



Spectroscopic and Biocidal Study of Co(II), Cu(II) and Ni(II) Chelates of Nitrogen and Sulphur Containing Schiff Base Derived from 6-methyl-2-phenyl-4H-chromen-4-one

B.K. RAI*, S. N. VIDYARTHI¹, PUJA SINHA², VINEETA SINGH³ and SANJIV KUMAR¹

*Department of Chemistry, L. N. T. College, Muzaffarpur, India.

B.R.A. Bihar University, Muzaffarpur, India.

¹Department of Chemistry, J. P. University, Chapra

²FNS Academy, +2 Govt. School, Guljarbag, Patna

³BNR +2 Govt. School, Guljarbag, Patna

*Corresponding author E-mail: binodkr_rai@yahoo.co.in

(Received: October 25, 2012; Accepted: December 29, 2012)

ABSTRACT

In the present paper, a series of complex of the type $[MLX_2]$ where M = Co(II), Ni(II) and Cu(II), L = 6-methyl-2-phenyl-4H-chromen-4-thiosemicarbazone (MPCT) have been synthesized. Their structure were confirmed by means of IR, electronic spectra, elemental analysis and molar conductance, coupled with magnetic susceptibility measurements. All the compounds were assayed for antibacterial activities against one gram positive bacterial strain *Bacillus subtilis* and one gram negative bacterial strain *Escherichia coli*, using disc diffusion technique. It was observed on comparison with reference to antibiotic and fungicides. The complexes were found to be more effective than ligands.

Key word: MPCT/ Cobalt(II)/ Nickel(II)/ Copper(II)/ Complexes.

INTRODUCTION

Schiff bases have the ability to act as coordinating ligands and the polynuclear complexes derived from Schiff bases find variety of applications in analytical and biological systems¹⁻¹². Schiff base complexes of transition metals are of great interest and have extensively been studied over past few decades¹³⁻¹⁶. Keeping in view the importance of Schiff base complexes of transition metal and in continuation of earlier work¹⁷⁻³¹ on

Schiff base coordination compounds, the present work was undertaken to study the complexes of Co(II), Ni(II) and Cu(II) ions with bioactive ligands. In the present paper, we report a series of new Co(II), Ni(II) and Cu(II) complexes of Schiff base 6-methyl-2-phenyl-4H-chromen-4-thiosemicarbazone. The complexes have general molecular formula $[MLX_2]$; where M = Co(II), Ni(II) and Cu(II); L = 6-methyl-2-phenyl-4H-chromen-4-thiosemicarbazone (MPCT) and X = Cl⁻, Br⁻, I⁻ and NO₃⁻.

EXPERIMENTAL

All the reagents and solvents were of analytical grade and were obtained from BDH and used as received.

Physical measurements

Analytical data were collected on Perkin Elmer-2400 CHNS/O elemental analyzer. Melting point were taken in open capillary tube and are uncorrected. IR spectra (KBr discs, 4000-200 cm^{-1}) were recorded using Perkin-Elmer-577 spectrophotometer. The molar conductance measurements were carried out at room temperature on Systronics conductivity meter model 303 using DMF as a solvent. The electronic spectra were recorded on Cary 2390 spectrophotometer in the 10000-25000 cm^{-1} and magnetic susceptibility of the samples were made on a Gouy balance using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant.

Preparation of the ligand

The hot ethanolic solution (20 ml) of 6-methyl-2-phenyl-4H-chromen-4 one and hot ethanolic solution of semicarbazide hydrochloride dissolved in sodium acetate was mixed slowly with constant stirring. This mixture was refluxed (80-90°C) for 3-4 h. On cooling, colourless precipitate was formed, which was filtered, washed and dried under vacuum over phosphorus pentoxide, yield 62%, m.p 180±1°C.

Preparation of the complexes

Hot ethanolic (20 ml) solution of ligand (3.09 g, 0.01 mol) and hot ethanolic solution of corresponding metal salt (0.005 mol) were mixed together with constant stirring. The mixture was refluxed for 2-3 h at 70-90°C. On cooling coloured complex was precipitated out. It was filtered, washed with cold ethanol and dried under vacuum over phosphorus pentoxide; Yield-58%.

RESULTS AND DISCUSSION

I.R. spectra

The I.R. spectrum of the ligand MPCT exhibit strong and broad band at 3160 cm^{-1} which is assigned³²⁻³⁴ to $\nu_{\text{N-H}}$. In the spectra of the complexes, this band is unaffected which indicates non participation of either primary amino or secondary

amino group in the coordination. IR spectrum of the ligand MPCT exhibits a strong and medium band at 1475 cm^{-1} assignable³¹⁻³⁵ to $\nu_{\text{C=N}}$. In the spectra of the complexes this band shows red shift with slightly reduced intensity. The shift of the band and change in intensity proposes coordination of the azomethine N with metal ion. The infrared spectrum of the ligand shows a strong and broad band at 800 cm^{-1} assigned^{32,33,37} to $\nu_{\text{C=S}}$. In the spectra of the complexes this band also shows red shift indicating coordination takes place through thione S atom of thiosemicarbazone moiety.

The conclusive evidence of bonding of ligand to metal ion through oxygen atom of either nitrate or perchlorate ion, N atom of azomethane group and thione S of thiosemicarbazone moiety is supported by the appearance of bands^{31,33,37} due to, $\nu_{\text{M-O}}$ at 500-510 cm^{-1} , $\nu_{\text{M-S}}$ at 390-405 cm^{-1} , $\nu_{\text{M-N}}$ at 435-450 cm^{-1} respectively. The evidence of metal-halogen linkage is supported by the low molar conductance values³⁷ of the complexes in the range 2.3-6.7 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ and appearance of a band in the region 315-275 cm^{-1} which assigned^{31,32,35} to $\nu_{\text{M-X}}$.

Nitrate complexes show characteristic medium intensity bands at 1300 and 1140 cm^{-1} with a separation of 140 cm^{-1} due to monodentate coordinated nitrate³⁹ group.

On the basis of above discussion on IR spectral data, it is proposed that the ligand MPCT acts in a neutral bidentate manner. The remaining coordination positions of metal ions are satisfied by negative ions, such as Cl^- , Br^- , I^- or NO_3^- .

Biocidal study

Schiff base MPCT and their metal complexes have been evaluated for their antimicrobial activity against *E. coli* and *B. subtilis* by disc diffusion method⁴³ at concentrations 50 and 25 mg ml^{-1} using streptomycin as control. On comparison with reference to antibiotic, the complexes were found to be more effective than free ligand. Further, it is also observed that the order of activity for complexes are: $\text{Cu(II)} > \text{Ni(II)} > \text{Co(II)}$ and also nitrate complexes have effective biocidal effect than metal-halide complexes which is supported by literature⁴⁴⁻⁴⁶.

Table-1: Analytical, colour, mol. wt., magnetic susceptibility values, conductivity measurement and decomposition temperature of ligand MPCT and its metal complexes

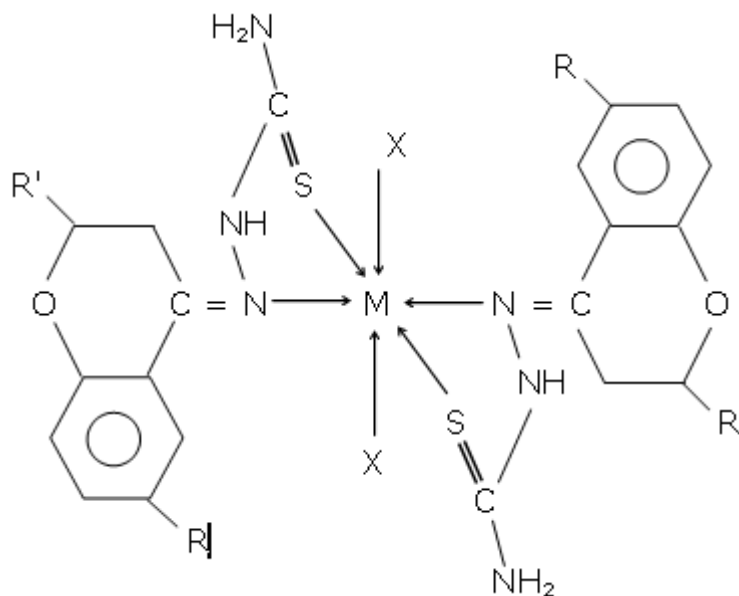
Compounds (Colour)	Yiel d%	Molar mass	% Analysis found (calculated)				DT °C.	μ_{eff} B.M	Ω_{in} cm ² mol ⁻¹	λ_{max} electronic cm ⁻¹
			M	C	N	H				
MPCT (Colourless)	68	309		65.79 (66.01)	13.42 (13.50)	4.78 (4.85)				
[Co(MPCT) ₂ Cl ₂] (Deep brown)	74	747.93	7.80 (7.87)	54.38 (54.55)	11.14 (11.23)	3.96 (4.01)	4.96	4.7	9300, 13500, 19700	
[Co(MPCT) ₂ Br ₂] (Yellow)	70	836.24	6.94 (7.04)	48.64 (48.76)	9.91 (10.03)	3.49 (3.56)	5.03	4.6	9200, 13900, 19300	
[Co(MPCT) ₂] (Deep green)	72	930.73	6.27 (6.33)	43.72 (43.83)	8.94 (9.02)	3.27 (3.22)	5.24	5.1	9800, 14500, 19800	
[Co(MPCT) ₂ (NO ₃) ₂] (Deep green)	70	800.93	7.28 (7.35)	50.83 (50.94)	10.49 (10.46)	3.68 (3.74)	504	5.3	9700, 14200, 19500	
[Ni(MPCT) ₂ Cl ₂] (Yellowish blue)	74	747.71	7.69 (7.85)	54.42 (54.56)	11.10 (11.23)	3.97 (4.01)	3.13	6.1	12400, 18300 , 25700	
[Ni(MPCT) ₂ Br ₂] (Yellow)	71	836.57	6.94 (7.01)	48.63 (48.77)	9.93 (10.04)	3.50 (3.58)	3.16	6.7	12100, 18400, 24700	
[Ni(MPCT) ₂] (Red)	73	930.51	6.22 (6.30)	43.76 (43.84)	8.94 (9.02)	3.15 (3.22)	3.18	6.4	12800, 19000, 25500	
[Ni(MPCT) ₂ (NO ₃) ₂] (Green)	75	800.71	7.26 (7.33)	50.78 (50.95)	10.37 (10.49)	3.68 (3.74)	3.24	6.3	12700, 18700 , 25300	
[Cu(MPCT) ₂ Cl ₂] (Green)	70	752.54	8.37 (8.44)	54.10 (54.21)	11.07 (11.16)	3.92 (3.98)	1.87	3.1	13600, 18300	
[Cu(MPCT) ₂ Br ₂] (Greenish yellow)	70	841.35	7.46 (7.55)	48.38 (48.49)	9.89 (9.98)	3.48 (3.56)	1.91	2.4	12700, 17900	
[Cu(MPCT) ₂ (NO ₃) ₂] (Green)	70	805.54	7.67 (7.88)	50.49 (50.64)	10.30 (10.42)	3.66 (3.72)	1.88	2.3	13100, 18700	

DT = Decomposition Temperature

Table 2: Salient features of IR spectral bands of ligand MPCT and its metal complexes

Compounds	$\nu_{\text{N-H}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C=S}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-S}}$	$\nu_{\text{M-X}}$
MPCT	3160 s,b	1475 s,m	800 s,b				
[Co(MPCT) ₂ Cl ₂]	3160 s,b	1455 s,m	770 s,s		410 m	395 m	305 m
[Co(MPCT) ₂ Br ₂]	3160 s,b	1450 s,m	765 s,s		430 m	390 m	250 m
[Co(MPCT) ₂ I ₂]	3160 s,b	1445 s,m	770 s,s		415 m	405 m	270 m
[Co(MPCT) ₂ (NO ₃) ₂]	3160 s,b	1445 s,m	770 s,s	505 m	450 m	405 m	
[Ni(MPCT) ₂ Cl ₂]	3160 s,b	1440 s,m	775 s,s		445 m	400 m	325 m
[Ni(MPCT) ₂ Br ₂]	3160 s,b	1440 s,m	765 s,s		435 m	395 m	295 m
[Ni(MPCT) ₂ I ₂]	3160 s,b	1440 s,m	770 s,s		445 m	405 m	275 m
[Ni(MPCT) ₂ (NO ₃) ₂]	3160 s,b	1445 s,m	765 s,s	510 m	440 m	390 m	
[Cu(MPCT) ₂ Cl ₂]	3160 s,b	1440 s,m	765 s,s		445 m	395 m	315 m
[Cu(MPCT) ₂ Br ₂]	3160 s,b	1445 s,m	770 s,s		440 m	395 m	285 m
[Cu(MPCT) ₂ (NO ₃) ₂]	3160 s,b	1445 s,m	770 s,s	500	445 m	390 m	

m = medium, s = strong, b = broad



M = Co(II) and Ni(II); X = Cl⁻, Br⁻, I⁻ and NO₃⁻; M = Cu(II); X = Cl⁻, Br⁻, and NO₃⁻; R = CH₃; R' = Phenyl

Fig. 1: [M(MPCT)X₂]

Electronic spectra and magnetic susceptibility of the complexes

The electronic³⁸ spectral and magnetic^{39,40} susceptibility values tentatively proposes octahedral geometry of Co(II), Ni(II) and Cu(II) complexes.

ACKNOWLEDGEMENTS

The authors are grateful to the U.G.C. for providing financial assistance under Minor Research Project.

REFERENCES

1. Ghiladi M., Larsen F. B., Mckenzie C. J., Sotofte I. and Tuchogues J. P., *J. Chem Soc., Dalton Trans*, 1687 (2005).
2. Chakraborty J., Nandi M., Mayer Figge G., Sheldrick W. S., Sorace L., Bhaumik A. and Banerjee P., *Eur. J. Inorg. Chem.*, 5033 (2007).
3. Eryleben A. and Hermann J., *J. Chem. Soc., Dalton Trans.*, 569 (2000).
4. Biswas P., Ghosh M., Dutta S. K., Florke U. and Nag K., *Inorg. Chem.*, **45**: 4830 (2006).
5. Mishra L. and Sinha R., *Indian J. Chem., Sect.A*, **29**: 1131 (2000).
6. Mukhopadhyay and Rau D., *Indian J. Chem., Sect.A*, **40**: 228 (2001).
7. Krishnankutty K. and Ummathur M. B., *J. Indian Chem. Soc.*, **83**: 633 (2006).
8. Dubey R.K., *J. Indian Chem. Soc.*, **83**: 1087 (2006).
9. Saritha P., Reddy B. S. and Jayatyagaraju, *J. Indian Chem. Soc.*, **83**: 1204 (2006).
10. Gulloli M., Casella L., Pasini A. and Ugo R., *J. Chem. Soc., Dalton Trans.*, 339 (1977).
11. Muslim L., Roth W. and Erienmeyor H.H., *Acta Chem. Helv.*, **36**: 36 (1983).
12. Vyas R. R. and Mehata R.N., *J. Indian hem. Soc.*, **68**: 294 (1991).
13. Gruber S.J., Harris C.M. and Sinn E., *Inorg. Chem.*, **7**: 268 (1968).
14. Gruber S. J., Harris C. M. and Sinn E., *J. Inorg. Nuclei Chem.*, **30**: 1805 (1968).
15. Gruber S. J., Harris C. M. and Sinn E., *J. Inorg. Nuclei Chem.*, **18**: 3469 (1979).
16. Fachinetti G., Floriani C., Zanzzi P.F., and A. R. Zanzari, *Inorg. Chem.*, **18**: 3469 (1979).
17. a) Rai B. K., *Asian J. Phys.*, **16**: 71 (2007)
b) Rai B. K., Rai H. C., Singh Shiv Pujan, Tomar Rashmi, Prakash Om and Sahi Poonam, *Asian J. Phys.*, **26**: 76 (2007).
18. B.K. Rai, Rachana Kumari and Amrita Thakur., *Orient. J. Chem.*, **28**(2): 943-948 (2012).
19. Rai B. K. and Sharma K., *Asian J. Chem.*, **20**: 137 (2008).
20. Rai B. K., Rai Rajeshwar, Sahi Poonam and Rana Swaty, *Asian J. Chem.*, **30**: 143, 149 (2008).
21. a) Rai B. K., Hussain Z., Singh U. P., Prasad S. N., Prasad A and Mishra P.M., *J. Ultra Chem.*, **4**: 53 (2008)
b) Rai B. K. and Prasad S. N., *J. Ultra Chem*, **4**: 71 (2008)
c) Rai B. K. and Kumar A., *J. Ultra Chem.*, **4**: 179 (2008).
22. a) Rai B. K., *J. Ind. Council Chem.*, **25**: 137 (2008)
b) Rai B. K., Baluni A., Prasad A., Thakur R. and Prakash P., *Asian J. Chem*, **21**: 3708, 3713 (2009).
23. a) Rai B. K. and Vinayak, *J. Ultra Chem*, **5**: 67 (2009)
b) Rai B. K., Kumar A., Ravishankar, *J. Ultra Chem*, **5**, 73 (2009)
c) Rai B. K., Kumari S., Singh R. K., Prasad A., Sinha M. Prasad and Mishra P. M., *J. Ultra Chem*, **5**: 83 (2009).
24. a) Prasad A. and Rai B. K., *Orient J. Chem.*, **25**: 175 (2009)
b) Rai B. K., Ravishankar and Pandey S., *Asian J. Chem.*, **21**: 5409 (2009).
25. a) Rai B. K., Prasad A., Vinayak, Singh S. P. and Jha S. 'Sunit', *Asian J. Phys.*, **18**: 63 (2009).
b) Rai B. K., Singh Vineeta, Vinayak, Singh S. P. and Jha S. 'Sunit', *Asian J. Phys.*, **6**:18, 67 (2009).
26. Rai B. K., Kumar H., Sharma M. and Rastogi V. K., *J. Indian Chem Soc.*, **87**: 1241 (2010).
27. a) Rai B. K., *Asian J. Chem.*, **22**: 2761 (2010).
b) Rai B. K. and Kumar Chandan, *Asian J. Chem.*, **22**: 5613 (2010).
c) Rai B. K. and Singh Sateydeo, *Asian J. Chem.*, **22**: 5619 (2010).
d) Rai B. K. and Sharma K. K., *Asian J. Chem.*, **22**: 5625 (2010).
e) Rai B. K., *J. ind. Council Chem.*, **27**, 68 (2010).
28. a) Kishore K. R. and Rai B. K., *Asian J. Chem.*, **22**: 8055 (2010).
b) Rai B. K. and Kumar Bimal, *Asian J. Chem.*, **22**: 8073 (2010).
c) Rai B. K. and Singh S., *Orient J. Chem.*, **26**: 989 (2010).
d) Rai B. K. and Kumar Chandan, *Orient J. Chem.*, **26**: 1019 (2010)

- e) Rai B. K. and Kumar Bimal, *Orient J. Chem.*, **26**: 1097 (2010).
29. a) Rai B. K., Sinha Puja, Vidyarthi S. N. and Singh Vineeta, *Asian J. Chem.*, **23**: 4629 (2011).
b) Rai B. K. and Kumar Bimal, *Asian J. Chem.*, **23**: 4635 (2011)
c) Rai B. K., Singh Vineeta, Vidyarthi S. N. and Sinha Puja, *Asian J. Chem.*, **23**: 4638 (2011).
30. a) Rai B. K. and Anand Puja, *Orient J. Chem.*; **28**: 525 (2012)
b) Rai B. K., Kumari Rachana and Thakur Amrita, *Orient J. Chem.*, **28**: 943 (2012).
c) Rai B. K., Vidyarthi S. N., Sinha Puja, Singh Kalyan Chandra, Sahi Shashi Bhushan and Jha Javvir, Sharan, *Orient J. Chem.*, **28**: 1365 (2012).
d) Rai B. K., Vidyarthi S. N., Amit Singh Rabindra, Bhardwaj Nithish and Ojha Avinash, *Orient J. Chem.*, **28**: 1403 (2012).
31. a) Rai B. K. and Anand Rahul, *Asian J. Chem.*, **25**: 480 (2013).
b) Rai B. K., Thakur Amrita and Divya, *Asian J. Chem.*, **25**: 583 (2013).
c) Rai B. K., Vidyarthi S. N., Kumari Punam, Kumari Suman, Kumari Laxmi and Singh Rajkishore, *Asian J. Chem.*, **25**: 941 (2013).
d) Rai B. K. and Kumar Arun, *Asian J. Chem.*, **25**: 1169 (2013).
33. Mohir Kumar and Shamim Ahmad., *Orient. J. Chem.*, **26**(4): 1455-1459 (2010).
34. Silverstein Robert and Webster X. Francis, "Spectrometric Identification of Organic Compounds", 6th ed., John Wiley & Sons (2008).
35. Kemp William, "Organic Spectroscopy", 3rd ed., Palgrave, New York (2008).
36. Gudasi K. B., Patil S. A., Vadavi R. S., Shenoy R. V. and Patil R. S., *J. Serb. Chem. Soc.*, **17**: 526 (2006).
37. Agarwal R. K., Agarwal H. and Chakraborti I., *Synth. React. Inorg. Metal Org. Chem.*, **25**: 679 (1995).
38. Ferraro J. R., "Low Frequency Vibration of Inorganic and Coordination Compound", Plenum Press, New York.
39. Boghaei D. M. and Zadeegan N. Lashani, *Synth. React. Inorg. Metal-Org. Chem*, **30**: 1393 (2000).
40. Addison C. C., Logan N., Wallwork S. C. and Barmer D. C., *Quart. Rev.* (1971).
41. Krishna C. H., Mahapatra C. M. and Dash A. K., *J. Inorg. Nucl. Chem.*, **39**: 1253 (1977).
42. B. N. Figgis, "Introduction to Ligand Field", Wiley Eastern Ltd., New Delhi, 279 (1976).
43. Carlin R. L. and Dryneveledt A. J. Van, "Magnetic Properties of Transition Metal CCompounds", Springer Verlag, New York, (1997).
44. Mukherjee P. K., Saha K., Giri S. N., Pal M. and Saha B. P., *Indian J. Microbiology*, **35** (1995).
45. Parashar R. K. and Sharma R. C., *J. Inorg. Biochem*, **28**: 225 (1987).
46. Rainsford K. D. and Whitehouse M. W., *J. Pharmacol*, **28**: 83 (1976).
47. Nishant N., Ahmad S. and Ahmad R. T., *J. Appl. Polym. Sci.*, **100**: 928 (2006).