

Structural and Antifungal Characterization of Co(II), Ni(II) and Cu(II) Complexes with Schiff Bases

B.K. RAI*, AKHILESH BALUNI†, ANUKUL PRASAD‡, R. THAKUR¶ and PREM PRAKASH§

Department of Chemistry, LNT College, Muzaffarpur-842 002, India

E-mail: binodkr_rai@yahoo.co.in

Complexes of the type $[M(\text{ANFTS})_2]X_2$ where ANFTS = 2-acetyl naphtho[2-1-b]furan thiosemicarbazone, $M = \text{Co(II)}$, Ni(II) and Cu(II) ; $X = \text{Cl}^-$, Br^- , I^- , NO_3^- and ClO_4^- ; have been synthesized and characterized on the basis of elemental analysis, molar conductance, magnetic moment, thermal analysis, IR and electronic spectral data. The results are in consistent with tridentate chelation of ligand with azomethine N, oxygen atom of the furan ring of the ligand and thione sulphur atom of thiosemicarbazone as bonding sites as inferred from IR spectra while the complexes of above stoichiometry are proposed to be octahedral environment. The high value of molar conductance suggests the complexes are found to be electrolytic in nature of the 1:2 type.

Key Words: ANFTS, Co(II), Ni(II) and Cu(II) complexes, Antifungal activity.

INTRODUCTION

Heterocyclic compounds such as furan and its derivative are versatile pharmacophores possessing a variety of biological activities^{1,2}. They also play important roles in natural products, non-linear optics^{3,4} and supramolecular chemistry. Substituted furan ring are important compounds for synthesis purpose and as starting material obtained pharmaceutically and industrially important compounds⁵. In continuation of our earlier recent⁶⁻¹³ work on Schiff base metal complexes with heterocyclic based ligand, we herein report the synthesis and characterization of metal complexes of Co(II), Ni(II) and Cu(II) with 2-acetyl naphtho[2,1-b]furan thiosemicarbazone (ANFTS).

EXPERIMENTAL

All the chemicals used were either E-Merck or BDH quality. 2-Acetyl naphtho[2-1,b]furan was prepared by reported method¹⁴. Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer. The electronic spectra recorded on a Shimadzu 160A

*Department of Chemistry, Pandit Balkrishna Navin P.G. College, Shajapur-465 001, India.

†Department of Chemistry, M.M. Das Mahila College, Sirsia-843 108, India.

‡Holy Mission Senior Secondary School, Muzaffarpur-842 001, India.

¶Research Scholar, Department of Chemistry, J.P. University, Chapra-841 301, India.

spectrophotometer. Molar conductance data were made on systronics conductivity meter model 303 using DMF as a solvent. Magnetic susceptibility measured by a Guoy balance using mercury tetrathiothiocyanato cobaltate as a calibrant. The metal contents were determined using standard procedures¹⁵. The analytical data, colour, magnetic susceptibility, decomposition temperature, conductivity value and electronic spectra have been recorded in Table-1.

TABLE-1
ANALYTICAL, COLOUR, MAGNETIC MOMENT, CONDUCTIVITY VALUE,
ELECTRONIC SPECTRA AND DECOMPOSITION TEMPERATURE OF
LIGAND ANFTS AND THEIR METAL COMPLEXES

Compd. (colour)	Analysis found (calcd.)				μ_{eff} (BM)	Ω_m (ohm ⁻¹ cm ² mol ⁻¹)	λ_{max} electronic (cm ⁻¹)	DT
	M	C	N	H				
ANFTS (Colourless)	–	63.48 (63.60)	14.89 (14.84)	9.22 (9.18)	–	–	–	–
[Co(ANFTS) ₂]Cl ₂ (Yellowish red)	8.41 (8.46)	51.63 (51.72)	12.13 (12.07)	3.77 (3.73)	5.16	126.3	13300 19500	310
[Co(ANFTS) ₂]Br ₂ (Dark green)	7.56 (7.50)	45.74 (45.87)	10.64 (10.70)	3.35 (3.31)	5.06	118.9	13500 20100	314
[Co(ANFTS) ₂]I ₂ Dark (Green)	6.76 (6.70)	40.89 (40.96)	9.51 (9.55)	2.91 (2.96)	5.24	119.3	13700 19400	317
[Co(ANFTS) ₂](NO ₃) ₂ (Deep green)	7.82 (7.86)	48.15 (48.06)	11.26 (11.21)	3.32 (3.47)	4.91	124.3	13200 19500	323
[Co(ANFTS) ₂](ClO ₄) ₂ (Light green)	7.20 (7.15)	43.61 (43.69)	10.24 (10.19)	3.18 (3.15)	4.81	128.3	13360 20200	289
[Ni(ANFTS) ₂]Cl ₂ (Deep blue)	8.47 (8.43)	51.62 (51.74)	12.11 (12.07)	3.76 (3.73)	3.24	136.3	10600 15300 24300	294
[Ni(ANFTS) ₂]Br ₂ (Deep brown)	7.41 (7.48)	45.76 (45.88)	10.62 (10.70)	3.36 (3.31)	3.31	134.3	10800 15300 24200	291
[Ni(ANFTS) ₂]I ₂ Deep (Blue)	6.73 (6.68)	40.88 (40.97)	9.50 (9.56)	2.93 (2.95)	3.44	130.2	10400 15600 24500	293
[Ni(ANFTS) ₂](NO ₃) ₂ (Deep green)	7.79 (7.84)	48.14 (48.08)	11.28 (3.47)	3.43 (3.47)	3.48	134.8	10700 15800 24400	317
[Ni(ANFTS) ₂](ClO ₄) ₂ (Green)	7.17 (7.12)	43.58 (43.70)	10.23 (10.19)	3.18 (3.15)	3.59	135.9	10500 16200 24800	320
[Cu(ANFTS) ₂]Cl ₂ (Green)	9.12 (9.07)	51.27 (51.38)	11.92 (11.99)	3.75 (3.71)	1.83	113.6	11300 14300	303
[Cu(ANFTS) ₂]Br ₂ (Deep brown)	8.08 (8.04)	45.49 (45.60)	10.59 (10.64)	3.26 (3.29)	1.84	112.9	11400 14200	313
[Cu(ANFTS) ₂](NO ₃) ₂ (Deep green)	8.47 (8.43)	47.67 (47.77)	11.01 (11.08)	3.48 (3.45)	1.78	111.8	11700 14000	319
[Cu(ANFTS) ₂](ClO ₄) ₂ (Green)	7.61 (7.66)	43.53 (43.44)	10.17 (10.13)	3.10 (3.13)	1.77	108.3	11600 15000	326

DT = Decomposition temperature.

Preparation of ligand ANFTS: A suspension of 2-acetyl naphtho[2-1,b]furan (2.10 g, 0.01 m) in hot dioxane (20 mL) was treated with thiosemicarbazone hydrochloride (1.28 g, 0.01 m) dissolved in 10 % ethanolic solution of sodium acetate. The resulting reaction mixture were heated on waterbath for 4 h when a crystalline colourless solid began to separate. It was heated for further 0.5 h for complete precipitation. It was cooled, filtered, washed with aqueous ethanol, dried and crystallized with methyl alcohol. Yield 65-70 %, m.p. 241 °C.

Preparation of complexes: The complexes of Co(II), Ni(II) and Cu(II) were formed by heating ethanolic solution of respective metal salt with the ethanolic solution of the ligand ANFTS. The resulting reaction mixture were refluxed on water bath for 3-4 h. The procedure carried out in each case was similar with slight variation of timing of reflux. On cooling solid coloured complexes separated out which were filtered washed with ethanol, dried and recrystallized with dimethyl formamide. Yield in all cases 60-65 %.

RESULTS AND DISCUSSION

The IR spectra of the ligand ANFTS exhibits a broad band of medium intensity at 3440 cm^{-1} which may be assigned¹⁶ to $\nu(\text{N-H})$. The spectra of the complexes exhibit this band without much change in position and intensity clearly indicating non-involvement of nitrogen atom of either amino or imino group in the coordination with metal ion. The spectrum of the ligand ANFTS exhibits a sharp and strong band at 1485 cm^{-1} which can be assigned¹⁷ to $\nu(\text{C=N})$. In the spectra of the complexes, this band has shifted to a lower frequency region with slightly reduced intensity. The shift of the band and change in intensity suggest coordination of azomethine nitrogen of thiosemicarbazone moiety to the metal ion. The other IR band of structural significance in the spectra of the ligand ANFTS, appears *ca.* 820 cm^{-1} which can be assigned¹⁸ to $\nu(\text{C=S})$ group. This band also suffered downward shift by $20\text{-}30\text{ cm}^{-1}$ in the complexes indicating the coordination may takes place through thione S atom of thiosemicarbazone moiety. The next IR spectra of the ligand ANFTS exhibit in the range $1200\text{-}1000\text{ cm}^{-1}$ has shifted towards the lower frequency side in all complexes indicating the involvement of furan oxygen in the complex formation.

The coordination through azomethine N atom, thione sulphur of thiosemicarbazone moiety and oxygen atom of the furan ring are further confirmed by the presence of three bands in the far ir regions, $560\text{-}535$, $470\text{-}430$ and $385\text{-}360\text{ cm}^{-1}$ which may be assigned^{19,20} to $\nu(\text{M-O})$, $\nu(\text{M-S})$ and $\nu(\text{M-N})$, respectively.

Electronic spectra and magnetic susceptibility of the complexes: The complexes of Co(II) display two bands in the regions $20200\text{-}13200\text{ cm}^{-1}$ which proposes octahedral²¹ geometry of the Co(II) complexes. The proposed geometry of the complexes are further supposed^{22,23} by high μ_{eff} value of the complexes in the range $4.81\text{-}5.24\text{ BM}$. The electronic spectra of all the Ni(II) complexes exhibit three bands in regions, $10400\text{-}24800\text{ cm}^{-1}$, which proposes octahedral²¹ geometry of the Ni(II) complexes. The geometry of Ni(II) complexes is further supported by the μ_{eff} value

in the range 3.24-3.60 BM. The Cu(II) complexes display two ligand field bands in the region, 11300-11700 and 14000-15000 cm^{-1} which proposes octahedral²¹ geometry of the Cu(II) complexes (Table-2).

TABLE-2
INFRARED SPECTRAL DATA FOR LIGAND ANFTS AND
ITS METAL COMPLEXES

Compounds	$\nu(\text{N-H})$	$\nu(\text{C=N})$	$\nu(\text{C=S})$	$\nu(\text{M-O})$	$\nu(\text{M-NS})$	$\nu(\text{M-N})$
ANFTS	3440 m,b	1485 s,b	820 s,b	–	–	–
[Co(ANFTS) ₂]Cl ₂	3440 m,b	1460 m,b	785 m,b	555 m	465 m	365 m
[Co(ANFTS) ₂]Br ₂	3440 m,b	1455 m,b	790 m,b	560 m	470 m	375 m
[Co(ANFTS) ₂]I ₂	3440 m,b	1450 m,b	785 m,b	550 m	460 m	360 m
[Co(ANFTS) ₂](NO ₃) ₂	3440 m,b	1460 m,b	790 m,b	545 m	465 m	370 m
[Co(ANFTS) ₂](ClO ₄) ₂	3440 m,b	1460 m,b	795 m,b	540 m	470 m	380 m
[Ni(ANFTS) ₂]Cl ₂	3440 m,b	1455 m,b	795 m,b	535 m	440 m	370 m
[Ni(ANFTS) ₂]Br ₂	3440 m,b	1450 m,b	790 m,b	545 m	430 m	360 m
[Ni(ANFTS) ₂]I ₂	3440 m,b	1460 m,b	795 m,b	540 m	435 m	380 m
[Ni(ANFTS) ₂](NO ₃) ₂	3440 m,b	1455 m,b	790 m,b	550 m	445 m	385 m
[Ni(ANFTS) ₂](ClO ₄)	3440 m,b	1460 m,b	795 m,b	540 m	450 m	375 m
[Cu(ANFTS) ₂]Cl ₂	3440 m,b	1455 m,b	790 m,b	545 m	470 m	360 m
[Cu(ANFTS) ₂]Br ₂	3440 m,b	1455 m,b	795 m,b	550 m	450 m	370 m
[Cu(ANFTS) ₂](NO ₃) ₂	3440 m,b	1460 m,b	790 m,b	535 m	460 m	360 m
[Cu(ANFTS) ₂](ClO ₄)	3440 m,b	1455 m,b	795 m,b	540 m	465 m	380 m

Antifungal activity: The ligand ANFTS and its complexes with Co(II), Ni(II) and Cu(II) have been screened for their antifungal activity against *A. niger* and *C. albicans* at concentrations at 25 and 50 mg mL^{-1} by following paper disc plate method²⁴. The minimum inhibitory concentration values are listed in Table-3.

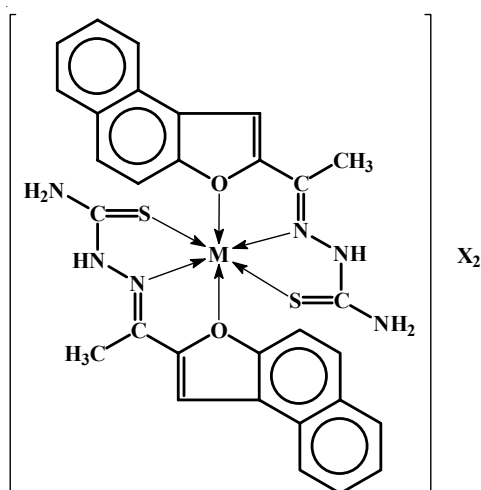
TABLE-3
ANTIFUNGAL ACTIVITY OF THE LIGAND ANFTS AND
ITS METAL COMPLEXES OF Co(II), Ni(II) AND Cu(II)

Compounds	MIC mg mL^{-1}	
	<i>A. niger</i>	<i>C. albicans</i>
ANFTS	21	24
[Co(ANFTS) ₂]Cl ₂	36	44
[Co(ANFTS) ₂]Br ₂	31	37
[Ni(ANFTS) ₂]Cl ₂	38	42
[Ni(ANFTS) ₂]Br ₂	37	48
[Cu(ANFTS) ₂]Cl ₂	46	54
[Cu(ANFTS) ₂]Br ₂	49	57

Conductivity measurements: Molar conductance value of the complexes were measured in the solvent DMF and all the complexes were found to be electrolytic²⁵ in nature of 1:2 type and conductivity values are in the range 108.3-136.3 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$.

Conclusion

Thus, on the basis of above studies it may be concluded that the complexes possess the octahedral geometry around the central metal ion as shown in Fig. 1.



[M(ANFTS)₂]X₂; M = Co(II), Ni(II) and Cu(II); X = Cl⁻, Br⁻, I⁻, NO₃⁻ and ClO₄⁻

Fig. 1

REFERENCES

1. R.J. Sundberg, in eds: A.R. Katritzky and C.W. Rees, *Comprehensive Heterocyclic Chemistry*, Pergamon, Oxford, Vol. 4, p. 329 (1984).
2. J.S. Yadav, B.V.S. Reddy, B. Eeshwaraiah and M.K. Gupta, *Tetrahedron Lett.*, **45**, 5873 (2004).
3. D.L. Boger, C.W. Boyee, M.A. Labriti, C.A. Sehon and Q. Jin, *J. Am. Chem. Soc.*, **121**, 54 (1999).
4. C.E. Hewton, M.C. Kimber and D.K. Taylor, *Tetrahedron Lett.*, **43**, 3199 (2002).
5. S. Onitsuka, H. Nishino and K. Kurusawa, *Tetrahedron Lett.*, **41**, 3149 (2000).
6. B.K. Rai, *J. Indian Coun. Chem.*, **23**, 13 (2006).
7. B.K. Rai and K. Sharma, *Orient. J. Chem.*, **22**, 645 (2006).
8. B.K. Rai, P. Choudhary, U.P. Singh, P. Sahi, Z. Hussain and S. Rana, *Orient. J. Chem.*, **23**, 271, 291 (2007).
9. B.K. Rai, I. Kostava, S.P. Ojha, R. Tomar and V.K. Rastogi, *Asian J. Phys.*, **16**, 29 (2007).
10. B.K. Rai, *Asian J. Phys.*, **16**, 71 (2007).
11. B.K. Rai, H.C. Rai, S.P. Singh, R. Tomar and O. Prakash, *Asian J. Phys.*, **16**, 76 (2007).
12. B.K. Rai and K. Sharma, *Asian J. Chem.*, **20**, 137 (2008).
13. B.K. Rai, R. Rai, P. Sahi and S. Rana, *Asian J. Chem.*, **20**, 143, 149 (2008).
14. Akhilesh Baluni, Ph.D. Thesis, Spectral Studies of Co(II), Ni(II) and Cu(II) Complexes with Nitrogen and Sulphur Containing Ligands, B.R.A. Bihar University, Muzaffarpur, India, p. 64 (2003).
15. A.I. Vogel, *A Textbook of Quantitative Chemical Analysis* Revised by J. Bessett, R.C. Denny, J.H. Jeffery and J. Mendham, ELBS, London, edn. 5 (1996).

16. M.S. Patil and J.R. Shah, *J. Indian Chem. Soc.*, **58**, 944 (1981).
17. R.K. Agarwal and K. Arora, *Polish J. Chem.*, **67**, 219 (1993).
18. R.K. Agarwal, H. Agarwal and I. Chakraborti, *Synth. React. Inorg. Met.-Org. Chem.*, **25**, 679 (1995).
19. M. Goldstein and D. Unsworth, *Inorg. Chim. Acta*, **4**, 370 (1970).
20. D.M. Adams, *Metal Ligand and Related Vibrations*, E. Arnold Publications, London (1967).
21. C.H. Krishna, C.M. Mahapatra and B.K. Dash, *J. Inorg. Nucl. Chem.*, **39**, 1253 (1977).
22. B.N. Figgis, *Introduction to Ligand Fields*, Wiley Eastern Ltd., New Delhi, India, p. 279 (1976).
23. R.L. Carlin and A.J. Van Dyneveledt, *Magnetic Properties of Transition Metal Compounds*, Springer Verlag, New York (1997).
24. A.W. Baur, W.M. Kirby, J.C. Sherris and M. Turk, *Am. J. Clin. Pathol.*, **45**, 493 (1966).
25. C. Singh, H.K. Parwana, G. Singh and R.S. Jolly, *Asian J. Chem.*, **12**, 1 (2000).

(Received: 25 June 2008;

Accepted: 17 February 2009)

AJC-7244

**11TH INTERNATIONAL CONFERENCE ON THE CHEMISTRY OF
SELENIUM AND TELLURIUM, ICCST-11**

1 — 6 AUGUST 2010

OULU, FINLAND

Contact:

Prof. Risto Laitinen,
Department of Chemistry, P.O. Box 3000,
University of Oulu, Oulu 90014, Finland.
Tel:+358-8-5531611, Fax:+358-8-5531603,
e-mailristo.laitinen@oulu.fi