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SYNTHESIS AND PHYSICOCHEMICAL STUDIES OF NITROGEN, OXYGEN AND SULPHUR DONOR SCHIFF BASE COMPLEXES OF COBALT (II), NICKEL (II)AND COPPER(II)

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ABSTRACT

Hexacoordinated complexes of the general formula [M(DMPT)$_2$X$_2$], where M is Cobalt(II), Nickel(II) and Copper(II), DMPT is 2,6-dimethyl-4-pyrone thiosemicarbazone (neutral bidentate Schiff base); X is Cl^-, Br^-, I^-, NO_3^-, ClO_4^- have been synthesized. The complexes were characterized by elemental analysis, magnetic susceptibility, molar conductance, spectral analysis (IR, electronic). An Octahedral geometry has been assigned to all these complexes. The ligand and complexes have been screened for their antibacterial and antifungal activities.

KEYWORDS : DMPT/ Co(II), Ni(II), Cu(II)/ Antifungal activity

Schiff base ligand exhibits an important and interesting biological activities such as anti-bacterial, anti-fungal and anti-tumor activities. The roles of Schiff base complexes of transition metals in chemistry and biochemistry suggest that considerable potential exists for their chelation reaction representing an exclusively beginning in the direction. In continuation of previous studies on Schiff base chelates of biological significance (Rai, 2008) the present work deals with synthesis and characterization of complexes of Co(II), Ni(II) and Cu(II) with Schiff base 2,6-dimethyl-4-pyrone thiosemicarbazone (DMPT)

Experimental

All the chemicals and solvents were of reagent grade and were used without further purification.

Physical Measurement

The complexes were analysed using standard methods. Analytical data (C, H, N) were collected on Perkin Elmer- 2400 CHNS/O elemental analyzer. Molar conductance was measured using a systronics conductivity meter model 303 using Ca.10−3 M solution in DMF. Spectroscopic data were obtained using following instruments; IR spectra, Perkin Elmer model- 577 (KBr disc 4000-200 cm^{-1}), electronic spectra, Cary 2390, Magnetic measurements of the samples were made on a Guoy balance using mercury tetraisothiocyanato cobaltate as the calibrant.

Synthetic Procedures

Preparation of the Bidentate Schiff Base Ligand

The compound 2,6-dimethyl-4-pyrone was synthesized by earlier reported method .

The Schiff base was prepared by the condensation reaction of equimolar quantity of 2,6-dimethyl-4-pyrone and thiosemicarbazide hydrochloride in ethanol. Ethanolic solution of 2,6-dimethyl-4-pyrone and thiosemicarbazide hydrochloride were mixed together in 1:1 ratio. The contents were shaken vigorously and were refluxed for 1h. Colourless Schiff base was obtained which was washed thoroughly with water and recrystallized with tetrahydrofuran. m.p. 126 ±1ºC Yield 75%-80%.

General Method for the Preparation of Metal Complexes

The following general method was adopted for the preparation of the halide complexes of Co(II), Ni(II) and Cu(II).

The complexes were prepared by reacting respective metal halides (0.005g) of Co(II), Ni(II) and Cu(II) in ethanol with the ethanolic solution of the ligand 2,6-dimethyl-4-pyrone thiosemicarbazone in molar ratio of 1:2. The resulting reaction mixture was refluxed on a water bath for 2-3 h. The procedure carried out in each case of similar with slight variation of timing of reflux. The precipitated complexes were filtered, washed with aqueous ethanol and dried in air oven. Yield 70%-75%.

The following general method was adopted for the preparation of nitrate and perchlorate complexes. By adding

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a ethanolic solution of respective metal nitrate or metal perchlorate (0.05g) to a hot ethanolic solution of ligand 2,6-dimethyl-4-pyrone thiosemicarbazone with vigorous stirring. The resulting solution was heated on a water bath for 2 h. The precipitated complexes were filtered, washed several times with ethanol and then dried in air oven. Yield 70%-75%.

RESULTS AND DISCUSSION

Infrared Spectra

The relevant vibrational bands and assignments of the ligand and metal complexes are listed in table-1.

IR spectrum of the ligand DMPT exhibits a medium broad band at 3460 cm^{-1} assigned to $\nu_{N\text{-}H}$. In the spectra of the complexes this band appears without any change confirming the non participation of either primary or secondary amino group in coordination. The >C=N (azomethine) (Rana et al., 2002) and >C=S (Agarwal et al.,1995) observed at 1500 cm^{-1} and 800 cm^{-1} respectively, in the spectrum of the Schiff base ligand DMPT shows a downward shift (~1470,770) in all the complexes. These suggest participation of the azomethine N and thione S atom of thiosemicarbazone moiety of Schiff base ligand DMPT in coordination. The linkage through azomethine N and Sulphur atoms of thiosemicarbazone moiety is supported by the appearance of bands in the far IR region 530-505, 470-440 and 410-390 cm^{-1} assigned to $\nu_{M\text{–}O}$, $\nu_{M\text{–}S}$, $\nu_{M\text{–}S}$, respectively. The coordination through metal halogen is confirmed by the appearance of a band in the region 325–270 cm^{-1}which assigned to $\nu_{M\text{–}X}$ (X= Cl^{-} or Br^{-} or I^{-}). These assignments are supported by literature (Nakamato,1976). The evidence of metal halogen linkage is further confirmed by the low value of molar conductance in the range 2.6 – 4.8 ohm^{-1} cm^{2} mol^{-1}. The bands at 1541 and 1420 cm^{-1} with a separation of 121 cm^{-1} suggest mono-coordinated nitrate group (Addison et al.,1971).

A strong band at 620 cm^{-1} and a medium intensity band at 1140 cm^{-1} observed in the spectrum of the perchlorate complexes indicating a monodentately coordinated perchlorate group (Harikumaran and Prabhakaran, 2000).

Magnetic Susceptibility and Electronic Spectral Studies

The electronic spectra of all the complexes have been recorded in the region 10,000-25,000 cm^{-1} and 22600-22000 cm^{-1} assignable to the transitions $^4T_{2g}$ (F) $\leftarrow$ $^4T_{1g}$(F), $^4A_{2g}$(F)$\leftarrow$$^4T_{1g}$(F) and $^4T_{1g}$(P) $\leftarrow$ $^4T_{1g}$(F) respectively. The above mentioned spectral bands indicate octahedral geometry for Co(II) complexes (Mane et al., 2000). The Octahedral geometry of Co(II) complexes is also supported by magnetic susceptibility value in the range 4.83- 5.11 B.M. The Ni(II) complexes exhibit three absorption bands in the region 10500-10100, 16200-15300 and 24600-24000 cm^{-1} respectively assignable to $^3T_{2g}$(F)$\leftarrow$$^3A_{2g}$(F), $^3T_{1g}$(F) $\leftarrow$ $^3A_{2g}$(F) and^3 T_{1g}(P) $\leftarrow$ $^3T_{2g}$(F) transition respectively. The above mentioned spectral bands proposes octahedral geometry for Ni(II) complexes (Mishra, Khare and Gautam,2002). It is also supported by magnetic susceptibility values of the complexes of the complexes in the range 3.13-3.20 B.M. The Cu(II) complexes exhibit two broad bands in the region 11400-11000 cm^{-1} and 14600-14100 cm^{-1} assigned to transitions $^2T_{2g}$(F) $\leftarrow$ ^2E_g and charge transfer band respectively which proposes octahedral geometry for Cu(II) complexes (Sacconi,1968). The magnetic moment values for Cu(II) complexes are found in the range 1.86-1.92 B.M.

Conductivity Measurement

Molar conductance values of the complexes of Co(II), Ni(II) and Cu(II) were found to be in the range 2.6-4.8 ohm^{-1}mol^{-1}cm^{-2} in DMF proposes their non electrolytic[37] nature. The molar conductance values also supported the structure assigned on the basis of physico-chemical and spectroscopic measurements.

Antimicrobial Activity

The ligand DMPT and its complexes of Co(II), Ni(II) and Cu(II) complexes were screened for their antibacterial activity against bacteria, *Eschericia coli* and antifungal activity against *Aspergillus niger* by disc diffusion technique (Mukherjee et al.,1995) using DMF as solvent at concentration of 50 mg (Mehta et. al.,1997). The activity was compared with known standard drugs, tetracycline and diethane Z-78, respectively at same concentration of 50 mg.

Table 1: Analytical, Colour, Molecular Formula, Magnetic Susceptibility, Electronic Spectral Values, Molar Conductivity and Decomposition Temperature of the ligand DMPT and its Complexes

Compound (Colour)	Mol. wt.	%Analysis found (Calculated)				μ_{eff} B.M.	λ_{max} electronic cm^{-1}	Ω_m ohm^{-1} cm^2 mol^{-1}	DT (in °C)
		M	C	N					
DMPT (colourless)	197		58.03 (58.18)	25.53 (25.45)	6.76 (6.66)				
[Co(DMPT)$_2$Cl$_2$] (Brown)	529.93	13.04 (12.92)	41.89 (42.11)	18.56 (18.42)	4.44 (4.82)	5.9	13700, 19300, 22000	3.1	260
[Co(DMPT)$_2$Br$_2$] (Brown)	612.75	10.82 (10.73)	35.12 (34.98)	15.22 (15.30)	3.93 (4.00)	5.7	13500, 19600, 22400	3.0	266
[Co(DMPT)$_2$I$_2$] (Deep Brown)	706.74	9.24 (9.16)	30.07 (29.87)	12.93 (13.06)	3.38 (3.42)	5.11	13100, 19100, 22300	2.8	253
[Co(DMPT)$_2$(NO$_3$)$_2$] (Dark Brown)	576.93	11.56 (11.48)	37.57 (37.43)	16.31 (16.37)	4.21 (4.28)	5.8	12900, 19000, 22400	2.7	257
[Co(DMPT)$_2$ (ClO$_4$)$_2$] (Brown)	651.93	10.09 (10.02)	32.83 (32.65)	14.20 (14.28)	3.82 (3.74)	4.83	13750, 19500, 22600	2.9	267
[Ni(DMPT)$_2$Cl$_2$] (Chocolate)	523.71	12.96 (12.88)	42.27 (42.13)	18.36 (18.43)	4.76 (4.82)	3.16	10500, 10600, 24000	2.6	250
[Ni(DMPT)$_2$Br$_2$] (Red)	612.53	10.63 (10.70)	34.89 (35.02)	15.22 (15.31)	3.92 (4.00)	3.14	10200, 16300, 24300	3.4	235
[Ni(DMPT)$_2$I$_2$] (Reddish Brown)	706.52	9.20 (9.13)	29.99 (29.80)	12.94 (13.07)	3.34 (3.42)	3.19	10100, 16000, 24400	3.7	230
[Ni(DMPT)$_2$(NO$_3$)$_2$] (Brownish red)	576.71	11.52 (11.45)	37.29 (37.21)	16.31 (16.35)	4.17 (4.29)	3.17	10300, 15600, 24600	3.9	240
[Ni(DMPT)$_2$ (ClO$_4$)$_2$] (Deep red)	651.71	10.04 (9.98)	32.70 (32.66)	14.35 (14.29)	3.69 (3.74)	3.13	10400, 15300, 24500	4.1	210
[Cu(DMPT)$_2$Cl$_2$] (Blue)	528.54	13.61 (13.67)	41.21 (41.33)	17.93 (18.08)	4.71 (4.77)	1.90	11300, 14300	4.3	230
[Cu(DMPT)$_2$Br$_2$] (Blue)	617.35	11.40 (11.48)	35.90 (34.69)	15.26 (15.13)	4.02 (3.97)	1.92	11400, 14600	4.7	220
[Cu(DMPT)$_2$(NO$_3$)$_2$] (Blue)	581.54	12.36 (12.27)	37.12 (37.00)	16.37 (16.29)	4.20 (4.25)	1.86	11200, 14100	4.5	235
[Cu(DMPT)$_2$(ClO$_4$)$_2$] (Deep blue)	656.54	10.85 (10.72)	32.24 (32.40)	14.26 (14.17)	3.77 (3.71)	1.88	11000, 14200	4.8	236

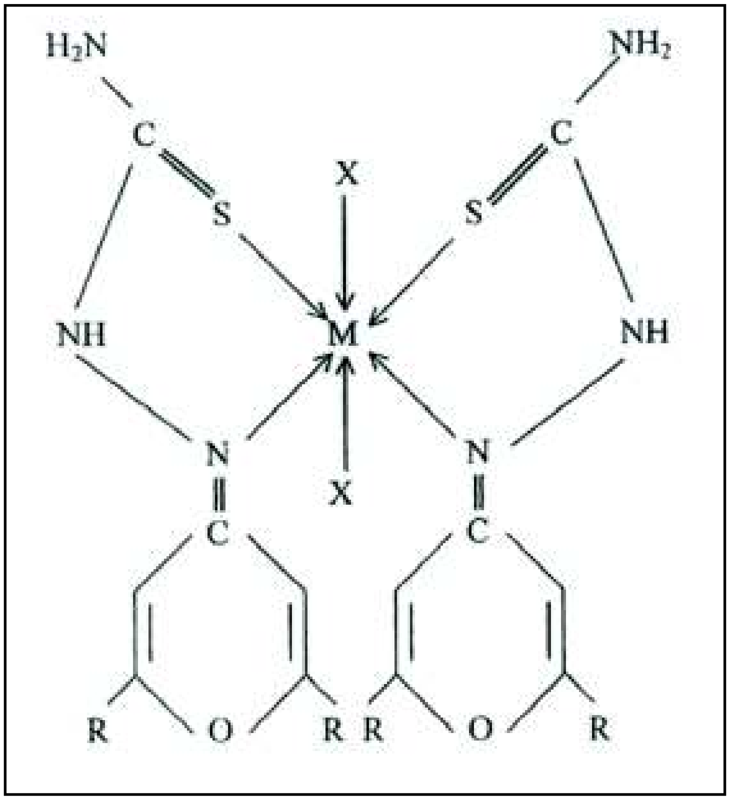
DT = Decomposition temperature

[M(DMPT)$_2$X$_2$]

M = Co(II) and Ni(II); X = Cl$^-$, Br$^-$, I$^-$, NO$_3^-$ and ClO$_4^-$;

M = Cu(II) ; X = Cl$^-$, Br$^-$, NO$_3^-$ and ClO$_4^-$; R = Methyl

It was observed that on comparison with references to antibiotic and fungicides the complexes were found to be more effective than ligands. The data indicates antibacterial and antifungal activity of complexes were found to be in the order Cu(II) > Ni(II) > Co(II). It is established from the literature that the metal complexes shows enhanced antimicrobial activity than free ligand. This is due to chelation which reduces the polarity of metal ion due to partial sharing of its positive charge with ligand (Nishant et al., 2006). The chelation increases lipophilic



$[M(DMPT)_2X_2]$

character in the complexes and results in the enhancement of fungicidal and antibacterial activity.

CONCLUSION

Thus on the basis of above studies it is concluded that the ligand DMPT acts in a bidentate manner and coordination is proposed through azomethine N and thione S of thiosemicarbazone moiety. The remaining center of metal ion is satisfied by negative ions such as Cl^-, Br^-, I^-, NO_3^- or ClO_4^-. The geometry of the Co(II), Ni(II) and Cu(II) complexes are proposed to be octahedral in nature as shown in figure.

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