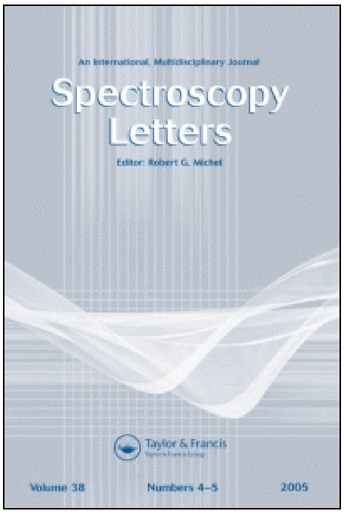

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

NMR and Other Spectroscopic Studies of Isonicotinoyl Based Hydrazones and Their Ternary Complexes

Vanita Purl[a]; B. V. Agarwala[a]
[a] Department of Postgraduate Studies and Research in Chemistry, Rani Durgavati University, Jabalpur, India

To cite this Article Purl, Vanita and Agarwala, B. V.(1994) 'NMR and Other Spectroscopic Studies of Isonicotinoyl Based Hydrazones and Their Ternary Complexes', Spectroscopy Letters, 27: 9, 1097 — 1113
To link to this Article: DOI: 10.1080/00387019408006968
URL: http://dx.doi.org/10.1080/00387019408006968

SPECTROSCOPY LETTERS, 27(9), 1097-1113 (1994)

NMR AND OTHER SPECTROSCOPIC STUDIES OF ISONICOTINOYL BASED HYDRAZONES AND THEIR TERNARY COMPLEXES

Vanita Puri and B.V. Agarwala*
Department of Postgraduate Studies and Research in Chemistry,
Rani Durgavati University, Jabalpur - 482 001 (India)

ABSTRACT

The three isonicotinoyl hydrazone Schiff bases viz. anisaldehyde isonicotinoyl hydrazone(AINH), 2-furaldehyde isonicotinoyl hydrazone(FINH), 2-thiophenealdehyde isonicotinoyl hydrazone(TINH) have been synthesized and characterized on the basis of their elemental analysis, magnetic susceptibility, IR, electronic and nmr spectral studies. The ternary complexes of Ni(II) and Cu(II) with these hydrazones and neutral bidentate base phen and bipy are octahedral and the presence of acetate and/or water molecule is revealed by the study of their IR spectra, force constants and thermal degradation pattern. Suitable structures have been assigned to these ternary complexes.

INTRODUCTION

Ternary complex formation has received wide spread interest in the past few years because of involvement of mixed chelation in many biological processes[1]. The Cu(II) amino acid complexes in normal human serum is in the form of mixed-ligand complex containing L-histidine, L-threonine and Cu(II) in the ratio 1:1:1. During recent years interest in the diimine, bipyridine and phenanthroline compounds has been renewed on account of their redox and photo redox properties. In case of Cu(II) compounds of these ligands, several of them have shown antimicrobial effects[2]. Complexes of this class of of ligands have been reviewed by Mc-whennie and Miller and Lindoy and livingstone[3]. The occurance in these systems of the α-di-imine group $-N = C - C = N-$, permits electron delocalization in the chelate ring and as a result bipy, phen and their derivatives are considerably better acceptor than are simple pyridines. Substitution reaction of η^5 cyclopentadienyl ruthenium(II) complexes with heterocycles pyridine, α-picoline, bipy or phen are reported to form mixed-ligand complexes[4]. The reaction products have distorted octahedral structures as revealed by ^{1}H-nmr, uv-vis and IR spectroscopic studies. Keeping in view of their interesting structural feature and biological activity, ternary complexes of Ni(II) and Cu(II) with anisaldehyde isonicotinoyl hydrazone(AINH), 2-furaldehyde isonicotinoyl hydrazone(FINH), 2-thiophenealdehyde isonicotinoyl hydrazone (TINH) which fuction as a primary Schiff base ligand. All the complexes are analysed microanalytically and spectroscopic and magnetic data are incorporated to elucidate their structural characteristic.

EXPERIMENTAL DETAILS

Starting materials

2-Furaldehyde, 2-thiophenealdehyde, anisaldehyde, isonicotinic hydrazide (all Sisco), $Ni(CH_3COO)_2 \cdot 4H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$, dimethyl formamide, 2 2'-bipyridine and 1,10-phenanthroline (all E. Merck) were used.

Preparation of the complexes

The Schiff base ligands anisaldehyde isonicotinoyl hydrazone, 2-furaldehyde isonicotinoyl hydrazone and 2-thiophenealdehyde isonicotinoyl hydrazone were prepared[5,6] and characterised using TLC, IR, UV and NMR techniques. A 0.005M solution of the Schiff base ligand (1.28g of AINH/1.075g of FINH/1.16g of TINH) was prepared in minimum quantity of DMF and refluxed while stirring with 50 cm^3 0.005M ethanolic solution of the base (0.78g bipy/0.99g phen) on a magnetic stirrer (equipped with heater) for 2h. Subsequently 0.005M aqueous solution of metal salt (1.0g of $Cu(CH_3COO)_2.H_2O$; 1.24g of $Ni(CH_3COO)_2.4H_2O$) was added dropwise with stirring and the mixture refluxed for 4h on heating mantle. Bright coloured ternary complexes separated out which were filtered, washed with ethanol and ether and dried in vacuum over $CaCl_2$.

Physical measurements

The percentage of C,H,N were determined by microanalytical procedures on a Hitachi 2000 microanalyser. The infrared spectra of ligands were recorded on a Hitachi 270 Spectrophotometer in the range 4000–250 cm^{-1} using CsI pellets. ^1H NMR spectra of the ligands were recorded on a AMX-400 FTNMR spectrometer using d_6-DMSO as a solvent. The diffuse reflactance spectra of the complex in solid state were recorded employing Varian-Cray 2390 spectrophotometer in the range 200–1000 nm. The magnetic susceptibility measurements were carried out by using Faraday's method where, = –1.087 mg and H.dH/dZ = 7953.489. Metals were estimated in our laboratory gravimetrically. Thermogravimetric data were obtained using a V2.2A DuPont 9900 instrument and the weight loss was recorded in a nitrogen atmosphere at a heating rate of 10–15°C min^{-1}.

RESULTS AND DISCUSSION

^{1}H NMR spectral studies

The NMR spectra of the ligands dissolved in d_6-DMSO were recorded (shown in Fig.I) and TMS was used as an internal standard. Chemical shifts due to various protons have been assigned. Azomethinic proton H-C=N resonates at 8.4-8.7 ppm[7]. It confirms the condensation of aldehyde with hydrazide to form hydrazone Schiff base. Protons of pyridine ring of isonicotinoyl hydrazones resonates in the range 7.7-8.8 ppm respectively. In FINH signals due the furan ring protons appear at 7.0, 7.9, 6.7 ppm, respectively. Thiophene ring protons are shown at 7.5 and 7.2 ppm respectively.

Composition

The composition of the complexes are in agreement with the general formula [Cu(L)(B)(OAc)(H_2O)] where L = LaH = AINH, L_bH = FINH and L_cH = TINH in case of Ni(II) complexes one or two molecules of lattice water is also present as evidenced by IR spectral and thermogravimetric data thus pertaining to general formula [Ni(L)(B)(OAc)(H_2O)].nH_2O. The physical and analytical data colour, melting point and solubilities are given in Table I.

Infrared spectral analysis

By comparing the IR spectra of the free ligands with those of ternary complexes the following observations and inferences are made.

(i) The strong band due to ν (C=O) in AINH, FINH and TINH ternary complexes is absent which is present in each of the free ligand at 1647, 1629, 1675 cm-1 respectively.

Instead a new band appears due to ν(C-O) in all the metal complexes at 1170-1120[8] cm^{-1}.This confirms the complexation of the

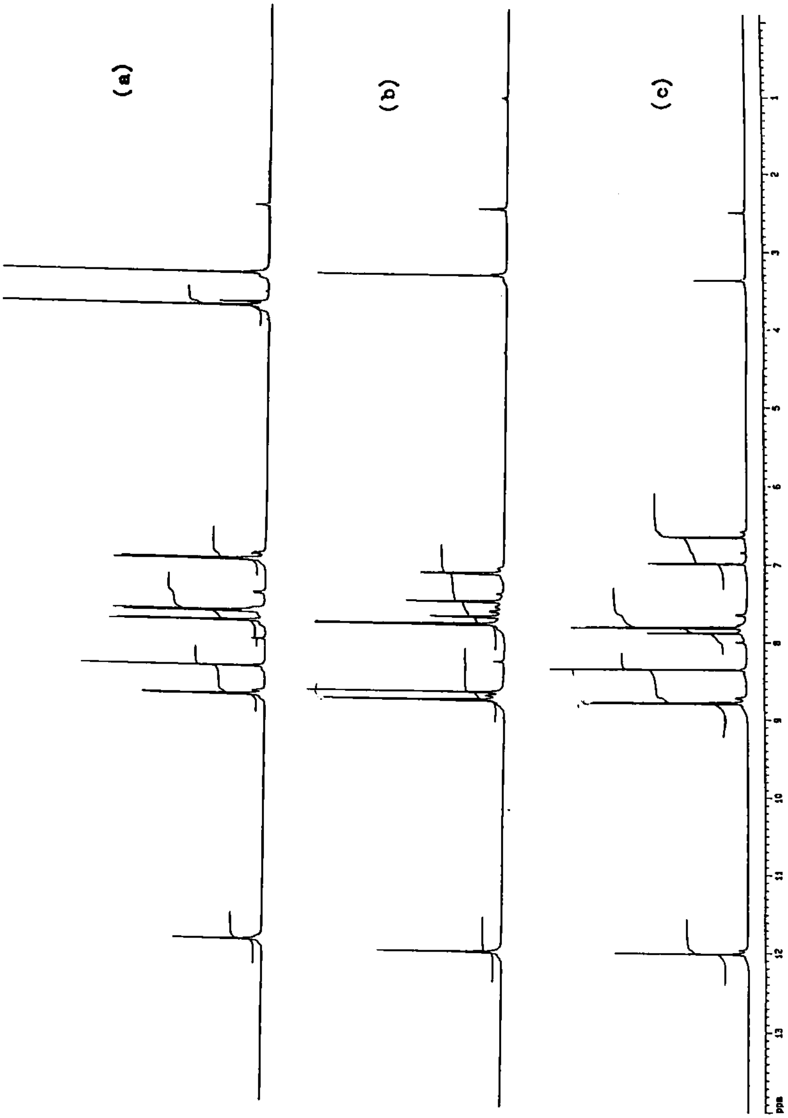

Fig.I : ^{1}H NMR spectra of (a) AINH (b) TINH (c) FINH.

Table-I : Physical characteristics and analytical data of mixed-ligand complexes with bipy and phen.

Compound	Colour	M.P. °C	Solubility	Carbon Found (Calcd)	Elemental hydrogen Found (Calcd)	Analysis nitrogen Found (Calcd)	(%) Metal Found (Calcd)
$[NiL_a(bipy)(OAc)(H_2O)].H_2O$ Ia	Yellowish Green	>360	DMF,DMSO	49.32 (51.10)	3.92 (4.43)	13.35 (12.41)	9.47 (10.37)
$[CuL_a(bipy)(OAc)(H_2O)]$ IIa	Brown	>360	Insoluble	49.70 (52.33)	3.80 (4.17)	11.30 (12.55)	10.63 (11.51)
$[NiL_a(phen)(H_2O)].H_2O$ IIIa	Yellowish Green	288	DMF,DMSO	52.40 (55.48)	3.94 (4.78)	12.60 (11.55)	9.32 (10.00)
$[CuL_a(phen)(OAc)(H_2O)]$ IVa	Brown	296	Insoluble	56.17 (56.72)	4.12 (4.55)	13.90 (11.80)	10.33 (11.03)
$[NiL_b(bipy)(OAc)(H_2O)].2H_2O$ Ib	Yellowish	>360	DMF,DMSO	42.95 (46.55)	3.32 (4.24)	13.18 (12.92)	10.03 (10.81)
$[CuL_b(phen)(OAc)(H_2O)]$ IVb	Brown	>360	Insoluble	52.40 (54.31)	3.38 (4.52)	13.50 (12.66)	12.01 (12.43)
$[NiL_c(bipy)(OAc)(H_2O)].H_2O$ Ic	Yellowish Green	>360	DMF,DMSO	43.55 (46.71)	3.46 (3.88)	12.34 (12.96)	10.32 (10.83)
$[CuL_c(bipy)(OAc)(H_2O)]$ IIc	Dark Green	>360	Insoluble	48.6 (47.87)	3.84 (3.60)	14.80 (13.28)	11.54 (12.05)

L_aH = AINH; L_bH = FINH; L_cH = TINH.

ligand via enolic form with metal ion in case of all the ternary complexes with AINH, FINH and TINH. It is further supported by appearance of new band ν(M-O) in the region 530-500 cm^{-1} in all the complexes[9].

(ii) The negative shift in ν(C=N) as compared to the ligand in the complexes indicate coordination through azomethinic nitrogen. This is shifted to 1570-1560 cm^{-1} from 1596 cm^{-1} in the complexes with AINH and to 1565-1560 cm^{-1} from 1619 and 1609 cm^{-1} in the complexes with FINH and TINH. This is further evidenced by the presence of new bands in the spectra of complexes at 1510-1500 cm^{-1} due to azomethinic moiety i.e. $>C=N-N=C<$[10].

(iii) The positive shift in the ν(N-N) from 1017-1026 cm^{-1} to 1055-1050 cm^{-1} in the complexes further supports the presence of the coordination through azomethinic nitrogen. It is further confirmed by appearance of ν(M-N)[11,12] in the region 410-320 cm^{-1}.

(iv) The appearance of new bands at 1590 cm^{-1} and 1370-1360 cm^{-1} due to ν_{as} and ν_s (COO) of acetate aion[13] $\Delta\nu$ = 220 cm^{-1}. The separation frequency of two bands is greater than that of free ion i.e. 144, which is for undidentate **coordinated acetate ion. This is in agreement with studies carried out by other investigators[14].**

(v) The bands observed in all the complexes at 3400-3200 cm^{-1}, 1660-1650 cm^{-1}, 860-820 cm^{-1}, 650-570 cm^{-1} attributable to antisymmetric and symmetric OH strectching, bending, rocking and wagging vibrations respectively[14]. This confirms the presence of the coordinated water molecules in all the complexes.

(vi) The band due to ν(C-O-CH$_3$) in the AINH complexes remain unaltered indicating its non-participation in complex formation. The methoxy group is not present in the other two hydrazone Schiff bases (FINH, TINH). The ν(C–S–C) of the thiophene ring[15] appear at 1310 cm^{-1} in the complexes of TINH and bipy/phen. It remains at the same position as in the parent ligand indicating its nonparticipation in the coordination. Similarly ν(C–O–C) at 1010 cm^{-1} of the furan ring remains unaltered on complexation indicating its non involvement in coordination[16].

(vii) The characteristic band confirming the coordination of bipy or phen molecule is observed in the spectra of all mixed-ligand complexes. The bands appearing at 580–560 cm^{-1}, 760–700 cm^{-1}, 1010–1090 cm^{-1}, 1470–1400 cm^{-1} confirm the coordination of bipy molecule[17]. The bands due to coordinated phen molecule[18] appear at 580–530 cm^{-1}, 750–690cm^{-1}, 910–860 cm^{-1}, 1470–1410 cm^{-1}. However new bands in the region 260–210 cm^{-1} due to ν(M–N) of phen and bipy further confirm its bidentate coordination to metal ion[14]. This is in addition to above bands confirming the presence of diimine in ternary complexes.

The foregoing facts suggest the bonding sites of the ligands are azomethine nitrogen, enolic oxygen and two ring nitrogen atoms of the heterocyclic base. Force constants of various bonds (Table II) further confirm the coordination. In addition to these acetate ion and water molecule is also coordinated to attain octahedral geometry.

Magnetic data and diffuse reflectance spectral analysis

The experimental magnetic moment values (Table III) for mixed-ligand Ni(II) complexes formed with bipy, and AINH is 3.62 B.M. The corresponding values are 3.51 B.M. and 3.44 B.M. for FINH and TINH ternary complexes. In almost all its six coordinate complexes, nickel(II) has a pseudoctahedral stereochemistry with

Table-II : Force constants of various bonds

Complex	Bond	Wave number (cm^{-1})	Force Constant K(Nm^{-1})
Ni-AINH & bipy	Ni - O	520	200.42
	Ni - N	400	106.60
	Ni - N(bipy)	260	45.06
Cu-AINH & bipy	Cu - O	510	195.95
	Cu - N	385	100.29
	Cu - N(bipy)	220	32.74
Ni-AINH & phen	Ni - O	510	264.30
	Ni - N	400	106.60
	Ni - N(phen)	210	29.40
Cu-FINH & phen	Cu - O	530	211.60
	Cu - N	390	102.90
	Cu - N(phen)	240	38.97
Ni-TINH & bipy	Ni - O	540	296.39
	Ni - N	320	68.27
	Ni - N(bipy)	230	35.26

a spin triplet as ground state since the ground state in O_h symmetry is A_{2g} and the next excited state $^3T_{2g}$ is generally well separated in energy. In ternary Ni(II) complexes formed with AINH and phen/bipy exhibit three bands at 10,240 cm^{-1}, 16,667 cm^{-1} and 24, 390 cm^{-1} and assigned to be ν_1, ν_2 and ν_3, respectively. The bands are observed at same positions for Ni(II) complex with FINH and bipy. Although similar spectra are obtained in case of Ni(II) complexes formed with TINH, bipy/phen, but two bands are observed at 10, 204 cm^{-1}, 24, 390 cm^{-1} assigned to be ν_1 and ν_3 respectively. The band due to ν_2 is not observed in their spectra.

The spectral data together with magnetic data reveal an octahedral geometry for Ni(II) complexes[19]. The value of Racah parameter B(796 cm^{-1}) is less than free ion value (1030 cm^{-1})

Table–III : Magnetic susceptibility Measurement data of mixed-ligand complexes with bipy/phen.

Complex	m(mg)	F'(mg)	$\chi_g \times 10^{-6}$	$\chi_M' \times 10^{-3}$	T(°K)	μ(BM)
Ni(II)-TINH-bipy	1.194	0.080	8.463	4.885	300.3	3.44
Ni(II)-FINH-bipy	1.492	0.104	8.731	5.086	300.3	3.51
Ni(II)-AINH-bipy	1.341	0.100	9.456	5.410	300.3	3.62
Cu(II)-FINH-phen	1.027	0.026	3.231	1.855	300.3	2.12
Cu(II)-AINH-phen	1.941	0.048	3.109	1.793	300.3	2.08

and nephlauxetic ratio β(0.77) and β^{o}(29%). The value of B is less than that for free ion suggesting a considerable orbital overlap and delocalisation of electron in the metal ligand bond ν_2/ν_1 value of 1.63 is close to those (1.64-1.8) expected[20] for octahedral geometry. Similar conclusion is drawn for octahedral ternary complexes of Ni(II) with N-pyridyl anthranilic acid and 2-picolinic acid and 2-furoic acid[21].

Cu(II) complexes

Copper(II) ternary complexes formed with FINH/AINH and phen exhibit magnetic moment 2.12 and 2.08 B.M. respectively. The theoretical spin-only magnetic moment value ($\mu_{S.O}$) of the individual separated copper(II) ion is 1.73 B.M. This higher value is obtained because of mixing of some orbital angular momentum from the excited states in an octahedral field.

The bivalent oopper has ^2D ground state which splits into two terms under the influence of an octahedral field[22]. In an octahedral Cu(II) complex, only one band is expected due to $^2T_{2g} \leftarrow {}^2E_g$ transition[23]. Undistorted octahedral Cu(II) complexes are rather uncommon due to John Teller distortion, giving rise to one band or a broad envelope of bands[24]. The copper(II) complex with TINH and bipy exhibits a high intensity band at (23255 cm^{-1}). Its complex with bipy and AINH exhibit band at (23255 cm^{-1}). This may be assigned to charge transfer or intra ligand transition.

The band $^2T_{2g} \leftarrow {}^2E_g$ appears as a shoulder in all the complexes in the region 18518-15151 cm^{-1}. This is the same as it has been reported for other distorted octahedral Cu(II) complexes[11].

Thermogravimetric analysis

The presence of one molecule of coordinated water has been confirmed in case of ternary complexes of Ni(II), Cu(II) with

TABLE IV THERMAL DATA OF TERNARY COMPLEXES OF AINH COMPLEXES

DECOMPOSITION REACTION	TEMP. RANGE (°C)	EXP. % WEIGHT LOSS	CALCD. % WEIGHT LOSS
$[NiL_2(OAc)(bipy)(H_2O)].H_2O$ ---> $[NiL_2(OAc)(bipy)(H_2O)]$	40-75	3.15	3.19
$[NiL_2(OAc)(bipy)(H_2O)]$ ---> $[NiL_2(OAc)(bipy)]$	75-210	3.15	3.19
$[NiL_2(OAc)(bipy)]$ ---> $[NiL_2(bipy)]$	210-300	10.50	10.42
$[NiL_2(bipy)]$ ---> $[NiL_2]$	300-360	22.90	27.69
$[NiL_2(OAc)(phen)(H_2O)].H_2O$ ---> $[NiL_2(OAc)(phen)(H_2O)]$	40-80	3.00	2.97
$[NiL_2(OAc)(phen)(H_2O)]$ ---> $[NiL_2(OAc)(phen)]$	80-220	2.95	2.97
$[NiL_2(OAc)(phen)]$ ---> $[NiL_2(phen)]$	220-360	9.75	9.74
$[NiL_2(phen)]$ ---> $[NiL_2]$	360-400	33.00	33.71
$[CuL_2(OAc)(bipy)(H_2O)]$ ---> $[CuL_2(OAc)(bipy)]$	40-170	3.15	3.26
$[CuL_2(OAc)(bipy)]$ ---> $[CuL_2(bipy)]$	170-290	10.72	10.71
$[CuL_2(bipy)]$ ---> $[CuL_2]$	290-340	28.60	28.35
$[CuL_2(OAc)(phen)(H_2O)]$ ---> $[CuL_2(OAc)(phen)]$	50-270	2.70	3.03
$[CuL_2(OAc)(phen)]$ ---> $[CuL_2]$	270-310	42.30	9.95

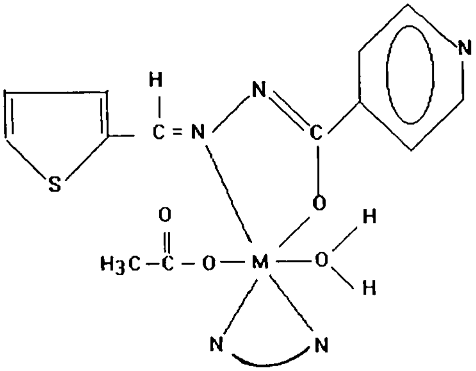

FIG. II STRUCTURE OF COMPLEX
$[M(L_c)(OAc)(B)(H_2O)].nH_2O$
M = Ni(II), Cu(II)
L_cH = TINH
n = 0,1
N–N = bipy/phen

AINH, FINH, TINH and bipy. One additional molecule of lattice water is present in the ternary complexes of Nickel(IIIa). In its complex with FINH and bipy two molecules of lattice water are present. In the copper complexes (IIa, IIc, IVa, IVb) no lattice water is present as no water molecule is lost upto 120°C. The acetate ion is coordinated in all these ternary complexes and is indicated by the weight loss.

Similar degradation pattern (Table IV) is observed in case of all these complexes. First the complexes loose lattice water upto 120°C, then coordinated water is lost depending upon the stability of the complex, it is followed by the loss of acetate molecule upto 360°C and bipy and phenanthroline at still higher temperatures. Probably the residue can be impure metal oxide. The degradation pattern along with temperature of each complex is given in table (IV). The values of weight loss calculated for H_2O, acetate and bipy are very close to values of weight loss obtained experimentally.

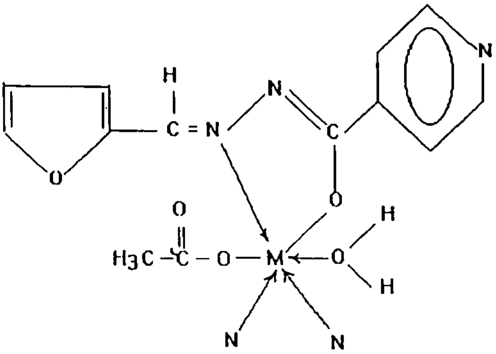

FIG. III STRUCTURE OF COMPLEX
$[M(L_b)(OAc)(B)(H_2O)].nH_2O$
M = Ni(II),Cu(II)
L_bH = FINH
n = 0,2
N–N- bipy/phen

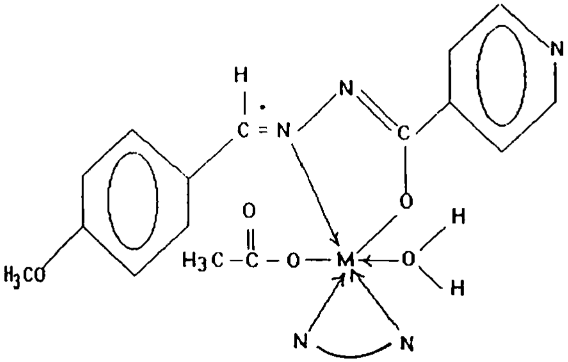

FIG. IV STRUCTURE OF COMPLEX
$[M(L_a)(OAc)(B)(H_2O)].nH_2O$
M = Ni(II),Cu(II)
L_aH = AINH
n = 0,1
N–N= biby/phen

Critical study of all the physicochemical data along with their degradation pattern and colour of the ternary complexes give enough evidence of their structure shown in Fig.(II-IV). The ternary complexes of Cu(II) and Ni(II) formed with AINH, FINH, TINH and a heterocyclic base (bipy/phen) are six coordinate. The bonding site of the hydrazone Schiff base ligands are azomethine nitrogen and enolic oxygen indicating to be monobasic and bidentate chelating species. The two nitrogen atoms of the bidentate heterocyclic base bipy/phen take part in coordination for which extra evidences are already elaborated. Additional coordination sites are occupied by OAc/H_2O lattice or coordinated in the case of Cu(II) and Ni(II) complexes.

ACKNOWLEDGEMENT

The authors thank Prof. C.L. Khetrapal, Bangalore for providing NMR facilities and to the University Grants Commission, New Delhi **for the financial assistance.**

REFERENCES

1. Sigel, H. "Metal Ions in Biological System" Marcel Dekker, N.Y.) 1982, 12.

2. Mcwhinnie, W.R. and Miller, J.D., Adv. Inorg. Chem. Radiochem., 1969, 12, 135.

3. Lindoy, L.F. and Livingstone, S.E., Coord. Chem. Rev., 1967, 2, 173.

4. Rao, K.M., Mishra, L. and Agarwala, U.C., Polyhedron, 1987, 6, 1383.

5. Reddy, P.S.N., Agarwala, B.V., Acta Chim. Acad. Sci. Hung. **1990, 127, 269.**

6. Chatterjee, P., Srivastava, O.P., 4th Int. Conf. on Bioinorg. Cambridge, MA (USA), 1989.

7. Agarwala, B.V. and Hingorani, S., Inorg.Chim. Acta, 1990, 176, 149.

8. Ibrahim, K.M., Rakha, T.H., Abaallan, A.M. and Hassanian, M.M., Indian J. Chem., 1993, 32A, 361.

9. Speca, A.N., Karayanis, N.M. and Pytlewski, L.L., Inorg. Chim. Acta, 1974, 8, 87.

10. Biradar, N.S., Kulkarni, V.H., J. Inorg. Nucl. Chem., 1971, 133, 2451.

11. Beecraft, B.,Campbel, M.J.M. and Grzeskow iak, R., J. Inorg. Nucl. Chem., 1974, 36, 55.

12. Agarwala, B.V., Hingorani, S., Puri, Vanita, Khetrapal, C.L., Naganagowda, G.A., Transt. Met. Chem., 1994, 19, 25.

13. Schafer, L., Burnvoll, J. and Cyvin, S.J., J. Mol. Struct., 1972, 11, 459.

14. Nakamoto, K.,"Infrared spectra of Inorganic and Coordination Compounds"(Wiley Interscience, New York) 1978).

15. Mukhedkar, V.A., Bhagwat, U.A. and Mukhedkar, A.J., J. Chem. Soc. Dalton Trans., 1982, 1899.

16. Shrivastava, V.S. and Saxena, G.C., J. Indian Chem. Soc., 1976, 63, 578.

17. Inskeep, R.G., J. Inorg. Nucl. Chem., 1962, 24, 763.

18. Paryzek, W.R. and Jankowska, F., Inorg. Chim. Acta, 1987, 1, 34.

19. Lever, A.B.P.,"Inorganic Electronic Spectroscopy,"(Elsevier, New York), 1968.

20. Cotton, F.A. and Wilkinson, G., Advanced Inorganic Chemistry (Wiley-Interscience), 5th Ed. 1988.

21. Nagar, R. and Sharma, R,C., J. Indian Chem. Soc., 1989, 66, 335.

22. Larkuorthy, L.F. and Patel, K.G., J. Inorg. Chem., 1970, 2, 1263.

23. Owen, J.,Proc. Roy. Soc., 1955, 183, 227.

24. Gerloch, M., Inorg. Chem., 1981, 20, 638.

Date Received: June 16, 1994
Date Accepted: July 21, 1994