

# SYNTHESIS OF Co(II), Ni(II), Cu(II), Fe(III), VO<sup>2+</sup> AND UO<sub>2</sub><sup>2+</sup> COMPLEXES DERIVED FROM A NEW BIS(PYRIDYLUREA) LIGAND. SPECTROSCOPIC CHARACTERIZATION, THERMAL, MAGNETIC AND 3D MOLECULAR MODELING STUDIES

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## ABSTRACT

Bis(pyridylurea) ligand, EBPU and its Co(II), Ni(II), Cu(II), Fe(III), VO<sup>2+</sup>, UO<sub>2</sub><sup>2+</sup> solid complexes were synthesized. Reaction of the ligand, EBPU with Co(II), Ni(II), Cu(II) and Fe(III) ions in presence of 8- hydroxyquinoline (8-HQ) afforded new mixed ligand complexes. The ligand and its metal complexes were characterized by elemental and thermal analyses, IR, <sup>1</sup>H NMR, electronic and mass spectra as well as conductance and magnetic susceptibility measurements. The spectroscopic data showed that the ligand, EBPU acts as bi- and tetradentate toward the metal ions, coordination via the pyridine -N, the carbonyl -O and/or the amidic -N atoms in a non-, mono- and bis-deprotonated form. The metal complexes exhibited tetrahedral, octahedral and square pyramidal geometrical arrangements. Kinetic and thermodynamic parameters for the different thermal decomposition steps of some complexes were calculated using Coats–Redfern equation. 3D molecular modeling of the ligand, EBPU and a representative complex were studied.

**Keywords:** Bis(pyridylurea) ligand; metal complexes; Spectroscopic; Thermal studies.

## INTRODUCTION

Amide bonds [—CONH—] are ubiquitous in biochemistry, because they provide the linkages that held together two of the most important types of biopolymers, nucleic acids and proteins. The interest in the study of amide complexes derived from their ability to model active sites present in some metallo-proteins,<sup>1, 2</sup> to act as effective catalysts for important organic transformations<sup>3</sup> and the search for better understanding of the physicochemical properties of such complexes, especially to modulate the structural, stereochemical and electronic properties of transition metal centers.<sup>4-6</sup> Pyridine urea ligands are a class of good candidates in the design and construction of supramolecular architectures because they effectively incorporate the urea groups for hydrogen bond formation and the pyridine moiety for coordination with metal ions.<sup>7</sup> Such ligands have been extensively used to construct various structures and functions through

cooperative binding of transition metals and anions.<sup>8, 9</sup> The coordination chemistry of pyridyl ureas and pyridinecarboxamides is extremely rich. Coordination via the pyridine nitrogen atoms, the carbonyl oxygen atoms and the amide nitrogen atoms of the ligands in a non-, mono- and bis-deprotonated form are known. Pyridinecarboxamides act as multidentate ligands towards transition metals<sup>10, 11</sup> and have also been employed in catalysis.<sup>12, 13</sup> Many derivatives of pyridine amide show anti-inflammatory, antipyretic and analgesic activities and they are useful in the treatment of atherosclerosis.<sup>14</sup> Some Pt (II) complexes with amide compounds demonstrated notable antitumour and anticancer activity.<sup>15, 16</sup> In the present work, a new ethylene-1,2-bis(3-pyridin-2-ylurea) ligand, EBPU and its metal complexes with vanadyl(II), iron(III), cobalt(II), nickel(II), copper(II) and uranyl(II) ions were synthesized. The structures of the ligand and

its metal complexes were characterized by elemental and thermal analyses, IR,  $^1\text{H}$  NMR, electronic, ESR and mass spectra as well as conductivity and magnetic susceptibility measurements at room temperature. Also, new mixed ligand complexes of the ligand, EBPU and 8-hydroxyquinoline (8-HQ) with  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  ions were synthesized and characterized. In addition, the kinetic and thermodynamic characteristics of the decomposition steps of some complexes have been studied employing Coats-Redfern equation. Finally, 3D molecular modeling of the ligand, EBPU and a representative complex were studied.

## MATERIALS AND METHODS

### Materials

Ethylchloroformate, 2-aminopyridine, ethylenediamine, anhydrous sodium acetate, EDTA,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{VOSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , hydrochloric, nitric and sulphuric acids were either Aldrich, BDH or Merck products. The organic solvents used, ethanol, DMF and diethylether, were spectroscopically pure and used without further purification.

### Analytical and physical measurements

FT-IR spectra were recorded on a Perkin-Elmer 293 spectrometer ( $4000\text{--}400\text{ cm}^{-1}$ ) in KBr pellets. Electronic spectra were recorded at room temperature on a Shimadzu model UV-1601 PC spectrophotometer (200–800 nm) as solutions in DMF. The  $^1\text{H}$ NMR spectrum of the ligand as a solution in  $\text{DMSO-d}_6$ , were recorded on a Varian (FT-290), 90 MHz spectrometer at room temperature using TMS as an internal standard. Mass spectra were recorded at 300 °C and 70 eV on a Shimadzu QP spectrometer model MS-5988. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a Johnson Matthey, Alfa products, Model MKI magnetic susceptibility balance. The effective magnetic moments were calculated from the expression  $\mu_{\text{eff}} = 2.828 (X_M T)^{1/2}$  B.M., where  $X_M$  is the molar susceptibility corrected using Pascal's constants for the diamagnetism of all atoms in the compounds.<sup>17</sup> The conductivities of complexes were measured as a solution in DMF ( $10^{-3}$  M) using WTWD-812 Weilheim-conductivity meter model LBR, fitted with a cell model LTA100. Microanalyses of carbon, hydrogen and nitrogen were carried out at the microanalytical center, Cairo University, Giza, Egypt. Analyses of the metals followed the dissolution of the solid complex in concentrated  $\text{HNO}_3$  and titrating the

metal solutions complexometrically using 0.001 M EDTA solution.<sup>18</sup> ESR spectra of the complexes were recorded on a Bruker, E500, X-band spectrometer. TGA measurements were carried out on a Shimadzu-50 thermal analyzer. Melting points of the compounds were determined using a Stuart melting points instrument.

### Synthesis of the ligand, EBPU

The ligand, EBPU was prepared in two steps,<sup>19</sup> scheme 1.

### Synthesis of ethylpyridine-2-carbamate (EPC)

Ethylchloroformate (1.09 g, 10 mmol) was added dropwise to 2-aminopyridine (0.94 g, 10 mmol) with one drop of piperidine, the reaction mixture was allowed to stand in ice-bath few minutes due to the exothermic behavior of the reaction, after that the reaction mixture was fused on a hot plate under reflux for 6 h. The product was allowed to cool till room temperature, solidified by ethanol and diethylether, filtered off and recrystallized from ethanol then dried under vacuum to give buff crystals, yield 44 %, m.p. 180 °C.

### Synthesis of ethylene-1,2-bis(3-pyridine-2-ylurea), the ligand, EBPU

A mixture of EPC (3.32 g, 20 mmol) and ethylenediamine (0.59 g, 10 mmol) in DMF (20 ml) was refluxed on a hot plate for 4 h. The reaction mixture was allowed to cool till room temperature, poured on crushed ice, filtered off and recrystallized from ethanol then dried under vacuum to give white crystals, yield 55%, m.p. 248 °C. The molecular formula of the ligand ( $\text{C}_{14}\text{H}_{16}\text{N}_6\text{O}_2$ , M.Wt = 300 g/mol) is in good agreement with the stoichiometry concluded from analytical data and mass spectra.

### Synthesis of the metal complexes

Ethanol solutions of the ligand, EBPU and the metal salt,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{VOSO}_4 \cdot \text{H}_2\text{O}$  or  $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  were mixed in a 1:1 and 1:2 (L:M) molar ratio. The resulting solutions were stirred for about 1 h then refluxed on a hot plate from 6 to 8 h. The solid complexes which separated out on hot were filtered off, washed with hot ethanol and diethylether and finally dried in vacuum desiccator over anhydrous  $\text{CaCl}_2$ .

### Synthesis of mixed ligand complexes

An ethanolic solution of the metal salt,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  or  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was added gradually to an ethanolic solution of the ligand, EBPU in the

molar ratio 1:2 (L:M). The resulting solutions were stirred for 0.5 h, then an ethanolic solution of 8-hydroxyquinoline (8-HQ) was added to the previous solution in the molar ratio 2:2 (8-HQ:M). The solutions were continuously stirred for 2 h then refluxed on a hot plate from 6 to 8 h. The solid complexes which separated out on hot were filtered off, washed with hot ethanol then diethylether and finally dried in vacuum desiccator over anhydrous  $\text{CaCl}_2$ .

### 3D molecular modeling studies

The 3D molecular modeling of the ligand, EBPU and a representative complex,  $[\text{Cu}_2(\text{EBPU})_2(\text{NO}_3)_3(\text{H}_2\text{O})]\text{NO}_3 \cdot \text{H}_2\text{O}$  was carried out on a Hyperchem 7.5 program.<sup>20</sup> It is an interactive graphics program that allows rapid structure building, geometry optimization with minimum energy and molecular display. It has ability to handle transition metal compounds.

## RESULTS AND DISCUSSION

### Characterization of the ligand, EBPU

The structure of the ligand, EBPU was investigated by elemental analyses, IR,  $^1\text{H}$  NMR, UV-Vis and mass spectra. Anal. Calcd. %: C, 56.00; H, 5.33; N, 28.00. Found %: C, 55.59; H, 5.04; N, 27.70. The IR spectrum ( $\text{cm}^{-1}$ ) of the ligand, table 2, showed bands at 3219 and 3090 that may be assigned to  $\nu(\text{NH})$ , strong band at 1682 characteristic of  $\nu(\text{C}=\text{O})$  amide. The IR spectrum of the ligand showed bands at 1584 and 1479 that may be due to the stretching frequencies of the pyridine ring.<sup>21, 22</sup>  $^1\text{H}$  NMR spectral data ( $\delta$  ppm) of the ligand relative to TMS in  $\text{DMSO-d}_6$  without and with  $\text{D}_2\text{O}$  give further support of the suggested structure of the ligand. The aromatic proton signals of pyridine rings were observed in the range 6.84-8.05, the signals observed at 8.46 and 9.20 may be assigned to the protons of NH groups and completely disappeared on adding  $\text{D}_2\text{O}$ . The electronic spectral data of the ligand ( $10^{-3}$  M in DMF), Table 3,  $\lambda_{\text{max}}$  (nm) showed three bands at 244, 291 and 430 which may be assigned to  $\pi-\pi^*$  transitions within the aromatic rings,  $\pi-\pi^*$  transitions within  $\text{C}=\text{O}$  and an intramolecular charge transfer (CT) transition within the whole molecule, respectively. The mass spectrum of the ligand, (figure 1), showed the molecular ion peak at  $m/e = 300$  amu, confirming its formula weight (F. W. = 300 g/mol). The mass fragmentation mode of the ligand, EBPU occurred through two main pathways, scheme 2, and supported the suggested structure of the ligand. The optimized structure of the ligand was given in (figure. 2) and structural parameters were evaluated by means of a semi-empirical molecular orbital calculations at the PM3 level

provided by Hyperchem 7.5 program. These data are found to be, surface area ( $\text{A}^{\circ 2}$ ) = 498.80, volume ( $\text{A}^{\circ 3}$ ) = 1001.22, HOMO energy (ev) = -9.334, LUMO energy (ev) = -0.360, heat of formation (Kcal/mol) = 13.13, electronic energy (ev) = -668960.38, dipole moment  $\mu$  (Debye) = 7.297 and bonds length  $\text{C}=\text{O}$  ( $\text{C}_8-\text{O}_{21}$  and  $\text{C}_{13}-\text{O}_{22}$ ) = 1.217  $\text{A}^{\circ}$ .

### Characterization of the metal complexes

Reactions of the ligand, EBPU with Co(II), Ni(II), Cu(II), Fe(III),  $\text{VO}_2^{2+}$  and  $\text{UO}_2^{2+}$  ions, in the molar ratio 1:1 or 1:2 (L:M), yielded mononuclear, binuclear or trinuclear complexes. All of the complexes prepared were stable at room temperature, non-hygroscopic, insoluble in common organic solvents except DMF. The elemental analyses of the metal complexes of the ligand, EBPU were agreed well with the proposed formulae, table 1.

The molar conductance values of the complexes in DMF ( $10^{-3}$  M solutions) were measured at room temperature and the results were listed in Table 1. The complexes **12**, **13** and **14** have molar conductance values in the range 29.1 - 34.2  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ . The values show that these complexes have non-electrolytic nature. The molar conductance values of the complexes **7** and **11** were 63.6 and 69.4  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ , respectively, suggesting 1:1 electrolytic nature. The complexes **3**, **6** and **9** have molar conductance values in the range 177.6 - 196.1  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ , suggesting 1:2 electrolytic nature. The molar conductance values of the complexes **4** and **10** were 233.5 and 205.9  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ , respectively, suggesting 1:3 electrolytic nature. The complexes **1**, **2**, **5** and **8** have molar conductance values in the range 279.0 - 316.5  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ , suggesting 1:4 electrolytic nature.<sup>23</sup>

### IR spectra and mode of bonding

The main bands of IR spectra of the metal complexes of ligand EBPU and their tentative assignments were listed in table 2. All metal complexes (except **9** and **12**) exhibit broad bands around 3543-3356  $\text{cm}^{-1}$  which assigned to  $\nu(\text{OH})$  of  $\text{H}_2\text{O}$  and / or EtOH molecules associated with the complexes and confirmed by elemental and thermal analyses. Two bands appearing at 1584 and 1479  $\text{cm}^{-1}$  are assigned to pyridine ring stretching vibrations in the free ligand, the first band showed a shift to lower wavenumber and the second band showed a shift to higher wavenumber which indicates the participation of the pyridine nitrogen atoms in coordination to the metal ions through the lone pair of electrons on the nitrogen.<sup>24</sup> In case of complexes **1** - **12**, the  $\nu(\text{C}=\text{O})$  band of the

coordinated ligand is doubled, one band being nearly coincident with the corresponding one of free ligand at  $1682\text{ cm}^{-1}$  and the other occurring at a lower frequency by  $60\text{--}66\text{ cm}^{-1}$ . This result has been interpreted in terms of the presence of both coordinated and noncoordinated (C=O) groups in the same ligand molecule.<sup>25</sup> This is confirmed by the existence of new bands at  $529\text{--}514\text{ cm}^{-1}$ , which could be assigned to  $\nu(\text{M}\text{--}\text{O})$  bands.<sup>26</sup> One of the  $\nu(\text{NH})$  bands of the coordinated ligand being nearly coincident with corresponding one of free ligand and the other shows slightly shift to a higher frequency and the intensity of this band has decreased suggesting coordination of the ligand with deprotonating of the amidic hydrogen's. For complexes **13** and **14**, the  $\nu(\text{C}=\text{O})$  band of the coordinated ligand being nearly coincident with the corresponding one of the free ligand confirming that C=O group is not involved in complex formation and the intensity of one NH (amidic) bands of the coordinated ligand has decreased showing coordination of the ligand with deprotonating of the amidic hydrogen's. This is supported by the existence of new bands at  $428\text{--}408\text{ cm}^{-1}$  which could be assigned to  $\nu(\text{M}\text{--}\text{N})$  bands.<sup>27</sup> The results reveal that the ligand, EBPU acts as bi- or tetradentate towards the metal ions via the pyridine - N, the carbonyl - O and / or the amide - N atoms in a non, mono- and bis- deprotonated form. The nitrate vibrations in complexes **2**, **4**, **5**, **7**, **8**, **10**, **11** and **12** at  $1411\text{--}1354$ ,  $1332\text{--}1281$  and  $1235\text{--}1224\text{ cm}^{-1}$  are indicative of the presence of monodentate nitrate groups<sup>28, 29</sup> since the separation of the two highest frequency bands (under  $C_{2v}$  symmetry) is small ( $<160\text{ cm}^{-1}$ ). The Presence of ionic  $\text{NO}_3^-$  ions in complexes **1** - **11** confirming by the appearance of the stretching vibration mode of ionic nitrate at  $1443\text{--}1379\text{ cm}^{-1}$ .<sup>30</sup> The  $\text{VO}_2^{2+}$  complex **13** displayed a strong band at  $985\text{ cm}^{-1}$ , assignable to  $\nu(\text{V}=\text{O})$  moiety.<sup>31</sup> The  $\text{UO}_2^{2+}$  complex **14** complex showed a new band at  $926\text{ cm}^{-1}$ , which may be assigned to the  $\nu_3(\text{O}=\text{U}=\text{O})$ , suggesting that the uranyl ion is linear.<sup>32</sup> The IR spectrum of the free 8-hydroxyquinoline (8-HQ) shows a strong band at  $1586\text{ cm}^{-1}$  due to the stretching vibration of the C=N group.<sup>33</sup> This band is shifted to a higher wavenumber on coordination for complexes **3**, **6**, **9** and **12** suggesting that the lone pair on nitrogen is involved in the formation of a bond with the metal ion. Moreover, the broad stretching vibration at  $3242\text{ cm}^{-1}$  due to O-H band of the free 8-HQ ligand.<sup>34</sup> was found to be absent in the latter complexes, suggesting the formation of a M-O bond with 8-hydroxyquinolate. Thus 8-

hydroxyquinoline in all mixed ligand complexes **3**, **6**, **9** and **12** is a bidentate chelating ligand.

### Electronic spectra and magnetic moment measurements

The electronic spectra of the metal complexes were measured in DMF solvent and the effective magnetic moments were determined. The data obtained are listed in table 3. The bands of the free ligand, EBPU showed slightly shifts in the spectra of all complexes as a result of complex formation.<sup>35, 36</sup> The electronic spectrum of Cu(II) complex **7** exhibited two bands at 560 and 644 nm, which can be assigned to  ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$  and  ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$  transitions within octahedral structure.<sup>37</sup> In addition, the magnetic moment of the complex **7** was 2.22 B.M. which are consistent with the proposed octahedral structure.<sup>38</sup> However, the complexes **8** and **9** showed a band at 641 and 692 nm, respectively, that can be assigned to  ${}^2\text{T}_2 \rightarrow {}^2\text{E}$  transition in tetrahedral geometries. The observed magnetic moment values of the complexes **8** and **9** were 2.18 and 2.12 B.M., respectively, which is consistent with one unpaired electron per Cu(II) ion, also confirming tetrahedral geometry.<sup>39</sup> The values showed the presence of some spin-spin interaction between Cu(II) ions in the different complexes. The effective magnetic moment values of Co(II) complexes, **1** and **2** were found to be at 3.95 and 4.12 B.M., respectively, These values are consistent with the presence of three unpaired electrons per the Co(II) ion in tetrahedral geometry.<sup>40</sup> The electronic spectra of the Co(II) complexes, **1** and **2** showed one band at 525 and 526 nm, respectively, the bands exhibit some shifts to lower wavelength than the expected value for tetrahedral complexes ( $600\text{--}700\text{ nm}$ )<sup>40</sup> which may be due to the formation of six coordinate species in DMF and the d-d transition bands shifted near 500 nm.<sup>40</sup> In case of the Co(II) complex **3**, the electronic spectra display a band at 535 nm which may be assigned to  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  transitions within octahedral structure.<sup>41</sup> The observed magnetic moment value of the complex **3** was found to be 3.56 B.M. which is less than expected for octahedral Co(II) complexes suggesting antiferromagnetic interaction between Co(II) ions. The effective magnetic moment value of Ni(II) complexes **4**, **5** and **6** were found to be in the range 2.47 - 2.58 B. M. These values indicated the presence of two unpaired electrons per the Ni(II) ion and confirming tetrahedral geometry<sup>42-44</sup> as in complex **5** or octahedral geometry as in complexes **4** and **6**.<sup>45</sup> The results indicated the presence of some spin - spin interaction between Ni(II) ions in these complexes. The electronic spectrum of Ni(II)

complex **5** showed a band at 556 nm, which can be assigned to  ${}^3T_1 \rightarrow {}^3T_1$  (P) transitions indicating tetrahedral geometry around Ni(II) ions, the shift of band to lower wavelength may be explained by the coordination of DMF solvent with Ni(II) ions in the complex and formation of octahedral structure. In case of the Ni(II) complexes **4** and **6** the electronic spectra display two bands at 563 and 667, 628 and 752 nm, respectively, which can be assigned to  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (P) and  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (F) transitions in an octahedral geometries. The electronic spectra of the Fe(III) complexes **10**, **11** and **12** showed one band in the range 531–577 nm corresponding to the  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  (G) transition, within the range reported for octahedral complexes.<sup>45</sup> The values of magnetic moments of the complexes **10**, **11** and **12** were 5.31; 5.56 and 5.76 B. M., respectively. These values reveal the presence of five unpaired electrons in the d-orbital per Fe(III) ion in a high spin octahedral geometry.<sup>46</sup> The lower values than expected magnetic moment (which is around 5.92 B. M.), perhaps due to antiferromagnetic interactions between Fe(III) ions in the complexes. The electronic spectrum of the  $VO^{2+}$  complex **13** showed an absorption band at 685 nm, that can be assigned to  ${}^2B_2 \rightarrow {}^2E$  ( $\nu_1$ ) or  ${}^2B_2 \rightarrow {}^2B_1$  ( $\nu_2$ ) transition in square-pyramidal geometry.<sup>47</sup> The magnetic moment value of the  $VO^{2+}$  complex **13** is 2.23 B.M. which is higher than the expected value for  $d^1$ -system, suggesting an orbital contribution.<sup>48</sup> The electronic spectrum of the  $UO_2(II)$  complex **14** showed a band at 590 nm which is attributed to an electronic transition from the apical oxygen atoms to f-orbital of the uranium(VI) ion or due to charge transfer transition from the ligand to uranium(VI) ion.<sup>49</sup> The uranyl complex **14** is diamagnetic as expected.

### ESR spectra

To obtain further information about the stereochemistry of the Cu(II) complexes, ESR spectra of the Cu(II) complexes (**7**, **8** and **9**) were recorded in the solid state at room temperature as shown in (figure 3) The X-band ESR spectrum of the Cu(II) complex **7** exhibits two signals at  $g_{\perp} = 2.072$  and  $g_{\parallel} = 2.261$ ,  $g_{av} = 1/3 (g_{\parallel} + 2 g_{\perp}) = 2.135$ . The shape of the ESR signals is consistent with the octahedral geometry around the Cu(II) ions in this complex.<sup>50, 51</sup> From the observed  $g$  - values, it is clear that  $g_{\parallel} > g_{\perp}$  which indicates that the unpaired electron is predominantly in the  $dx^2-y^2$  orbital<sup>52-54</sup> giving  ${}^2B_{1g}$  as the ground state. The complexes **8** and **9** exhibited sharp signals at  $g_{\perp} = 2.073$  and  $2.079$ ,  $g_{\parallel} = 2.271$  and  $2.254$ ,  $g_{av} = 2.139$  and  $2.137$ , respectively. The shape of signals and the  $g$  - values indicate tetrahedral

geometry around  $Cu^{2+}$  ions in these complexes. The  $g$  value is an important function for indicating covalent character of M-L bonds,<sup>55</sup> for ionic character,  $g_{\parallel} < 2.0023$  and for covalent character,  $g_{\parallel} > 2.0023$ . In the present complexes **7**, **8** and **9**, the  $g$  is more than 2.0023 indicating appreciable covalent character for the Cu-L bond.<sup>55</sup> In addition, the  $g$ -values are related by the expression,  $[G = (g_{\parallel} - 2.0023) / (g_{\perp} - 2.0023)]$ , which measures the exchange interaction between copper centers in the solid state. According to Hathaway,<sup>56, 57</sup> if the value of  $G$  is greater than four, the exchange interaction between a copper(II) centers in the solid state is negligible, whereas when  $G$  is lower than 4, a considerable exchange interaction is indicated in the solid complex. The calculated  $G$ -value of Cu(II) complexes **7**, **8** and **9** were 3.712, 3.801 and 3.282, respectively, which lower than 4, suggesting that there are copper-copper exchange interactions.<sup>58</sup>

### Mass spectra

The mass spectra for most of the complexes were performed to confirm the proposed formulae. The molecular ion peaks are coincident with the formula weights of the complexes, table 1. The mass spectra of the complexes,  $[Ni_2(EBPU)_2(NO_3)(H_2O)_3](NO_3)_3 \cdot 3H_2O$  (**4**);  $[Cu_2(EBPU)_2(NO_3)_3(H_2O)]NO_3 \cdot H_2O$  (**7**) and  $[Fe_2(EBPU)(8-HQ)_2(NO_3)_4]$  (**12**), as representative examples, are depicted in (figure 4) The mass spectra of the complexes **4**, **7** and **12** showed the molecular ion peaks at  $m/e$  1073.3, 1011.3 and 950.0, respectively, which agree with the formula weights of these complexes.

### Thermal studies

Thermogravimetric analysis (TGA) was mainly used to proof the associated water or solvent molecules to be in the inner or outer coordination sphere of the central metal ion.<sup>59</sup> Complexes **1**, **3**, **4**, **7**, **11** and **13** were taken as representative examples for thermal analysis. The results of TGA of these complexes were recorded in table 4. The following detailed description of the TG thermogram of the complex **3** is given as an example and the TG thermograms of other complexes were obtained similarly.

### TGA of complex **3** $[Co_2(EBPU)(8-HQ)_2(H_2O)_4](NO_3)_2 \cdot H_2O$

The TG thermogram of this complex involves four decomposition steps in the temperature

ranges 40 – 135, 136 – 291, 292 – 435 and 436 – 615 °C, scheme 3. The first step showed removal of the non-coordinated water molecule in addition to one coordinated water molecule (weight loss: found%, 4.25; calcd.%, 3.91). The second step showed loss of three coordinated water molecules in addition to two ionisable nitrate groups and a fragment part (C<sub>7</sub>H<sub>8</sub>N) of the ligand (weight loss: found%, 30.87 ; calcd.%, 30.88). The third step showed removal of another fragment part (C<sub>9</sub>H<sub>10</sub>N<sub>5</sub>O) of the ligand (weight loss: found%, 22.06 ; calcd.%, 22.18). In the last step, the complex undergoes decomposition of the final part (C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>) of the ligand within the temperature range up to 615 °C (weight loss: found%, 24.47 ; calcd.%, 25.01) leading to the formation of Co<sub>2</sub>O<sub>3</sub> (found 18.46 ; calcd.%, 18.03 %) as a final residue.

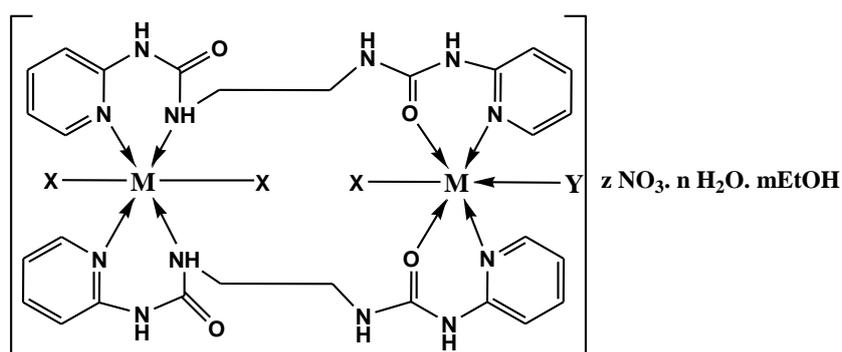
The thermodynamic and kinetic parameters for the different thermal decomposition steps in the complexes **1**, **3**, **4**, **7**, **11** and **13** were evaluated graphically by employing the Coats-Redfern equation.<sup>60</sup> The results of the order (n), the activation energy (E\*), the activation enthalpy ( $\Delta H^* = E^* - RT$ ), the activation entropy ( $\Delta S^* = R [\ln (Ah / K_B T) - 1]$ ) and the free energy of activation ( $\Delta G^* = \Delta H^* - T\Delta S^*$ ) of the decomposition steps for the chosen complexes are listed in table 5, where A is a pre-exponential factor, K is Boltzmann's constant and h is Plank's constant, respectively. The  $\Delta S^*$  values were found to be negative which indicated that the activated complex is more ordered than the reactant and/or the thermal decomposition reaction is slower than normal.<sup>61</sup> The positive sign of  $\Delta G^*$  revealed that the

decomposition steps are non-spontaneous processes.  $\Delta G^*$  values increase with increasing the order of the decomposition stages which indicates that at high temperatures the ligand decomposes and requires more energy for its rearrangement in the activated state<sup>62</sup> this may be attributed to the structural rigidity of the remaining complex after the expulsion of one and more ligands, as compared with the precedent complex, which required more energy for its rearrangement before undergoing any compositional change. The positive values of  $\Delta H^*$  means that the decomposition processes are endothermic.

### 3D Molecular modeling study

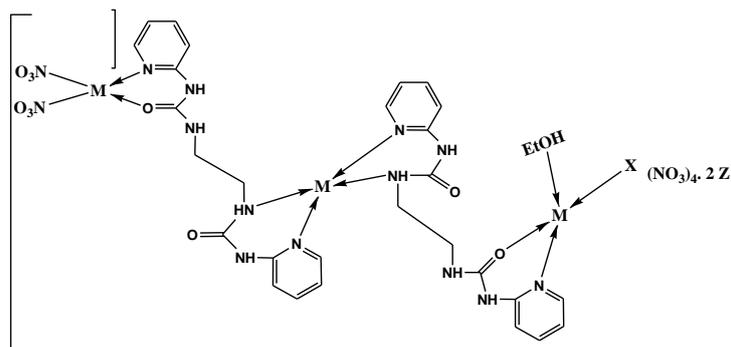
The molecular modeling of a representative complex, [Cu<sub>2</sub>(EBPU)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)] NO<sub>3</sub> .H<sub>2</sub>O (**7**) is shown in (figure 5) The C=O bonds (C<sub>12</sub>-O<sub>14</sub> and C<sub>28</sub>-O<sub>30</sub>) are longer by 0.024 Å than that in the free ligand, which indicate that the coordination take place through carbonyl groups with two O, N-donors of the ligand, EBPU at the equatorial positions in trans-arrangement to each other, is based on its octahedral structure.

from the interpretation of elemental and thermal analyses together with results of spectral data (infrared, electronic, mass and ESR) as well as magnetic susceptibility measurements at room temperature and conductivity measurements, it is possible to draw up the tentative structures of the metal complexes. The proposed structures of the metal complexes under study can be represented as follows:



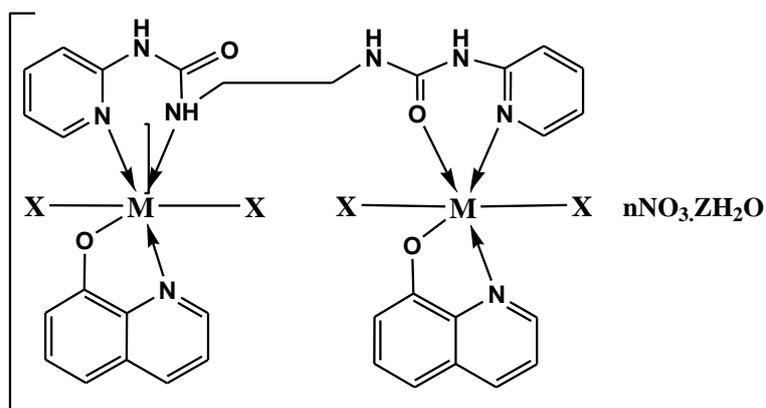
	M	X	Y	z	n	m
(1)	Co(II)	-	-	4	2	1
(7)	Cu(II)	NO <sub>3</sub> <sup>-</sup>	H <sub>2</sub> O	1	1	0

The proposed structures of the binuclear complexes (1) and (7)



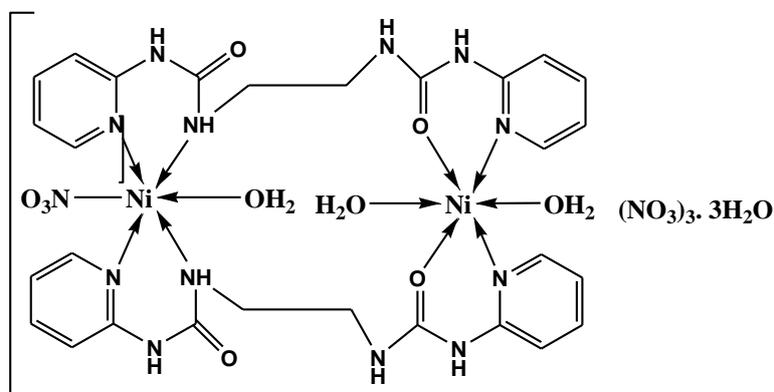
	M	X	Z
(2)	Co	EtOH	EtOH
(8)	Cu	H <sub>2</sub> O	H <sub>2</sub> O

The proposed structures of the trinuclear complexes (2) and (8)

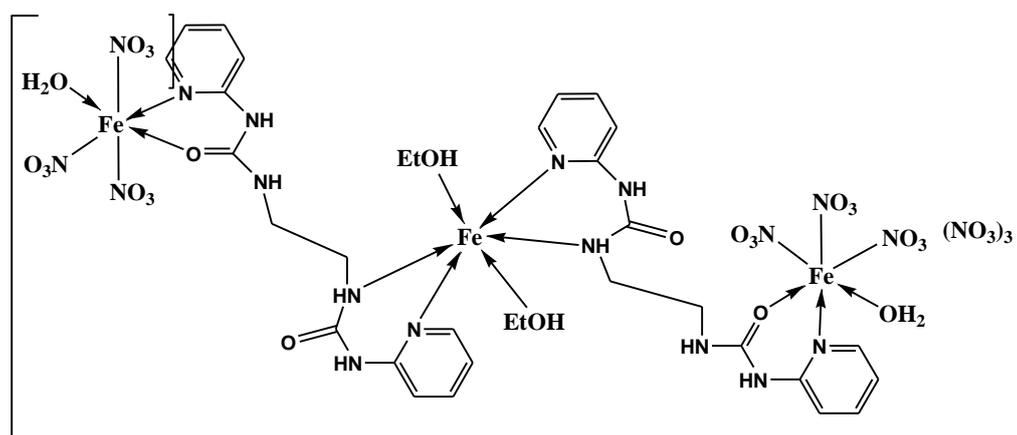
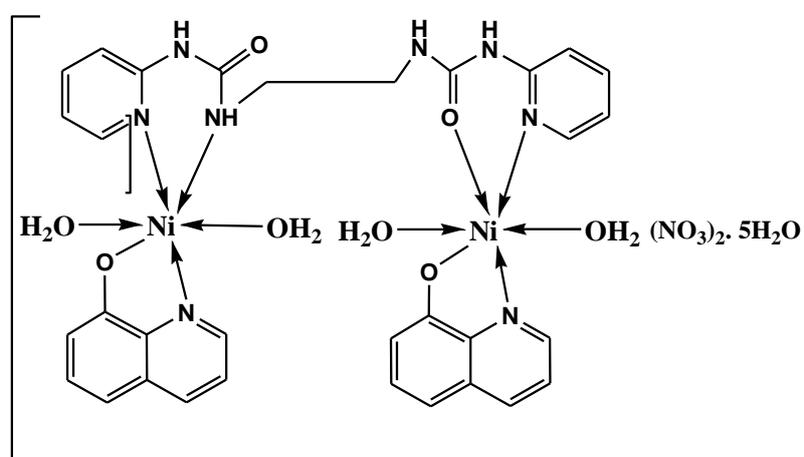
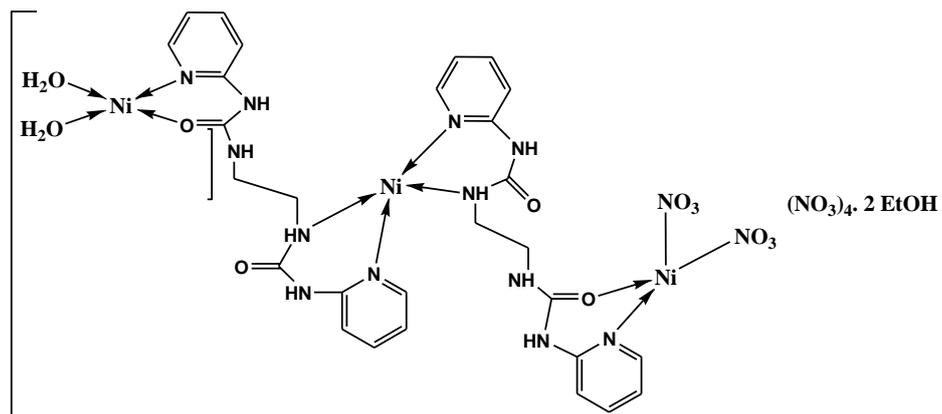


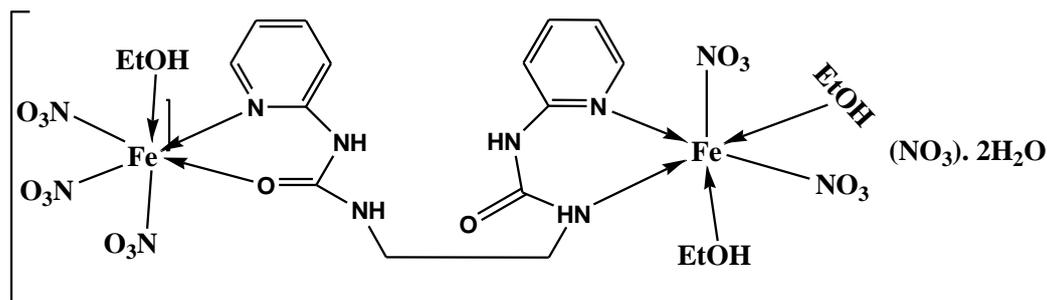
	M	X	n	z
(3)	Co(II)	H <sub>2</sub> O	2	1
(9)	Cu(II)	-	2	0
(12)	Fe(III)	NO <sub>3</sub> <sup>-</sup>	0	0

The proposed structures of the mixed ligand complexes (3), (9) and (12)

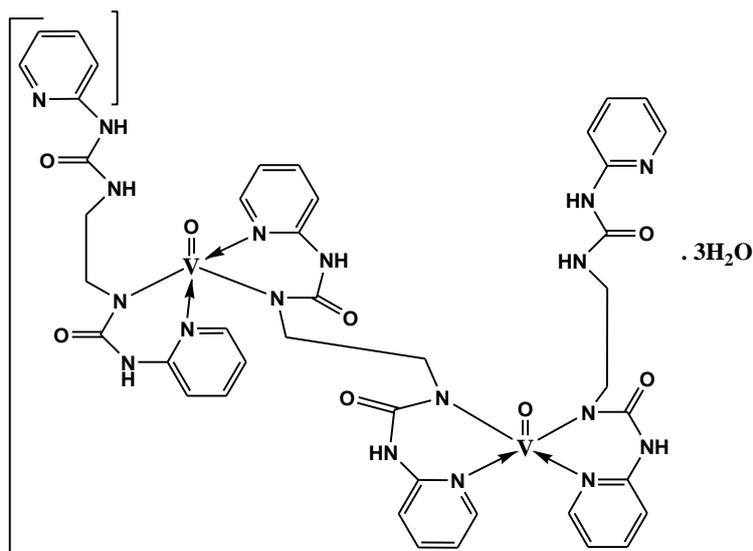


The proposed structure of the binuclear Ni(II) complex (4)

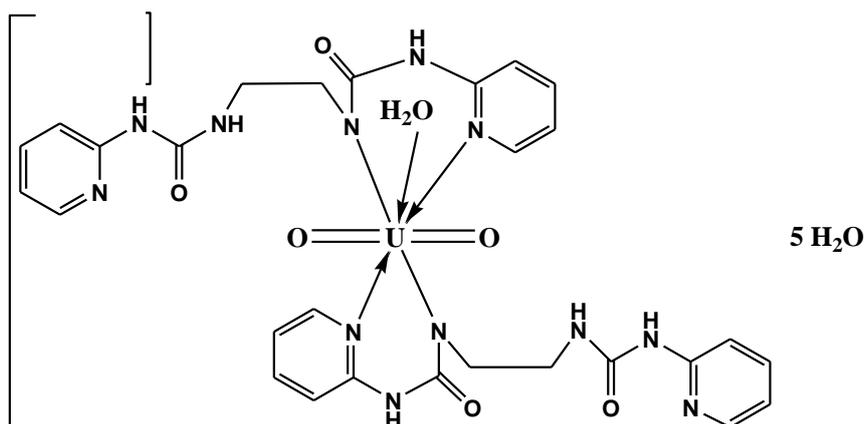




The proposed structure of the binuclear Fe(III) complex (11)



The proposed structure of the binuclear VO<sup>2+</sup> complex (13)



The proposed structure of the mononuclear UO<sub>2</sub><sup>2+</sup> complex (14)

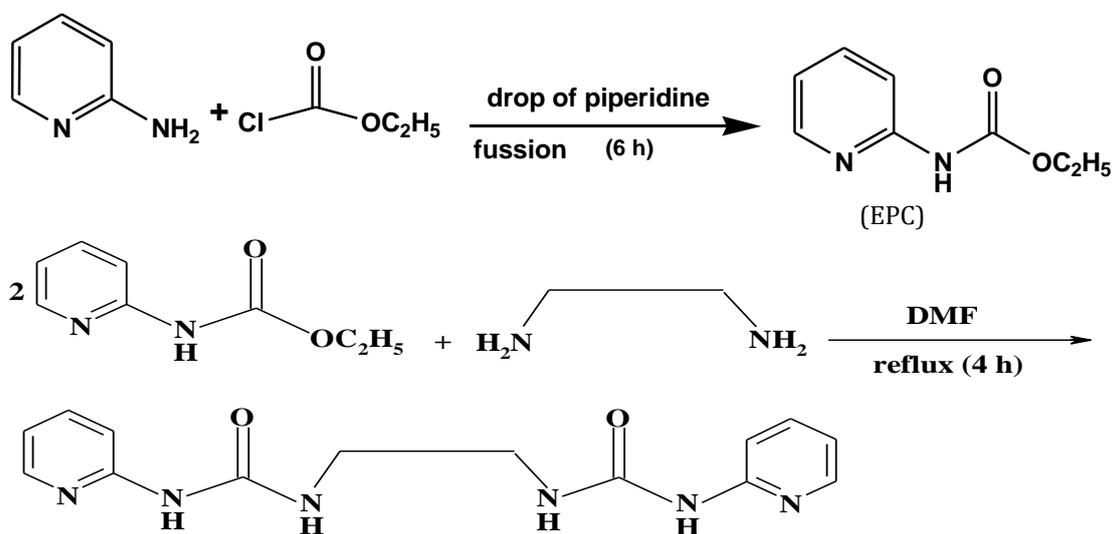
## CONCLUSION

A new ethylene-1,2-bis(3-pyridin-2-ylurea) ligand, EBPu and its metal complexes with vanadyl(II), iron(III), cobalt(II), nickel(II), copper(II) and uranyl(II) ions were synthesized

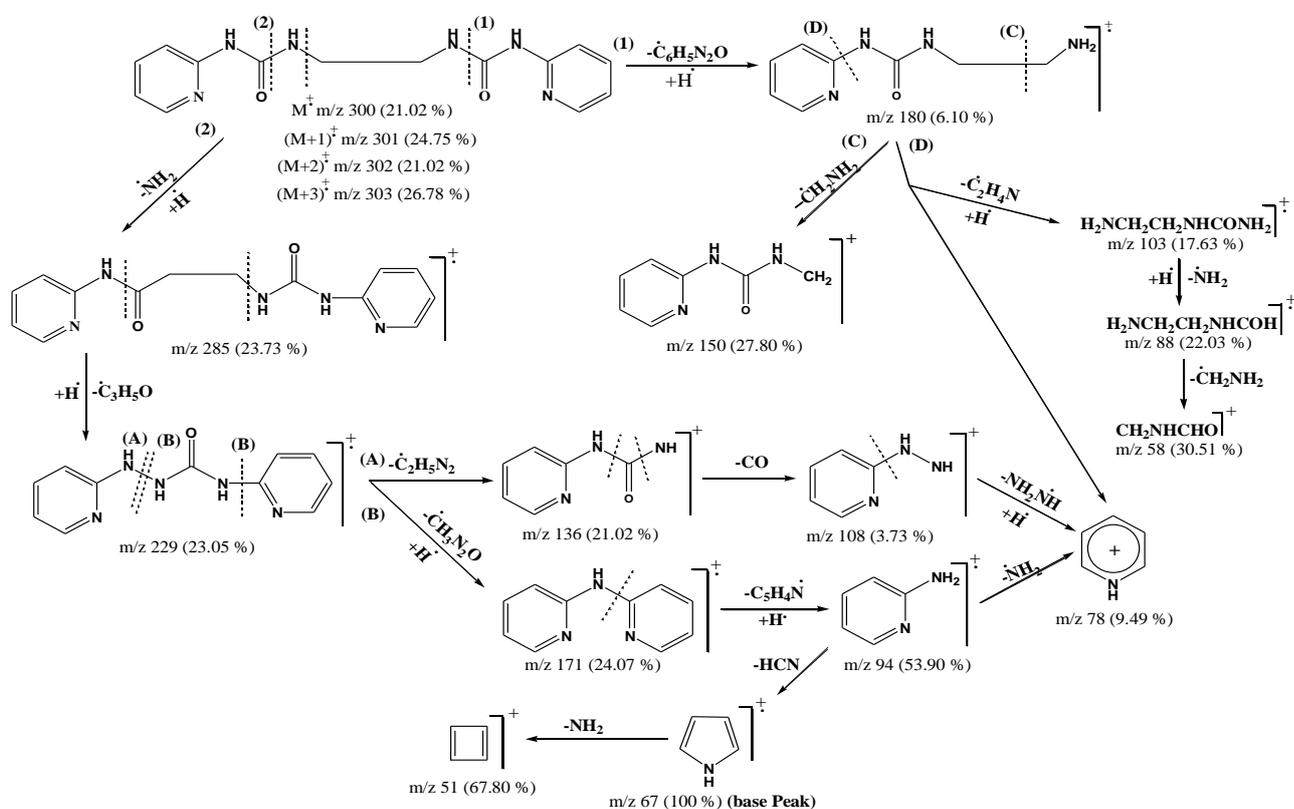
and characterized by different spectroscopic techniques. The ligand, EBPu acts as bi- and tetradentate toward the metal ions. 8-hydroxyquinoline in all mixed ligand complexes acts as a bidentate chelating ligand. The

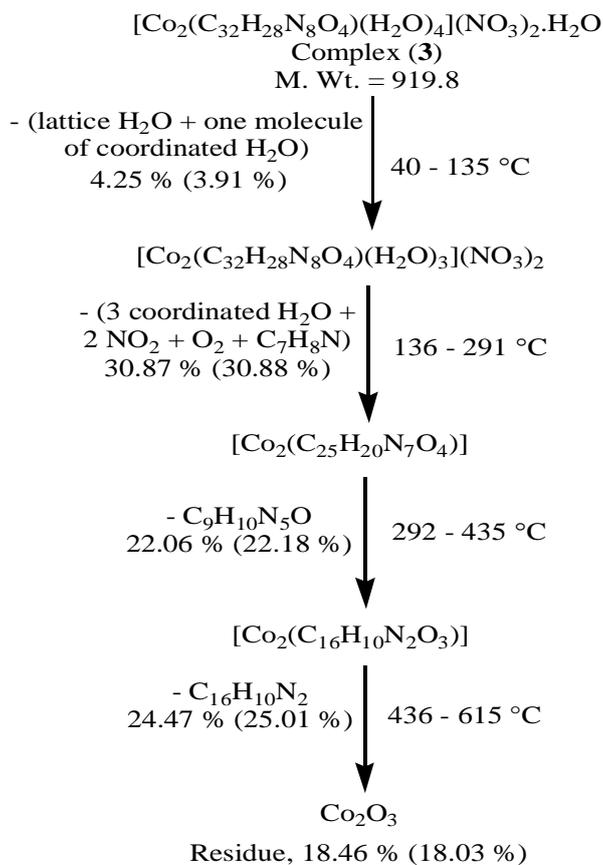
complexes exhibited tetrahedral, octahedral and square pyramidal geometrical arrangements. The thermodynamic and kinetic parameters for the different thermal decomposition steps in some of the complexes were evaluated graphically by employing the Coats-Redfern

equation. 3D molecular modeling of the ligand and a representative Cu(II) complex indicate that the coordination take place through carbonyl groups with two O, N-donor of the ligand.



**Scheme. 1: Synthesis of the ligand, EBP**





Scheme. 3: Proposed thermal decomposition pattern of the complex 3

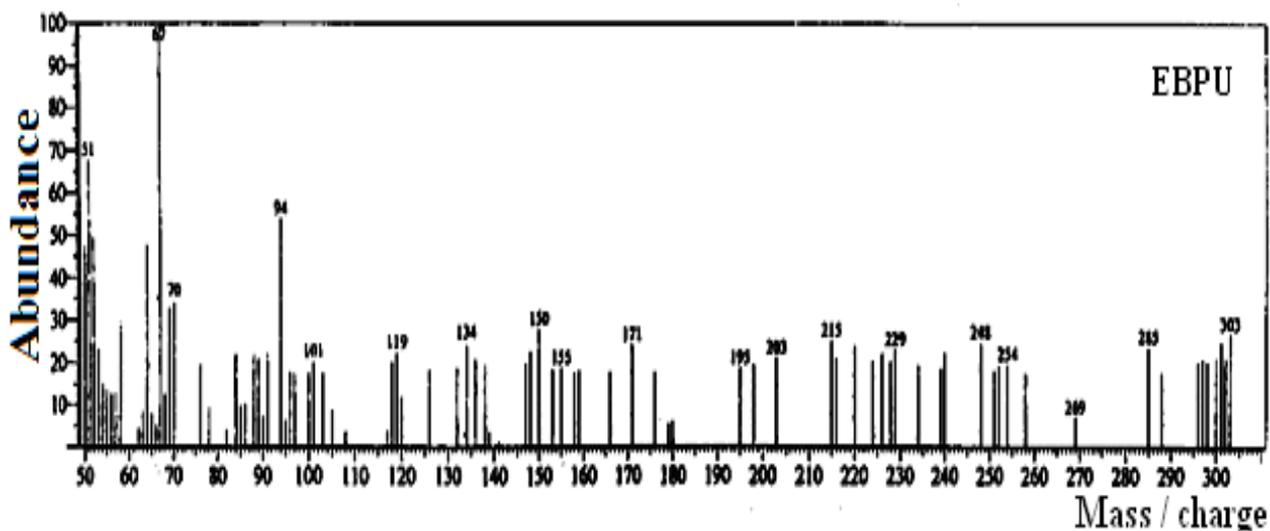


Fig. 1: Mass spectrum of the ligand EBPU

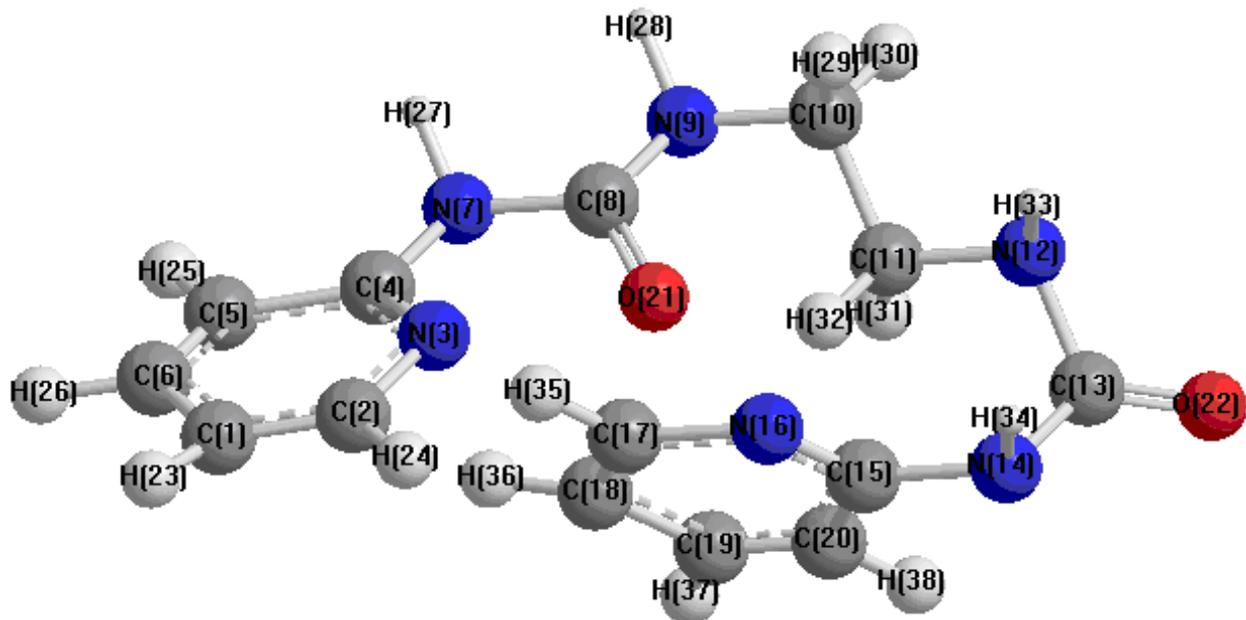
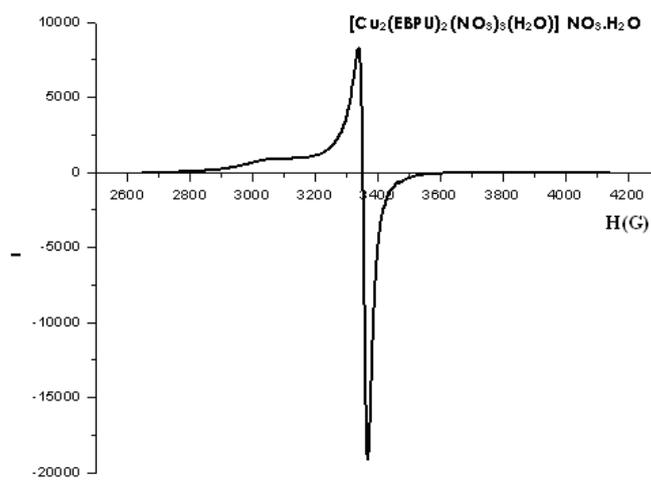


Fig. 2: The optimized structure of the ligand EBPU



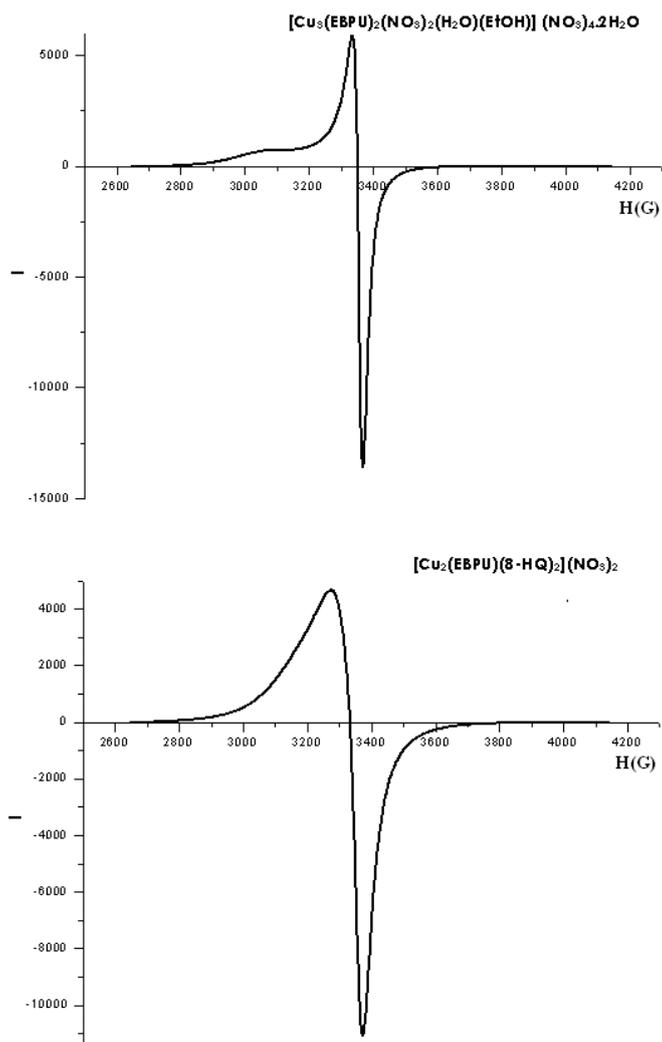
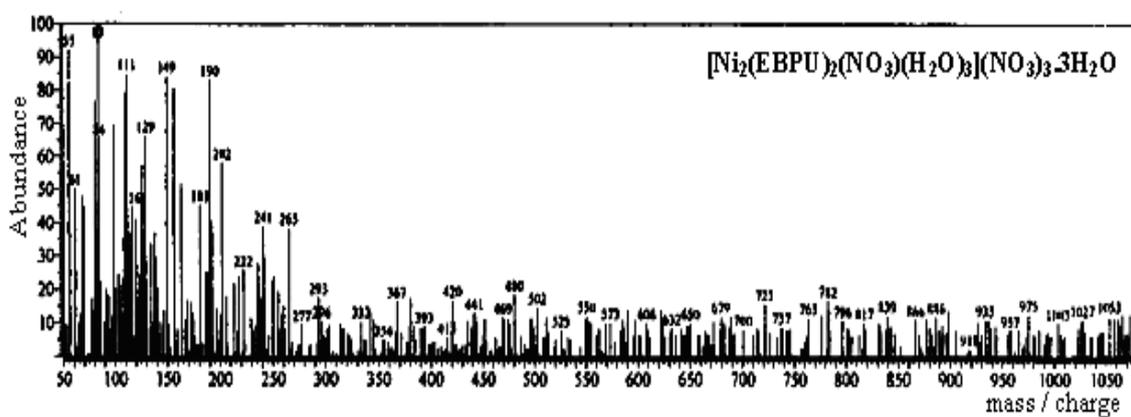


Fig. 3: X-band ESR spectra of Cu (II) complexes  $[\text{Cu}_2(\text{EBPU})_2(\text{NO}_3)_3(\text{H}_2\text{O})] \text{NO}_3 \cdot \text{H}_2\text{O}$  (7),  $[\text{Cu}_3(\text{EBPU})_2(\text{NO}_3)_2(\text{H}_2\text{O})(\text{EtOH})] (\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$  (8) and  $[\text{Cu}_2(\text{EBPU})(8\text{-HQ})_2](\text{NO}_3)_2$  (9)



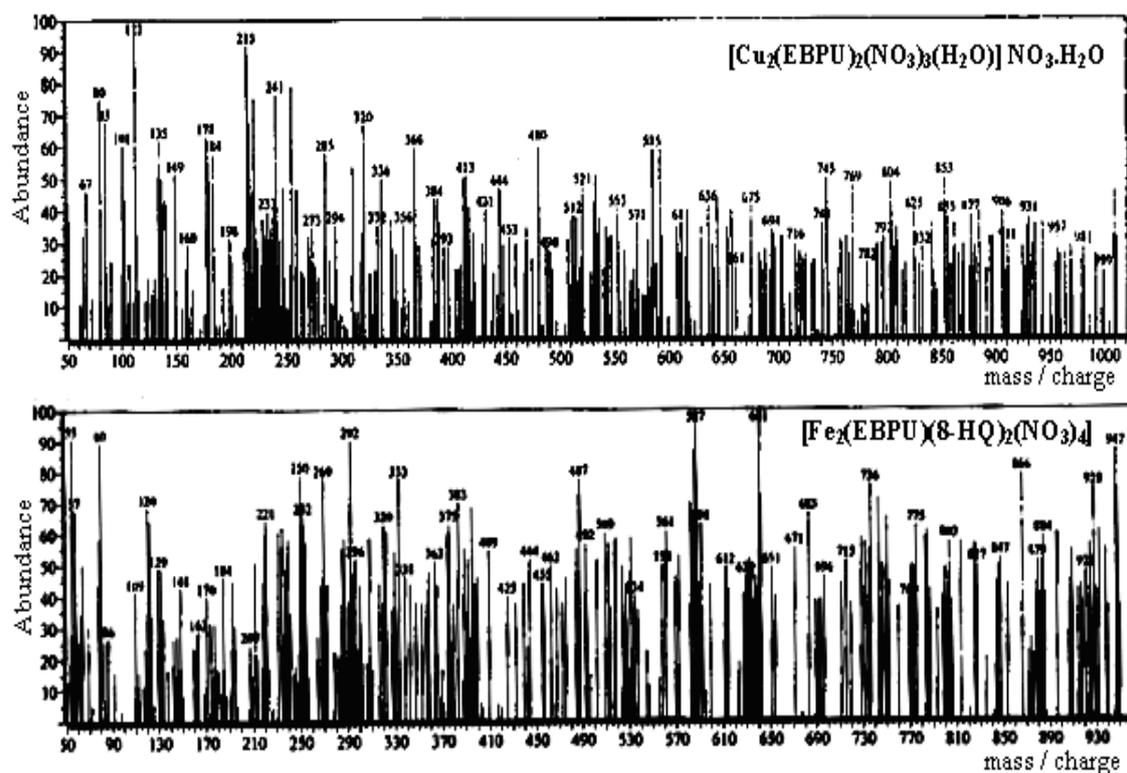


Fig. 4: Mass spectra of the  $[\text{Ni}_2(\text{EBPU})_2(\text{NO}_3)(\text{H}_2\text{O})_3](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$  (4),  $[\text{Cu}_2(\text{EBPU})_2(\text{NO}_3)_3(\text{H}_2\text{O})]\text{NO}_3 \cdot \text{H}_2\text{O}$  (7) and  $[\text{Fe}_2(\text{EBPU})(8\text{-HQ})_2(\text{NO}_3)_4]$  (12) complexes

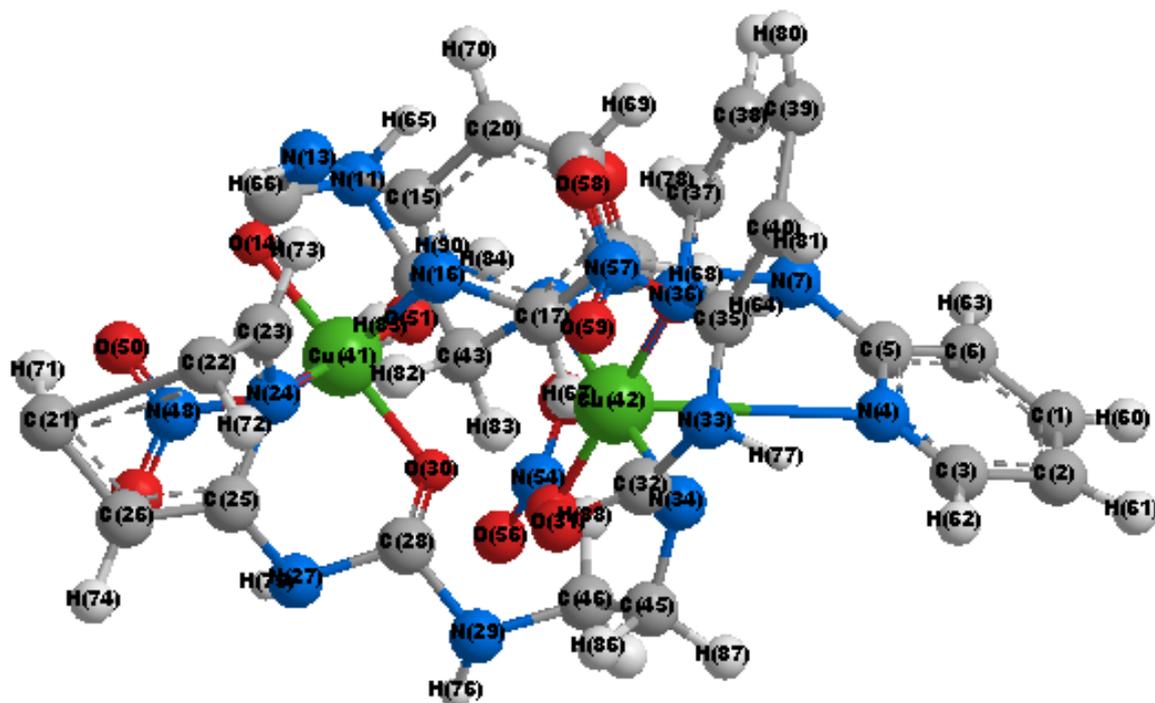


Fig. 5: 3D molecular modeling structure of complex (7)

**Table 1: Analytical and physical data of the metal complexes of the ligand EBPU**

Complex	Molecular formula	Colour	Yield (%)	m. p. (°C)	Elemental analysis, found (calcd)				Formula weight		$\Omega_m$ (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	
					(%C)	(%H)	(%N)	(%M)	Found <sup>a</sup>	calcd		
1	[Co <sub>2</sub> (EBPU) <sub>2</sub> ](NO <sub>3</sub> ) <sub>4</sub> .2H <sub>2</sub> O.EtOH	C <sub>30</sub> H <sub>42</sub> N <sub>16</sub> O <sub>19</sub> Co <sub>2</sub>	Pink	82.00	>300	34.14 (34.36)	4.34 (4.01)	21.01 (21.38)	10.27 (11.24)	—	1047.8	286.5
2	[Co <sub>3</sub> (EBPU) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> (EtOH) <sub>2</sub> (NO <sub>3</sub> ) <sub>4</sub> .2EtOH	C <sub>36</sub> H <sub>56</sub> N <sub>18</sub> O <sub>26</sub> Co <sub>3</sub>	Buff	81.25	>300	32.66 (32.42)	4.22 (4.20)	19.05 (18.91)	13.69 (13.26)	—	1332.7	316.5
3	[Co <sub>2</sub> (EBPU)(8-HQ) <sub>2</sub> ](H <sub>2</sub> O) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	C <sub>32</sub> H <sub>38</sub> N <sub>10</sub> O <sub>15</sub> Co <sub>2</sub>	brown	84.35	>300	41.12 (41.75)	4.02 (4.13)	15.17 (15.22)	13.69 (12.81)	—	919.8	182.0
4	[Ni <sub>2</sub> (EBPU) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> .3H <sub>2</sub> O	C <sub>28</sub> H <sub>44</sub> N <sub>16</sub> O <sub>22</sub> Ni <sub>2</sub>	Pale green	72.22	>300	31.86 (31.30)	4.11 (4.10)	20.60 (20.87)	10.24 (10.94)	1073.3	1073.4	233.5
5	[Ni <sub>3</sub> (EBPU) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (NO <sub>3</sub> ) <sub>4</sub> .2EtOH	C <sub>32</sub> H <sub>48</sub> N <sub>18</sub> O <sub>26</sub> Ni <sub>3</sub>	Pale green	70.62	>300	29.77 (30.09)	4.26 (3.76)	19.64 (19.75)	13.65 (13.80)	—	1276.1	279.0
6	[Ni <sub>2</sub> (EBPU)(8-HQ) <sub>2</sub> ](H <sub>2</sub> O) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> .5H <sub>2</sub> O	C <sub>32</sub> H <sub>46</sub> N <sub>10</sub> O <sub>19</sub> Ni <sub>2</sub>	Green	74.34	>300	38.39 (38.73)	3.95 (4.64)	— (14.12)	11.94 (11.84)	991.1	991.4	196.1
7	[Cu <sub>2</sub> (EBPU) <sub>2</sub> ](NO <sub>3</sub> ) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> .H <sub>2</sub> O	C <sub>28</sub> H <sub>36</sub> N <sub>16</sub> O <sub>18</sub> Cu <sub>2</sub>	Olive green	89.96	>300	33.04 (33.23)	3.68 (3.56)	21.60 (22.16)	12.92 (12.56)	1011.3	1011.0	63.6
8	[Cu <sub>3</sub> (EBPU) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (EtOH) <sub>2</sub> (NO <sub>3</sub> ) <sub>4</sub> .2H <sub>2</sub> O	C <sub>30</sub> H <sub>44</sub> N <sub>18</sub> O <sub>26</sub> Cu <sub>3</sub>	Greenish blue	87.19	>300	28.37 (28.51)	3.23 (3.49)	19.90 (19.96)	14.76 (15.09)	—	1262.5	291.0
9	[Cu <sub>2</sub> (EBPU)(8-HQ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	C <sub>32</sub> H <sub>28</sub> N <sub>10</sub> O <sub>10</sub> Cu <sub>2</sub>	Green	85.09	>300	45.37 (45.77)	3.25 (3.49)	16.75 (16.69)	14.77 (15.14)	840.3	839.0	177.6
10	[Fe <sub>3</sub> (EBPU) <sub>2</sub> ](NO <sub>3</sub> ) <sub>6</sub> (H <sub>2</sub> O) <sub>2</sub> (EtOH) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>	C <sub>32</sub> H <sub>48</sub> N <sub>21</sub> O <sub>35</sub> Fe <sub>3</sub>	Pale Brown	72.98	>300	26.51 (26.41)	3.23 (3.30)	— (20.22)	9.73 (11.55)	—	1454.0	205.9
11	[Fe <sub>2</sub> (EBPU)(NO <sub>3</sub> ) <sub>5</sub> (EtOH) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .2H <sub>2</sub> O	C <sub>20</sub> H <sub>38</sub> N <sub>12</sub> O <sub>25</sub> Fe <sub>2</sub>	Dark Brown	75.78	>300	24.46 (25.05)	3.25 (3.97)	16.54 (17.54)	11.35 (11.69)	958.3	958.0	69.4
12	[Fe <sub>2</sub> (EBPU)(8-HQ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>4</sub>	C <sub>32</sub> H <sub>28</sub> N <sub>12</sub> O <sub>16</sub> Fe <sub>2</sub>	Dark green	85.56	>300	40.73 (40.51)	2.99 (2.95)	— (17.72)	12.97 (11.81)	950.0	948.0	29.1
13	[(VO) <sub>2</sub> (EBPU) <sub>3</sub> ].3H <sub>2</sub> O	C <sub>42</sub> H <sub>50</sub> N <sub>18</sub> O <sub>11</sub> V <sub>2</sub>	Dark green	75.54	>300	46.84 (46.50)	5.24 (4.61)	23.26 (23.25)	— (9.39)	—	1083.8	34.2
14	[UO <sub>2</sub> (EBPU) <sub>2</sub> ](H <sub>2</sub> O) <sub>5</sub> .H <sub>2</sub> O	C <sub>28</sub> H <sub>42</sub> N <sub>12</sub> O <sub>12</sub> U	Yellow	75.60	>300	34.45 (34.43)	3.74 (4.30)	17.25 (17.21)	— (24.39)	—	976.0	28.4

<sup>a</sup> value obtained from mass spectra.**Table 2: Important IR spectral data and their assignment for the ligand EBPU and its metal complexes**

No.	Compound or complex	IR spectral bands (cm <sup>-1</sup> )						Other bands
		$\nu(\text{OH})$ (H <sub>2</sub> O/EtOH)	$\nu(\text{NH})$	$\nu(\text{C}=\text{O})$	Pyridine stretching vibrations	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	
	EBPU (H <sub>2</sub> L <sup>2</sup> )	—	3219, 3090	1682	1584, 1479	—	—	—
1	[Co <sub>2</sub> (EBPU) <sub>2</sub> ](NO <sub>3</sub> ) <sub>4</sub> .2H <sub>2</sub> O.EtOH	3462	3289, 3093	1679, 1618	1583, 1486	519	423	$\nu(\text{NO}_3^-)$ ionic 1384
2	[Co <sub>3</sub> (EBPU) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> (EtOH) <sub>2</sub> (NO <sub>3</sub> ) <sub>4</sub> .2EtOH	3462	3288, 3093	1678, 1617	1581, 1484	519	423	$\nu(\text{NO}_3^-)$ ionic, $\nu(\text{NO}_3^-)$ monodentate 1433 1400, 1329, 1234
3	[Co <sub>2</sub> (EBPU)(8-HQ) <sub>2</sub> ](H <sub>2</sub> O) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	3461	3290, 3093	1678, 1617	1579, 1485	517	414	$\nu(\text{NO}_3^-)$ ionic 1384
4	[Ni <sub>2</sub> (EBPU) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> .3H <sub>2</sub> O	3462	3290, 3093	1682, 1622	1583, 1486	519	427	$\nu(\text{NO}_3^-)$ ionic, $\nu(\text{NO}_3^-)$ monodentate 1435 1384, 1332, 1233
5	[Ni <sub>3</sub> (EBPU) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (NO <sub>3</sub> ) <sub>4</sub> .2EtOH	3465	3290, 3092	1682, 1621	1581, 1485	519	427	$\nu(\text{NO}_3^-)$ ionic, $\nu(\text{NO}_3^-)$ monodentate 1437 1394, 1330, 1231
6	[Ni <sub>2</sub> (EBPU)(8-HQ) <sub>2</sub> ](H <sub>2</sub> O) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> .5H <sub>2</sub> O	3462	3292, 3093	1682, 1622	1581, 1485	517	418	$\nu(\text{NO}_3^-)$ ionic 1384
7	[Cu <sub>2</sub> (EBPU) <sub>2</sub> ](NO <sub>3</sub> ) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> .H <sub>2</sub> O	3375	3281, 3091	1679, 1617	1565, 1483	520	428	$\nu(\text{NO}_3^-)$ ionic, $\nu(\text{NO}_3^-)$ monodentate 1432 1383, 1282, 1232
8	[Cu <sub>3</sub> (EBPU) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (EtOH) <sub>2</sub> (NO <sub>3</sub> ) <sub>4</sub> .2H <sub>2</sub> O	3543	3282, 3091	1681, 1617	1565, 1483	519	428	$\nu(\text{NO}_3^-)$ ionic, $\nu(\text{NO}_3^-)$ monodentate 1431 1354, 1281, 1232,
9	[Cu <sub>2</sub> (EBPU)(8-HQ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	—	3230, 3092	1680, 1616	1572, 1496	523	417	$\nu(\text{NO}_3^-)$ ionic 1379
10	[Fe <sub>3</sub> (EBPU) <sub>2</sub> ](NO <sub>3</sub> ) <sub>6</sub> (H <sub>2</sub> O) <sub>2</sub> (EtOH) <sub>2</sub> (N	3443	3272,	1679,	1581, 1483	529	417	$\nu(\text{NO}_3^-)$ ionic,

	$O_3)_3$		3093	1616				$\nu(NO_3^-)$ monodentate 1443 1384, 1284, 1235
11	$[Fe_2(EBPU)(NO_3)_5(EtOH)_3]NO_3 \cdot 2H_2O$	3390	3252, 3092	1678, 1616	1581, 1482	514	423	$\nu(NO_3^-)$ ionic, $\nu(NO_3^-)$ monodentate 1437 1411, 1310, 1224
12	$[Fe_2(EBPU)(8-HQ)_2(NO_3)_4]$	—	3283, 3092	1678, 1620	1576, 1500	514	417	$\nu(NO_3^-)$ monodentate 1384, 1292, 1233
13	$[(VO)_2(EBPU)_3] \cdot 3H_2O$	3356	3269, 3090	1686, 1647	1577, 1484	518	408	$\nu(V=O)$ 985
14	$[UO_2(EBPU)_2(H_2O)] \cdot 5H_2O$	3356	3268, 3091	1686, 1647	1577, 1486	518	408	$\nu(O=U=O)$ 926

## and magnetic moment values

No.	Compound or complex	Electronic spectral bands		$\mu_{eff}^a$ (B.M.)	$\mu_{compl}^b$ (B.M.)
		$\lambda_{max}$ (nm)	$\epsilon_{max}$ ( $mol^{-1}cm^{-1}L$ )		
	EBPU	244, 291, 430	3388, 3472, 5	-	-
1	$[Co_2(EBPU)_2](NO_3)_4 \cdot 2H_2O \cdot EtOH$	525	40	3.95	6.81
2	$[Co_3(EBPU)_2(NO_3)_2(EtOH)_2](NO_3)_4 \cdot 2EtOH$	526	67	4.12	10.27
3	$[Co_2(EBPU)(8-HQ)_2(H_2O)_4](NO_3)_2 \cdot H_2O$	535	746	3.56	6.45
4	$[Ni_2(EBPU)_2(NO_3)(H_2O)_3](NO_3)_3 \cdot 3H_2O$	563, 667	40, 13	2.58	5.06
5	$[Ni_3(EBPU)_2(NO_3)_2(H_2O)_2](NO_3)_4 \cdot 2EtOH$	556	20	2.47	6.01
6	$[Ni_2(EBPU)(8-HQ)_2(H_2O)_4](NO_3)_2 \cdot 5H_2O$	628, 752	52, 8	2.57	5.05
7	$[Cu_2(EBPU)_2(NO_3)_3(H_2O)] \cdot NO_3 \cdot H_2O$	560, 644	69, 45	2.22	3.14
8	$[Cu_3(EBPU)_2(NO_3)_2(H_2O)(EtOH)](NO_3)_4 \cdot 2H_2O$	641	149	2.18	3.99
9	$[Cu_2(EBPU)(8-HQ)_2](NO_3)_2$	692	561	2.12	3.70
10	$[Fe_3(EBPU)_2(NO_3)_6(H_2O)_2(EtOH)_2](NO_3)_3$	540	1022	5.31	9.2
11	$[Fe_2(EBPU)(NO_3)_5(EtOH)_3]NO_3 \cdot 2H_2O$	531	729	5.56	5.82
12	$[Fe_2(EBPU)(8-HQ)_2(NO_3)_4]$	577	817	5.72	6.67
13	$[(VO)_2(EBPU)_3] \cdot 3H_2O$	685	13	2.23	3.15
14	$[UO_2(EBPU)_2(H_2O)] \cdot 5H_2O$	590	27	-	-

<sup>a</sup>  $\mu_{eff}$  (B.M.) of one cationic species in the complex; <sup>b</sup>  $\mu_{eff}$  (B.M.) the total magnetic moments of all cations in the complex.

**Table 4: Results of thermogravimetric analysis (TGA)  
of some complexes of the ligand EBPU**

Complex No.	Molecular formula of the complex (M. Wt.)	Temperature Range (°C)	Wt loss % Found % (calcd %)	Decomposed product lost
1	$[\text{Co}_2(\text{EBPU})_2](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O} \cdot \text{EtOH}$ (1047.8)	73 - 163 164 - 303 304 - 521	6.09 (6.11) 45.79 (45.62) 27.40 (27.39) 20.92 (20.88)	lattice EtOH + one molecule of lattice H <sub>2</sub> O lattice H <sub>2</sub> O + 4 NO <sub>2</sub> + 2 O <sub>2</sub> + C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> + 2 C <sub>2</sub> H <sub>4</sub> C <sub>12</sub> H <sub>13</sub> N <sub>7</sub> O <sub>2</sub> Residue, Co <sub>2</sub> (C <sub>2</sub> H <sub>3</sub> N <sub>3</sub> O <sub>2</sub> )
3	$[\text{Co}_2(\text{EBPU})(8\text{-HQ})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (919.8)	40 - 135 136 - 291 292 - 435 436 - 615	4.25 (3.91) 30.87 (30.88) 22.06 (22.18) 24.47 (25.01) 18.46 (18.03)	lattice H <sub>2</sub> O + one molecule of coordinated H <sub>2</sub> O 3 coordinated H <sub>2</sub> O + 2 NO <sub>2</sub> + O <sub>2</sub> + C <sub>7</sub> H <sub>8</sub> N C <sub>9</sub> H <sub>10</sub> N <sub>5</sub> O C <sub>16</sub> H <sub>10</sub> N <sub>2</sub> Residue, Co <sub>2</sub> O <sub>3</sub>
4	$[\text{Ni}_2(\text{EBPU})_2(\text{NO}_3)(\text{H}_2\text{O})_3](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ (1073.4)	43 - 161 162 - 354 355 - 585	5.14 (5.03) 43.31 (42.67) 21.37 (21.15) 30.18 (31.15)	3 lattice H <sub>2</sub> O 3 coordinated H <sub>2</sub> O + 4 NO <sub>2</sub> + 2 O <sub>2</sub> + C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> C <sub>14</sub> H <sub>17</sub> N <sub>3</sub> Residue, Ni <sub>2</sub> (C <sub>4</sub> H <sub>7</sub> N <sub>7</sub> O <sub>4</sub> )
7	$[\text{Cu}_2(\text{EBPU})_2(\text{NO}_3)_3(\text{H}_2\text{O})] \text{NO}_3 \cdot \text{H}_2\text{O}$ (1011.0)	64 - 287 288 - 646	44.42 (43.52) 24.37 (23.94) 32.01 (32.54)	lattice H <sub>2</sub> O + coordinated H <sub>2</sub> O + 4 NO <sub>2</sub> + 2 O <sub>2</sub> + C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> C <sub>14</sub> H <sub>18</sub> N <sub>4</sub> Residue, Cu <sub>2</sub> (C <sub>2</sub> H <sub>3</sub> N <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>
11	$[\text{Fe}_2(\text{EBPU})(\text{NO}_3)_5(\text{EtOH})_3]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ (958.0)	29 - 274 275 - 531	54.16 (53.65) 9.85 (9.81) 36.02 (36.53)	2 lattice H <sub>2</sub> O + 3 coordinated EtOH + 6 NO <sub>2</sub> + 2 O <sub>2</sub> C <sub>5</sub> H <sub>6</sub> N <sub>2</sub> Residue, Fe <sub>2</sub> (C <sub>9</sub> H <sub>10</sub> N <sub>4</sub> O <sub>4</sub> )
13	$[(\text{VO})_2(\text{EBPU})_3] \cdot 3\text{H}_2\text{O}$ (1083.8)	108 - 426 427 - 674	71.58 (71.23) 9.11 (8.49) 19.55 (20.28)	3 lattice H <sub>2</sub> O + C <sub>35</sub> H <sub>38</sub> N <sub>14</sub> O <sub>4</sub> C <sub>5</sub> H <sub>4</sub> N <sub>2</sub> Residue, (VO) <sub>2</sub> (C <sub>2</sub> H <sub>2</sub> N <sub>2</sub> O <sub>2</sub> )

**Table 5: The order (n), temperature of decomposition and activation parameters (E\*, ΔH\*, ΔS\*, ΔG\*) for decomposition steps of some complexes of the ligand EBPU**

No.	Complex	Step	n	r	Thermodynamic activation parameters				
					E* (kJmol <sup>-1</sup> )	ΔH* (kJmol <sup>-1</sup> )	A (S <sup>-1</sup> )	ΔS* (kJmol <sup>-1</sup> K <sup>-1</sup> )	ΔG* (kJmol <sup>-1</sup> )
1	[Co <sub>2</sub> (EBPU) <sub>2</sub> ](NO <sub>3</sub> ) <sub>4</sub> .2H <sub>2</sub> O.EtOH	1 <sup>st</sup>	0.5	0.99998	7.22	3.99	1.209	-0.17826	73.09
		2 <sup>nd</sup>	0.66	0.982112	12.46	7.94	8.374	-0.18412	108.03
		3 <sup>rd</sup>	0.66	0.999592	13.84	8.26	8.522	-0.18573	132.97
3	[Co <sub>2</sub> (EBPU)(8-HQ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	1 <sup>st</sup>	0.66	0.999405	6.38	3.23	2.045	-0.17370	69.09
		2 <sup>nd</sup>	0.66	0.990188	9.94	5.45	1.225	-0.18090	103.24
		3 <sup>rd</sup>	0.66	0.997965	12.81	7.09	9.562	-0.18498	134.44
		4 <sup>th</sup>	0.66	0.999651	16.18	9.49	7.388	-0.18842	161.12
4	[Ni <sub>2</sub> (EBPU) <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>3</sub> ](NO <sub>3</sub> ) <sub>3</sub> .3H <sub>2</sub> O	1 <sup>st</sup>	0	0.999996	7.04	4.05	6.057	-0.18339	106.76
		2 <sup>nd</sup>	0.66	0.992078	12.24	7.62	8.862	-0.18383	109.71
		3 <sup>rd</sup>	0.66	0.999739	13.99	8.20	8.683	-0.18588	137.67
7	[Cu <sub>2</sub> (EBPU) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> (H <sub>2</sub> O)] NO <sub>3</sub> .H <sub>2</sub> O	1 <sup>st</sup>	0.66	0.981628	9.90	5.47	1.192	-0.18101	101.83
		2 <sup>nd</sup>	0.66	0.999861	12.13	7.36	9.975	-0.18312	112.43
11	[Fe <sub>2</sub> (EBPU)(NO <sub>3</sub> ) <sub>5</sub> (EtOH) <sub>3</sub> ]NO <sub>3</sub> .2H <sub>2</sub> O	1 <sup>st</sup>	0.66	0.980302	9.04	4.96	1.239	-0.18001	93.27
		2 <sup>nd</sup>	0.66	0.998977	11.88	6.34	1.073	-0.18375	134.37
13	[(VO) <sub>2</sub> (EBPU) <sub>3</sub> ].3H <sub>2</sub> O	1 <sup>st</sup>	0.66	0.987644	13.72	9.36	6.059	-0.18652	107.28
		2 <sup>nd</sup>	0.66	0.999066	14.81	8.07	8.685	-0.18714	159.81

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