPDPPS)_2]Cl_2$	3205 s, b	1735 s, b	1590 s, b	—	510 m	410 m	—
$[Co(CPDPPS)_2]Br_2$	3200 s, b	1745 s, b	1595 s, b	—	525 m	415 m	—
$[Co(CPDPPS)_2]I_2$	3205 s, b	1740 s, b	1585 s, b	—	520 m	425 m	—
$[Co(CPDPPTS)_2]Cl_2$	3265 s, b	—	1650 s, b	740 s, b	—	430 m	365 m
$[Co(CPDPPTS)_2]Br_2$	3260 s, b	—	1655 s, b	750 s, b	—	440 m	350 m
$[Co(CPDPPTS)_2]I_2$	3270 s, b	—	1650 s, b	755 s, b	—	410 m	355 m
$[Ni(CPDPPS)_2]Cl_2$	3205 s, b	1755 s, b	1585 s, b	—	525 m	425 m	—
$[Ni(CPDPPS)_2]Br_2$	3200 s, b	1740 s, b	1580 s, b	—	515 m	415 m	—
$[Ni(CPDPPS)_2]I_2$	3210 s, b	1745 s, b	1590 s, b	—	535 m	430 m	—
$[Ni(CPDPPTS)_2]Cl_2$	3270 s, b	—	1655 s, b	745 s, b	—	420 m	365 m
$[Ni(CPDPPTS)_2]Br_2$	3260 s, b	—	1650 s, b	750 s, b	—	415 m	380 m
$[Ni(CPDPPTS)_2]I_2$	3265 s, b	—	1645 s, b	740 s, b	—	425 m	355 m
$[Cu(CPDPPS)_2]Cl_2$	3210 s, b	1740 s, b	1585 s, b	—	530 m	415 m	—
$[Cu(CPDPPS)_2]Br_2$	3200 s, b	1750 s, b	1580 s, b	—	535 m	430 m	—
$[Cu(CPDPPTS)_2]Cl_2$	3265 s, b	—	1645 s, b	755 s, b	—	435 m	375 m
$[Cu(CPDPPTS)_2]Br_2$	3270 s, b	—	1650 s, b	750 s, b	—	430 m	380 m

s, b = strong and broad, m = medium.

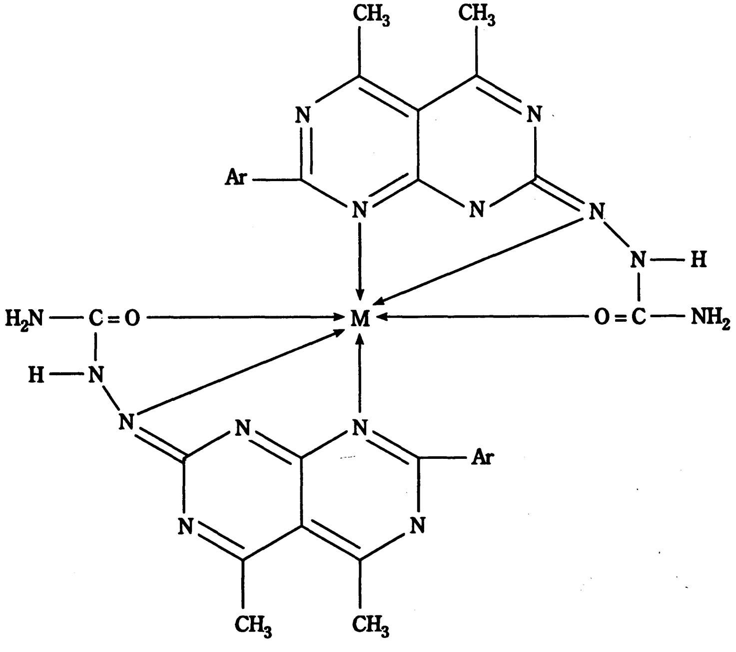
The IR spectra of the ligand CPDPPTS show strong and broad bands at 1680 cm^{-1} and at 780 cm^{-1} which can be assigned to ν(C=N) and ν(C=S)[11] respectively. In the spectra of the complexes, these bands show red shift clearly indicating that coordination takes place through thione sulphur as well as azomethine nitrogen of the thiosemicarbazone moiety. The coordination through O, N and S donor atoms is further confirmed by the occcurrence of three bands in the far infrared regions at 540–510 cm^{-1}, 440–410 cm^{-1} and 380–350 cm^{-1} which are assigned to ν(M—O)[12], ν(M—S)[13] and ν(M—N)[14] respectively.

Electronic Spectra and Magnetic Moment of the Complexes

The Co(II) complexes exhibit four electronic spectral bands at *ca.* 8730, 17300, 20300 and 28900 cm^{-1} assignable to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and $^4A_{2g}(F)$, $^4T_{1g}(P)$ and charge transfer transitions respectively, which corresponds to an octahedral configuration[15]. The proposed configurations are further supported[16] by high μ_{eff} value in the range 4.8–5.2 B.M. for all the Co(II) complexes. The Ni(II) complexes display absorption bands in the regions 8100–7600 cm^{-1}, 14900–14100 cm^{-1}, 25900–25100 cm^{-1} and 29300 cm^{-1} attributable to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ and charge transfer transitions indicating octahedral structure[17]. The proposed geometry of Ni(II) complexes is further confirmed[17] by the μ_{eff} value in the range 2.85–3.08 B.M. for all the complexes. The Cu(II) complexes exhibit bands 13900–13600 cm^{-1} and 27700–27100 cm^{-1}; the former may be assignable to $^3E_g \rightarrow {}^3T_{2g}$ transition and the latter can be attributed to L-M charge transfer band, suggesting thereby an octahedral geometry[18]. The proposed geometry of Cu(II) complexes is further confirmed[17] by the μ_{eff} value in the range 1.83–1.94 B.M. for all the complexes.

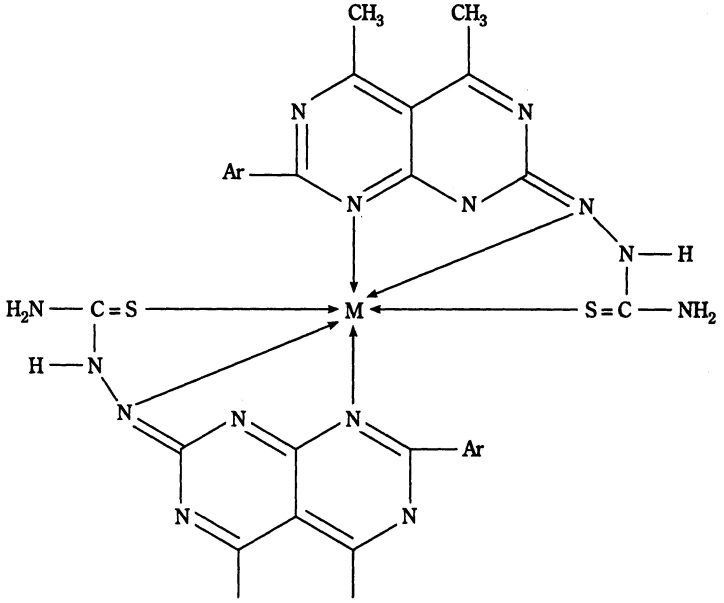
Conductivity of the complexes was measured in DMF and all the complexes have conductivity value in the range 120–135 ohm^{-1} cm^2 mol^{-1} indicating them to be electrolytic[19] in nature of 1 : 2 type.

Hence on the basis of elemental analysis, infrared spectra, electronic spectra, magnetic moment data and conductivity measurements the geometry of the complexes of the Co(II), Ni(II) and Cu(II) of the type $[M(CPDPPS)_2]X_2$ and $[M(CPDPPTS)_2]X_2$ can be presumed to have octahedral geometry as shown in Figs. 1 and 2.



$[M(CPDPPS)_2]X_2$; M = Co(II), Ni(II) and Cu(II); X = Cl^-, Br^- or I^-; Ar = *p*-chlorophenyl

Fig. 1



[M(CPDPPTS)$_2$]X$_2$; M = Co(II), Ni(II) and Cu(II); X = Cl$^-$, Br$^-$ or I$^-$; Ar = *p*-chlorophenyl

Fig. 2

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