Asian Journal of Chemistry; Vol. 26, No. 10 (2014), 3089-3094

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16823

Spectral Characterization and Biological Studies on Mixed Ligand Complexes of Cr(III), Ni(II) and Cu(II) Derived from 3-Aminopyridine and Nitrite Ion

K. DHAVEETHU[1], T. RAMACHANDRAMOORTHY[1] and K. THIRUNAVUKKARASU[2,*]

[1]PG and Research Department of Chemistry, Bishop Heber College (Autonomous), Tiruchirappalli-620 017, India
[2]National Centre for Catalysis Research, Indian Institute of Technology Madras, Chennai-600 036, India

*Corresponding author: Tel/Fax: +91 44 22574241: E-mail: kthirunavukkarasu@gmail.com

Received: 5 December 2013; *Accepted*: 3 February 2014; *Published online*: 10 May 2014; AJC-15187

Mixed ligand metal complexes of Cr(III), Ni(II) and Cu(II) complexes with 3-aminopyridine and nitrite ions have been synthesized by microwave irradiation technique. The metal complexes were characterized by elemental analyses, molar conductance, IR, Far-IR, electronic and EPR studies. The spectroscopic studies reveal the composition, different modes of bonding and electronic transition and probable geometry of the complexes. On the basis of characterization data, distorted octahedral geometry predicted for Cr(III) and Cu(II) complexes; distorted tetrahedral geometry predicted for Ni(II) complex. The organic ligand (3-aminopyridine) and the metal complexes were screened against pathogenic bacteria and fungi *in vitro*.

Keywords: 3-Aminopyridine, Nitro complex, Mixed ligand complexes, Biological activities, EPR.

INTRODUCTION

The biological activity of the aminopyridines and their transition metal complexes act as K^+ and Ca^{2+} channel inhibitors has been discussed in the literature[1,2]. 3-aminopyridine (3AP) possesses significant antiproliferative, antiinflammatory and antibacterial activities[3] and furthermore, an antitumor activity of its derivatives has also proposed[4]. Metal aminopyridine complexes are generally used as asymmetric catalysts for various reactions such as hydrogenation, cyclopropanation, epoxidation *etc*[5]. The versatile coordination modes of the ambidentate ligand nitrite ion (NO_2^-) were previously reported[6]. Metal nitrito complexes (M-ONO) are in general used as photochemical NO precursors[7].

The transition metal complexes have many applications in pharmaceutical industries, biology and medicine. They posses electrical, thermo chromic, catalytic, antibacterial and antifungal properties[8], Metal complexes of chromium, nickel and copper have a wide range of applications such as dyes and pigments[9]. Many drugs possess modified toxicological and pharmacological properties in the form of metal complexes and the most widely studied in this respect is the Cu(II) ion which has proved beneficial in many diseases such as tuberculosis, gastric ulcers, rheumatoid arthritis and cancers[10]. Copper complexes are currently being investigated for their potential anticancer activity. Moreover, coordination with copper often enhances the activity of various types of drugs such as antitumor and antiinflammatory agents[11]. Aminopyridines and their derivatives in most cases act as monodentate ligand which coordinates the metal ion through the nitrogen of the pyridine ring[12]. Numerous octahedral coordination compounds of Cr(III) are found in the literature as they are very stable. In fact they have played a prominent role in the development of coordination chemistry[13]. EPR of Cu(II) has been investigated in a wide symmetry environments, *viz*., octahedral[14], tetrahedral[15], square planar[16], square pyramidal[17], trigonal bipyramidal[18] *etc*.. The reason for this is ascribed to the Jahn-Teller effect arising from the unequal occupation of the eg pair of orbitals when d^9 ion is subjected to an octahedral crystal field. The EPR study gives very important information about the site symmetry of the transition metal ions[19].

With the view of these, the present work aims at the synthesis, spectral characterization and biological studies of Cr(III), Ni(II) and Cu(II) complexes derived from 3-aminopyridine and nitrite ion ligands as part of our continuing research on the study of aminopyridine-based metal complexes[20]. The organic ligand (3-aminopyridine) and their metal complexes were screened against pathogenic bacteria and fungi *in vitro*.

EXPERIMENTAL

All the chemicals used were of AR grade from Sigma-Aldrich Company and were used as received. Ethanol was distilled over calcium oxide before use. Microwave irradiations were used for the complex preparation from domestic microwave oven (model IFB-25 PG 1S) at 900W power for 10 s.

Synthesis of chromium(III) complex (1): An ethanolic solution (20 mL) of 3-aminopyridine (0.56 g, 6 mmol) was mixed with an ethanolic solution (20 mL) of $CrCl_3 \cdot 3H_2O$ (0.42 g, 2 mmol) were irradiated in a microwave oven for about 10 seconds. The resulting green solution was then added with ethanolic solution (20 mL) of sodium nitrite (0.40 g, 6 mmol) and irradiated for about 10 s.The resulting mixture was kept unaltered, the pale green coloured complex was separated out after a few hours. It was filtered, washed with cold ethanol and dried in a vacuum desiccator over anhydrous calcium chloride.

Synthesis of nickel(II) complex (2): An ethanolic solution (20 mL) of 3-aminopyridine (0.37 g, 4 mmol) was mixed with an ethanolic solution (20 mL) of $Ni(NO_3)_2 \cdot 6H_2O$ (0.36 g, 2 mmol) were irradiated in a microwave oven for about 10 seconds. The resulting pale blue solution was then added with ethanolic solution (20 mL) of sodium nitrite (0.26 g, 4 mmol) and irradiated for about 10 s. The resulting mixture was kept unaltered, the bluish-green coloured complex was separated out after a few hours. It was filtered, washed with cold ethanol and dried in a vacuum desiccator over anhydrous calcium chloride.

Synthesis of copper(II) complex (3): An ethanolic solution (20 mL) of 3-aminopyridine (0.38 g, 4 mmol) was mixed with an ethanolic solution (20 mL) of $Cu(NO_3)_2 \cdot 3H_2O$ (0.48 g, 2 mmol) were irradiated in a microwave oven for about 10 s. The resulting blue coloured solution was then treated with ethanolic solution (20 mL) of sodium nitrite (0.28 g, 4 mmol) and irradiated for about 10 seconds. The resulting mixture was kept unaltered, the blue-violet coloured complex was separated out after a few hours. It was washed filtered, with cold ethanol and dried in a vacuum desiccator over anhydrous calcium chloride.

The formation of complexes of $CrCl_3 \cdot 3H_2O/Ni(NO_3)_2 \cdot 6H_2O/Cu(NO_3)_2 \cdot 3H_2O$ with 3-aminopyridine (AP) and nitrite ion in ethanol is presented in the following reactions.

$$CrCl_3 \cdot 3H_2O + 3(3AP) + 3NaNO_2 \longrightarrow [Cr(3AP)_3(ONO)_3](\mathbf{1}) + 3NaCl + 2H_2O \quad (1)$$

$$Ni(NO_2)_2 \cdot 6H_2O + 2(3AP) + 2NaNO_2 \longrightarrow [Ni(3AP)_2(ONO)_2](\mathbf{2}) + 2NaNO_3 + 6H_2O \quad (2)$$

$$Cu(NO_3)_2 \cdot 3H_2O + 2(3AP) + 2NaNO_2 \longrightarrow [Cu(3AP)_2(ONO)_2](\mathbf{3}) + 2NaNO_3 + 3H_2O \quad (3)$$

Physical measurements: Elemental analyses (carbon, hydrogen and nitrogen) were analyzed using Elementar Vario EL III (Germany) model analyzer. The metal content was estimated by volumetric and Atomic Absorption Spectrometry. Molar conductance were measured in DMF on the Equiptronics, digital conductivity meter, (Model EQ-660), where the cell constant was calibrated with 0.1 M KCl solution and DMF was used as the solvent. The IR Spectra (4000-400 cm^{-1}) were taken at 27 ºC using Perkin Elmer spectrometer, model Spectrum X1 in KBr disc and Far-IR spectra were taken at 27 °C using FT-IR Thermo Nicolet (model 6700) spectrometer in which polyethylene was used as calibrant. The electronic spectra were recorded by the diffused reflectance technique on Varian Cary (model 5000) spectrophotometer. The EPR spectra of the solution samples were obtained at room temperature and at liquid nitrogen temperature using BRUKER EMX plus spectrometer on the X-band in the range of 3480 MHz.

Microbial studies: Cultures of phytopathogenic (Gram-negative) bacteria such as *Raoultella planticola* (MTCC, 2272), *Shigella flexineri* (MTCC,1457) and *Pseudomonas aeruginosa* (MTCC, 1688) and fungi such as *Aspergillus niger* (MTCC, 961) and *Candida albicans* (MTCC,183) were procured from Microbial type culture collection and gene bank, Chandigarh, India and maintained on slants of Potato Dextrose Agar (PDA) and Nutrient Agar (NA) media.

Antibacterial studies: The antibacterial and antifungal activities of the ligands (3-aminopyridine and nitrite ions) and their Cr(III), Ni(II) and Cu(II) complexes have been studied by well diffusion technique[21] and Agar plate technique[22], respectively. The antibacterial activities of the ligand (3-aminopyridine) and its metal complexes against test bacteria *R. planticola*, *S. flexineri* and *P. aeruginosa* at different concentrations were checked by well diffusion technique. Twenty milliliters of sterilized nutrient agar (NA) media was poured in each pettri-dish. After solidification 0.1 mL of test bacteria spreads over the medium using a spreader. The test compounds in measured quantities were dissolved in DMF to get concentrations of 100, 75, 50 and 25 $\mu g\ mL^{-1}$. Using sterile cork borer (6 mm in diameter), four holes were made in each dish, then tested compounds dissolved in DMF were poured into these holes. Finally, the dishes were incubated at 37 °C for 24 h where clear or inhibition zones detected around each hole. DMF was used as a control and streptomycin used as a standard drug under the same conditions for each organism and by subtracting the diameter of inhibition zone resulting with DMF from that obtained in each case, the antibacterial activities can be calculated as a mean of three replicates.

Antifungal studies: *A. niger* and *C. albicans* fungi were used as the test organism for which the growth inhibition capacity of the ligand (3-aminopyridine) and its complexes have been screened. According to the agar plate technique, the compounds were directly mixed to the DMF in different (400, 200, 100 $\mu g\ mL^{-1}$) concentrations. The discs measuring 5 mm in diameter were prepared from Whatman No. 1 filter paper sterilized by dry heat at 140 °C for 1 h. The sterilized discs were soaked with the fungus and were placed on the medium with the help of the inoculum needle. The discs were inverted and kept in an incubator at 27 °C for 72 h. The inhibation zones thus formed was measured (in mm) after 72 h. Chlorothalonil used as commercial fungicide and DMF served as control.

RESULTS AND DISCUSSION

All the metal complexes are stable under room temperature. The complexes are soluble in DMF and DMSO. On the basis of elemental analyses, the complexes were found to have the composition as shown in Table-1. The molar conductivity values for the mixed ligand complexes in DMF solvent (1×10^{-3} M) were in the range (19.7-22.4) $\Omega^{-1}\ cm^2\ mol^{-1}$ which assigned to be non-electrolytic nature.

Infrared spectra: The IR spectral frequency of the ligands (3AP and NO_2^-) and their metal complexes are given in Fig. 1. The IR spectral evidence concerning the aromatic character of the 3-aminopyridine summarized[23]. The most typical IR frequency bands of 3-aminopyridine in this study correspond to skeleton vibrations at 1586, 1486, 1439 cm^{-1} and out of plane

TABLE-1
ELEMENTAL ANALYSES AND MOLAR CONDUCTANCE OF 3-AMINOPYRIDINE AND THE COMPLEXES **1-3**

Compound	Colour	Yield (%)	Elemental analysis (%): Found (calcd.)				Λ_m (Ω^{-1} cm^2 mol^{-1})
			M	C	H	N	
$C_5H_6N_2$ (3AP)	Pale brown	–	–	63.45 (63.83)	6.32 (6.83)	29.76 (29.78)	–
$CrC_{15}H_{18}N_9O_6$ (**1**)	Pale green	76	11.69 (11.82)	39.94 (40.86)	3.45 (3.41)	28.56 (28.64)	21.3
$NiC_{10}H_{12}N_6O_4$ (**2**)	Bluish green	84	17.35 (17.33)	35.58 (35.43)	3.67 (3.54)	24.72 (24.80)	22.4
$CuC_{10}H_{12}N_6O_4$ (**3**)	Blue violet	87	18.52 (18.49)	34.86 (34.93)	3.37 (3.49)	24.41 (24.45)	19.7

frequencies at 800 and 706 cm^{-1}. In complex **1** skeleton vibrations and out of plane vibrations observed at 1598, 1428, 1422 and 803 cm^{-1}. In complex **2**, the peaks observed at 1487, 1439, 1372 and 800 cm^{-1} and in complex **3**, peaks observed at 1381 and 807 cm^{-1}. The peaks at 800, 803 and 800 cm^{-1} are characteristic for the *meta* substituted aromatic ring of the 3-aminopyridine. The frequency at 1631 cm^{-1} corresponds to the NH_2 scissoring mode, which was observed at 1598 cm^{-1} for complex **1**, 1625 cm^{-1} for complex **2** and 1625 cm^{-1} for complex **3**. The NH^- stretching region (3500-3100 cm^{-1}) of the 3-aminopyridine characterized by two bands assigned to the $\nu_{asym}(NH_2)$ and $\nu_{sym}(NH_2)$ bands observed at 3437 cm^{-1}. 3-Aminopyridine has two nitrogen atoms, each having lone pair electrons to donate. It is well known that when amino nitrogen atom involved in coordination, a drastic red shift will be observed in NH_2 stretching vibrations (Δ = 150-200 cm^{-1})[24]. Since red shift is not observed in NH_2 stretching vibrations, it is concluded that amino group nitrogen of 3-aminopyridine does not involve coordination in all the studied complexes.

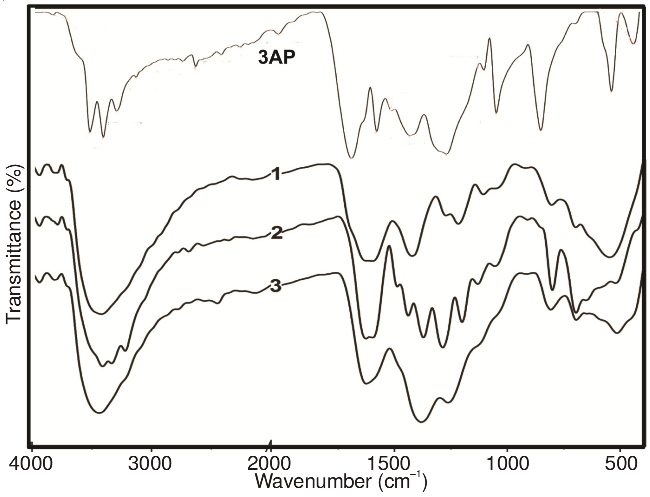


Fig. 1. IR spectra of the complexes **1**, **2** and **3**

The ring breathing mode observed at 909 cm^{-1} in the IR spectrum of micro-crystalline 3-aminopyridine, is observed at 917, 910 and 910 cm^{-1} in the spectra of **1**, **2** and **3**, respectively. This mode is known to be very sensitive to co-ordination of pyridine ring from endocyclic nitrogen lone pairs and increases in wave number on the co-ordination strength. Thus, it is concluded that ring nitrogen is involved in the coordination in the complexes studied. The nitrite group (NO_2^-) has three fundamental modes at 1358, 1262 and 838 cm^{-1} which are all active with infrared region. Upon coordination, the band positions are shifted as compared to the free nitrite ion frequencies. The shift exhibited by the asymmetric and symmetric stretching frequencies are used to indicate the mode of bonding of the nitrite group, whether it is coordinated through nitrogen atom (nitro) complex or through the oxygen atom (nitrito) complex[25].

In case of nitrito complexes, both $\nu_{asym}(NO_2)$ and $\nu_{sym}(NO_2)$ are at lower or higher values than the free nitrite ion frequencies[26]. The N-O bending band appears in the region between 850 and 750 cm^{-1}. The absorption bands observed at 560-500 and 467-410 cm^{-1} are attributed to ν(M-N) and ν(M-O), respectively[27]. The ν(M-N) stretching frequency also exhibited in the range of 290-230 cm^{-1} [28]. The presence of wagging mode ρ_w at 640 cm^{-1} is the evidence for the nitro complexes[29]. But in our studied complexes **1**, **2** and **3**, no bands assignable to wagging ρ_w for the pale green coloured complex **1**, bluish green complex **2** and blue-violet complex **3**. From the literature, all the nitrito complexes exhibit absorption bands in the 370-340 cm^{-1} region due to the M-ONO[30] which were observed in **1**, **2** and **3**. Thus, all the prepared complexes are nitrito in nature.

Magnetic moment and electronic spectra: The electronic spectra **1**, **2** and **3** complexes are given in Fig. 2. The solid diffused reflectance spectra of **1** show three bands at 15974 cm^{-1} (ν_1), 22124 cm^{-1} (ν_2) and 39063 cm^{-1} (ν_3). These bands can be assigned to the transitions $^4A_{2g(F)} \rightarrow {}^4T_{2g(F)}$, $^4A_{2g}$ (F) $\rightarrow {}^4T_{1g(F)}$ and $^4A_{2g(F)} \rightarrow {}^4T_{1g(P)}$, respectively. At room temperature, Cr(III) complex show magnetic moment corresponding to three unpaired electrons *i.e.*, 3.74 B.M[31]., in good agreement with that expected for octahedral Cr(III) complexes. The solid diffused reflectance spectra of **2** show broad peak around 15267 cm^{-1} (ν_1) with shoulder around 19608 cm^{-1}(ν_2), assigned to $^3T_{1(F)} \rightarrow {}^3T_{2(F)}$ and $^3T_{1(F)} \rightarrow {}^3T_{1(P)}$ transition probably indicating distorted tetrahedral geometry around nickel(II). The magnetic moment value 2.92 BM further supports a distorted tetrahedral environment around the Ni(II) ion[32].

The solid diffused reflectance spectra of **3** show three bands at 18182 cm^{-1} (ν_1), 27778 cm^{-1} (ν_2) and 39216 cm^{-1} (ν_3), respectively, suggesting an octahedral structure[33]. These bands can be assigned to the transitions $^2B_{1g} \rightarrow {}^2A_{1g}$ ($d_{x^2-y^2} \rightarrow d_{z^2}$), $^2B_{1g} \rightarrow {}^2B_{2g}$ ($d_{x^2-y^2} \rightarrow d_{zy}$) and $^2B_{1g} \rightarrow {}^2E_g$ ($d_{x^2-y^2} \rightarrow d_{xz}$, d_{zy}), respectively. The broadness of the bands is due to Jahn-Teller distortion which results from an odd number of electrons in the $d_{x^2-y^2}$ orbital[34]. The magnetic moment (1.91 BM) for the compound is higher than the spin only value for the copper ion, suggesting the presence of some orbital contribution to the magnetic moments.

Ligand field parameters: Inter electronic repulsion is expressed in terms of the Racah parameters B and C (Table-2). The parameter B is used to evaluate the difference in energy between states of the same spin multiplicity. However, both parameters are necessary for terms of different multiplicity. The energy of the first spin allowed transition directly gives the value of 10 Dq. The Racah parameter 'B' has been calculated from the relation:

TABLE-2
MAGNETIC MOMENT, ELECTRONIC SPECTRAL DATA AND LIGAND FIELD PARAMETERS OF THE COMPLEXES, **1** AND **3**

Complex	Magnetic moment (B.M)	Electronic bands (cm^{-1})	Possible assignments	Dq (cm^{-1})	B (cm^{-1})	β	C (cm^{-1})	ν_2/ν_1
1	3.74	15974 22124 39063	$^4A_2g(F) \rightarrow {}^4T_2g(F)$ $^4A_2g(F) \rightarrow {}^4T_1g(F)$ $^4A_2g(F) \rightarrow {}^4T_1g(P)$	1597.4	884.3	0.96	3979	1.39
3	1.91	18182 27778 39216	$^2B_1g \rightarrow {}^2A_1g$ $^2B_1g \rightarrow {}^2B_2g$ $^2B_1g \rightarrow {}^2Eg$	1818.2	--	--	--	1.53

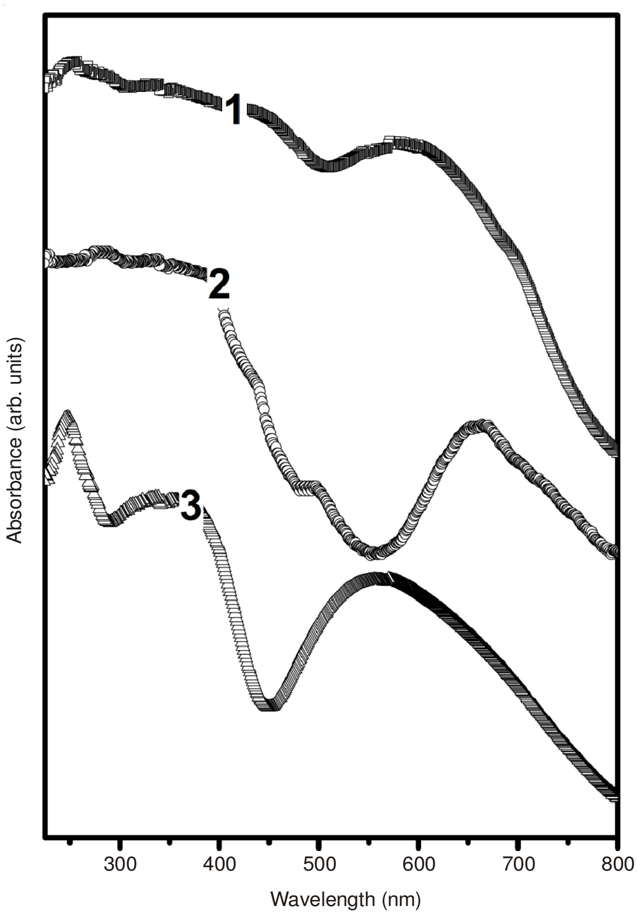


Fig. 2. Electronic spectra of the complexes **1**, **2** and **3**

$$B = \frac{\nu_2 + \nu_3 - 3\nu_1}{15} \qquad (4)$$

where, ν_1, ν_3 and ν_3 are the energies of the transitions. The nephelauxetic parameter 'β' obtained by using the relation:

$$\beta = \frac{B_{Complex}}{B_{Free\ Ion}} \qquad (5)$$

According to Jorgenson[35], decreased β values are associated with a reduction in the nuclear charge on the cation and the smaller charge experienced by the *d-d* electrons. For Cr(III), B free ion = 918 cm^{-1}; C/B = 4.50. The Cr(III) complex have a low Racah parameter 'B' value *i.e.* 884.3 which is 96 % of that of the free ion value 918 cm^{-1} and indicates a greater degree of covalency.

The effect of covalence is to reduce the positive charge on the metal ion as a consequence of the inductive effect to the ligand with reduce positive charge, the radial extension of the *d*-orbital increases, this decreases the electron-electron repulsion, lowering the energy of the 3_p states[36]. The resuting values of the Racah parameter B and the nephelauxetic ratio β suggest low amounts of electron delocalization between the metal and ligands and place the aminopyridine amongst the non π-bonding ligands in the nephelauxetic series[37].

EPR spectra: EPR spectra of **1**, **2** and **3** complexes are given in Fig. 3. EPR spectrum of the polycrystalline complex **1** was recorded at room temperature on the X-band at 9.86 GHz under the magnetic field 3480G (EPR of **2**, **3** also recorded under similar conditions). The parameter g is 1.97 which is well fitted with the predicted value (g = 1.98) for the octahedral geometry. The zero field splitting of the state be so large. Therefore, no zero field splitting observed and of may be taken to be isotropic[38]. The EPR spectrum of polycrystal line complex **2** shows the axial parameter g values (g = 2.94, 2.07 and 1.98) is well fitted with those of the tetrahedral Ni(II) complex[39] (g = 2.64, 2.02 and 1.95), which predicts tetrahedral environment around Ni(II) ion.

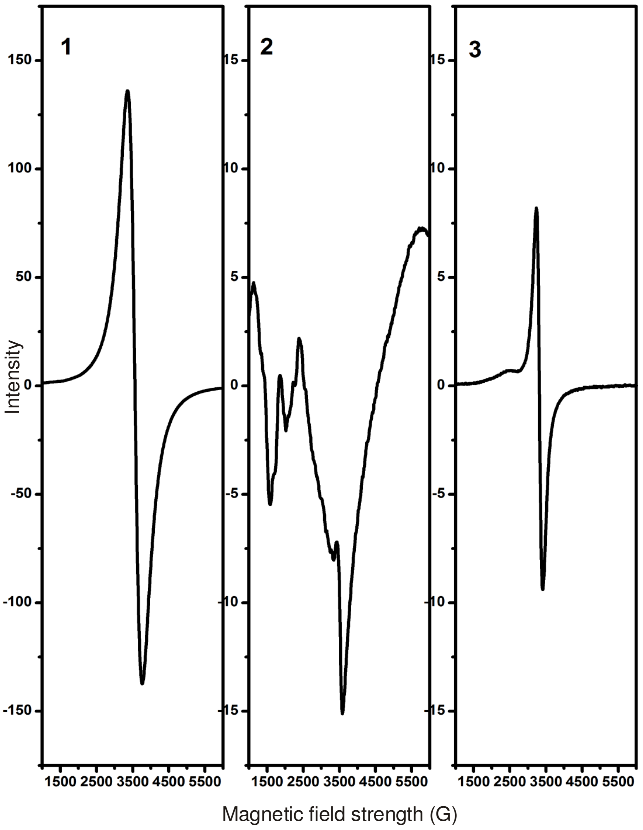
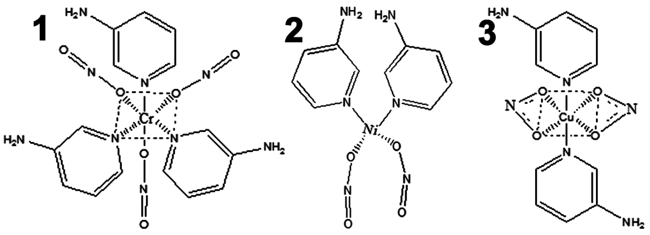


Fig. 3. EPR of the complexes **1**, **2** and **3**

The EPR spectrum of polycrystalline complex **3** shows not well resolved anisotropic signal because of static J.T. effect with g average at 2.231, which is consistent with an axially elongated octahedral geometry. The analysis of the spectra give the lande splitting factor $g\parallel = 2.368$ and $g\perp = 2.118$. Comparisons of g with the predicted value ($g\parallel = 2.368$ and $g\perp = 2.093$) which is relatively good[40]. The anisotropy in g shows the presence of a low symmetry ligand field component. The axial symmetry parameter, *i.e.* $G(g\parallel - g\perp)$ has been calculated. According to Hathaway *et. al.*, the G value measures the exchange interaction between metal centers in polycrystalline solids[41]. In present case $G < 4$, indicates considerable exchange interaction occurs in the complex. It has also been found that $g\parallel = 2.368 > g\perp = 2.118$ in accordance with the criterion of Kivelson and Neiman implying the presence of unpaired electron is localized $d_{x^2-y^2}$ orbital which indicates considerable exchange interaction[42] in the Cu(II) ion characteristic of the axial symmetry[43]. Thus, the complexes **1**, **2** and **3** could be formulated as $[Cr(3AP)_3(ONO)_3]$, $[Ni(3AP)_2(ONO)_2]$ and $[Cu(3AP)_2(ONO)_2]$, respectively. Suggested structures of the complexes **1**, **2** and **3** are given in **scheme-I**.



Scheme-1: Suggested structures of the complexes **1**, **2** and **3**

Antibacterial studies: The antibacterial results (Fig. 4) show that the metal complexes **1**, **2** and **3** are more active than free ligand 3-aminopyridine. From the figure, it is clear that the complex **2** and **3** shows excellent and moderate activity against *R. planticola*, *S. flexineri* and *P. aeruginosa*. The complex **1** shows poor activity against all type of bacteria. The antibacterial activity of all the complexes against *R. planticola* is completely reversed compared to the free ligand, 3-aminopyridine. In complex **1**, the activity is lowered due to the biochemical mechanism. Complexation enhances the activity against *R. planticola*, *S. flexineri*. The enhanced bacterial activity of the ligand on complexation may be explained by the chelation theory. This enhancement in the activity was suggested to be possibly due to an efficient diffusion of the metal complexes into the bacterial cell or interaction with the bacterial cell walls[44]. The antibacterial activity of the complexes shows the following order: 2 > 3 > 1 > 3-aminopyridine. In general complexes **2** and **3** show better antibacterial activity than the free organic ligand, 3-aminopyridine. Concentration plays a vital role, when concentration of the complexes increases the activity also increases.

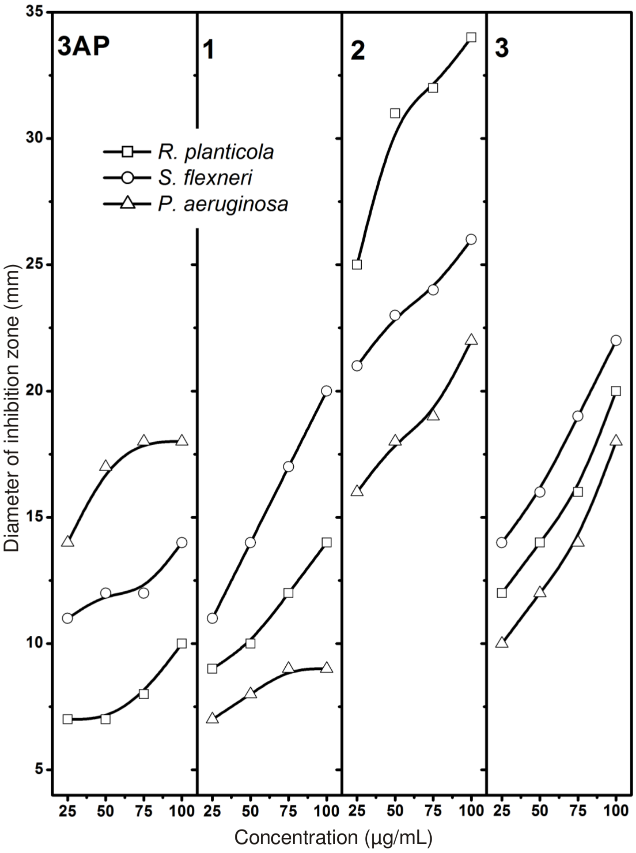


Fig. 4. Antibacterial activities of complexes **1**, **2** and **3** with the free ligand, 3AP against the bacteria, *R. planticola*, *S. flexineri* and *P. aeruginosa*

Antifungal activity: *Aspergillus niger* and *Candida albicans* fungi were used as the test organisms for which the growth inhibition capacity of the ligand (3-aminopyridine) and its complexes (**1-3**) have been screened (Table-3). From the antifungal activity data, complex **2** shows noble antifungal character against *Aspergillus niger* and complex **3** shows better activity against *Candida albicans*. Complex **1** shows the poor activity towards both the fungi *Aspergillus niger* and *Candida albicans*. The ligand 3-aminopyridine and co-ligand NO_2^- does

TABLE-3
ANTIFUNGAL ACTIVITY OF LIGANDS (NO_2^-, 3-AMINOPYRIDINE) AND THEIR METAL COMPLEXES **1-3**

Compound	Fungus tested	Fungal growth inhibition (in %) at concentrations (µg mL^{-1})		
		400	200	100
Ligand (NO_2^-)	*C. albicans*	--	--	--
	A. niger	--	--	--
Ligand (3AP)	*C. albicans*	10	--	--
	A. niger	12.5	--	--
1	*C. albicans*	--	--	--
	A. niger	37.5	25	--
2	*C. albicans*	25	--	--
	A. niger	50	37.5	25
3	*C. albicans*	50	30	10
	A. niger	25	25	12.5

not show any antifungal activity. The antifungal activity towards *Candida albicans* shows the following order: **3** > **2** > **1** > 3-aminopyridine while towards *Aspergillus niger* the activity shows the following order: **2** > **1** > **3** > 3-aminopyridine. In general, Complexation process increases the fungicidal activity of the ligand[45] as seen in the antibacterial activity. Antifungal character also a concentration dependent, when concentration increases the activity increases.

Conclusion

From elemental analyses and molar conductance data, the probable formulae of the complexes arrived. 3-Aminopyridine acts as monodentate ligand through the nitrogen of the pyridine ring. Nitrito ligand coordinate with the metal ion through oxygen atom in all the complexes **1-3** studied. From the IR and far-IR data revealed that complexes of **1**, **2** and **3** are nitrito in nature. Electronic spectral data showed that three well separated bands observed for complexes **1** and **3** predicts distorted octahedral environment around the Cr(III) and Cu(II) ion, further supported by EPR and magnetic studies; distorted tetrahedral geometry predicted for the complex **2**. The results of antibacterial and antifungal studies show that metal complexes possess noble antibacterial and antifungal activity than the free ligand 3-aminopyridine. The metal complexes **2** and **3** may be used as antibacterial and antifungal agents with careful precautions.

ACKNOWLEDGEMENTS

The authors are thankful to the Management of Bishop Heber College (Autonomous), Tiruchirappalli, for providing laboratory facilities and financial assistance; CECRI, Karaikudi, for recording EPR spectra; CIF, Pondicherry University, Pondicherry for recording IR, Far-IR and UV-visible spectra; Bishop Heber College (Autonomous), Tiruchirappalli, for microbial screening.

REFERENCES

1. G. Picolo, A.C. Cassola and Y. Cury, *Eur. J. Pharmacol.*, **469**, 57 (2003).
2. A. Akgul and I. Kaya, *Indian J. Biochem. Biophys*., **4**, 120 (2004).
3. F. Labrie, *J. Clin. Oncol*., **22**, 864 (2004).
4. G. Chelucci, *Coord. Chem. Rev*., **257**, 1887 (2013).
5. T. Chattopadhyay, M. Ghosh, A. Majee, M. Nethaji and D. Das, *Polyhedron*, **24**, 1677 (2005).
6. P.C. Ford, *Acc. Chem. Res*., **41**, 190 (2008).
7. J. Yuan, D.B. Lovejoy and D.R. Richardson, *Blood*, **104**, 1450 (2004).
8. M.A.S. Goher, A.K. Hafez, M.A.M. Abu-Youssef, A.M.A. Badr, C. Gspan and F.A. Mautner, *Polyhedron*, **23**, 2349 (2004).
9. A.M. Donia and H.A. El-Boraey, *Transition Met. Chem.*, **18**, 315 (1993).
10. M. Tumer, *Synth. React. Inorg. Met. Org. Chem*., **30**, 1139 (2000).
11. D.H. Brown, W.E. Smith, J.W. Teape and A.J. Lewis, *J. Med. Chem*., **23**, 729 (1980).
12. P.J. Blower, *Annu. Rep. Prog. Chem. Sect. A: Inorg. Chem*., **98**, 615 (2002).
13. J.E. Huheey, E.A. Keiter and R.L. Keiter, Inorganic Chemistry, Principles of Structure and Reactivity, Addison-Wesley Publishing Company, edn 4 (1993).
14. V.S.X. Anthonisamy and R. Murugesan, *Chem. Phys. Lett*., **287**, 353 (1998).
15. B.J. Hathaway and D.E. Billing, *Coord. Chem. Rev*., **5**, 143 (1970).
16. N. Wei, N.N. Murthy and K.D. Karlin, *Inorg. Chem*., **33**, 6093 (1994).
17. J. García-Lozano, J. Server-Carrió, E. Escrivà, J.-V. Folgado, C. Molla and L. Lezama, *Polyhedron*, **16**, 939 (1997).
18. D. Reinen and C. Friebel, *Inorg. Chem*., **23**, 791 (1984).
19. F. Köksal, I. Kartal and F. Ucun, *Solid State Commun*., **98**, 1087 (1996).
20. K. Dhaveethu, T. Ramachandramoorthy and K. Thirunavukkarasu, *J. Korean. Chem. Soc*., **57**, 341 (2013).
21. N. Raman, A. Kulandaisamy, C. Thangaraja and K. Jeyasubramanian, *Transition Met. Chem.*, **28**, 29 (2003).
22. A. Chaudhary and R.V. Singh, *Phosphorous Sulphur Silicon Rel. Elem*., **178**, 603 (2003).
23. P. Carmona, M. Molina and R. Escobar, *Spectrochim. Acta A*, **49**, 1 (1993).
24. M. Bakiler, I.V. Maslov and S. Akyuz, *J. Mol. Struct*., **475**, 83 (1999).
25. D.M.L. Goodgame and M.A. Hitchman, *Inorg. Chem.*, **3**, 1389 (1964).
26. F. Basolo and G.S. Hammaker, *Inorg. Chem*., **1**, 1 (1962).
27. M.N. Patel, S.H. Patel and P.B. Pansuriya, *Med. Chem. Res*., **20**, 1371 (2011).
28. D.G. Brewer, P.T.T. Wong and M.C. Sears, *Can. J. Chem*., **46**, 3137 (1968).
29. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, John Wiley & Sons: New York, pp. 151-155 (1963).
30. G. Blyholder and A. Kittila, *J. Phys. Chem*., **67**, 2147 (1963).
31. H.A. Santos silva, R.M. Carlos, A.J. Camargo, C.M.C. Picchi, R.H.A. Santos, B.R. McGarvey and D.W. Franco, *Inorg. Chim. Acta*, **357**, 3147 (2004).
32. S.U. Rehman, S. Rehman, M. Ikram and F. Ullah, *J. Saudi Chem. Soc*., **17**, 353 (2013).
33. B.N. Figgis, Introduction to Ligand Field Theory, Wiley Interscience, New York (1978).
34. A.B.P. Lever, Crystal Field Spectra, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, edn 1, p. 249 (1968).
35. L.S. Forster, C.J. Ballhausen, A.-M. Olson, T. Briggs, G.A.D. Haslewood and H. Flood, *Acta Chem. Scand*., **16**, 1385 (1962).
36. R.S. Drago, Physical Methods in Chemistry, W.B. Saunders & Company, London, p. 647 (1977).
37. B.N. Figgis, Introduction to Ligand Fields, Interscience: New York (1966).
38. B.N. Figgis, Introduction to Ligand Fields, John Wiley & Sons, Inc., New York, p. 304 (1976).
39. T. Matsumoto, M. Ito, M. Kotera and K. Tatsumi, *Dalton Trans*., **39**, 2995 (2010).
40. S. Mithira, B. Natarajan, S. Deepa, R.V.S.S.N. Ravikumar and P. Sambasiva Rao, *J. Mol. Struct*., **839**, 2 (2007).
41. B.J. Hathaway, J.N. Bradley and R.D. Gillard, Essays in Chemistry, Academic Press, New York, (1971).
42. M. Procter, B.J. Hathaway and P. Nicholls, *J. Chem. Soc. A*, 1678 (1968).
43. D. Kivelson and J. Neiman, *J. Phys. Chem*., **35**, 149 (1961).
44. S. Khan, S.A.A. Nami, K.S. Siddiqi, E. Husain and I. Naseem, *Spectrochim. Acta A*, **72**, 421 (2009).
45. G.G. Mohamed, N.A. Ibrahim and H.A.E. Attia, *Spectrochim. Acta A*, **72**, 610 (2009).