



Infrared spectroscopic interpretations on the reaction products resulted from the interaction between Co(II), Cu(II), Fe(III), Mn(II), Ni(II) and Zn(II) phosphate salts with urea at 85 °C

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ABSTRACT

The complexation mode of urea (U) with cobalt(II), copper(II), ferric(III), manganese(II), nickel(II), and zinc(II) phosphate salts at 85 °C temperature with 3-5 hrs has been studied by conductivity measurements and infrared spectroscopy. The high values of molar conductivity of the resulting urea complexes show them to be electrolytes in nature. The physical and spectral data were well explained in terms of the formation of $[Co_3(NH_2CONH_2)_6](PO_4)_2$, $[Cu_3(NH_2CONH_2)_4](PO_4)_2$, $[Fe(NH_2CONH_2)_6] PO_4$, $[Mn_3(NH_2CONH_2)_6](PO_4)_2$, $[Ni_3(NH_2CONH_2)_6](PO_4)_2$ and $[Zn_3(NH_2CONH_2)_4](PO_4)_2$. On the basis of the infrared spectral data and the values of stretching vibrational bands of both $-C=O$ and $-NH_2$ groups, the complexation of metal ions toward urea was distinguished.

Keywords: Urea, Transition metal phosphate, Conductance, Infrared spectra.

INTRODUCTION

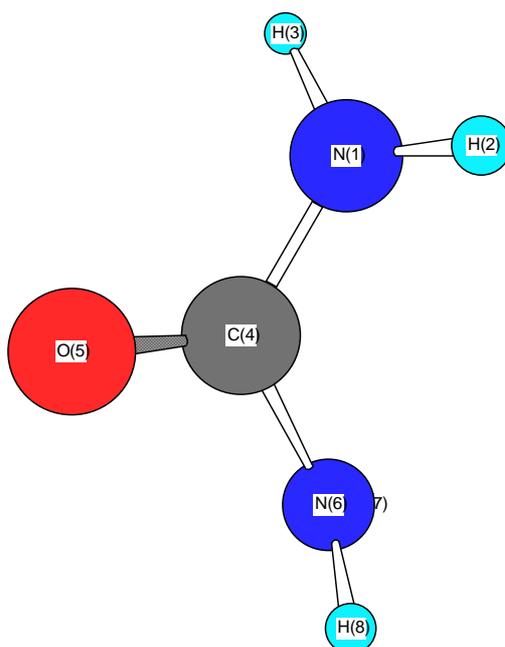
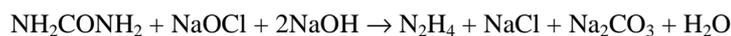
Carbamide, carbonyldiamide or the most famous name, urea (Scheme 1), CH_4N_2O , was first prepared by Wöhler [1] by evaporating a solution containing a mixture of potassium isocyanate and ammonium sulphate. Ammonium isocyanate, which is formed first, undergoes molecular rearrangement to give urea, as shown by the following reaction;



Urea may be prepared in the laboratory by the action of ammonia with carbonyl chloride, alkyl carbonates, chloroformates or urethans. Industrially [2-4], urea is prepared by allowing liquid carbon dioxide and liquid ammonia to interact, and heating the formed ammonium carbamate at 130-150 °C under about 35 atmospheric pressure. The carbamate is decomposed to form urea and water according to the following reaction;



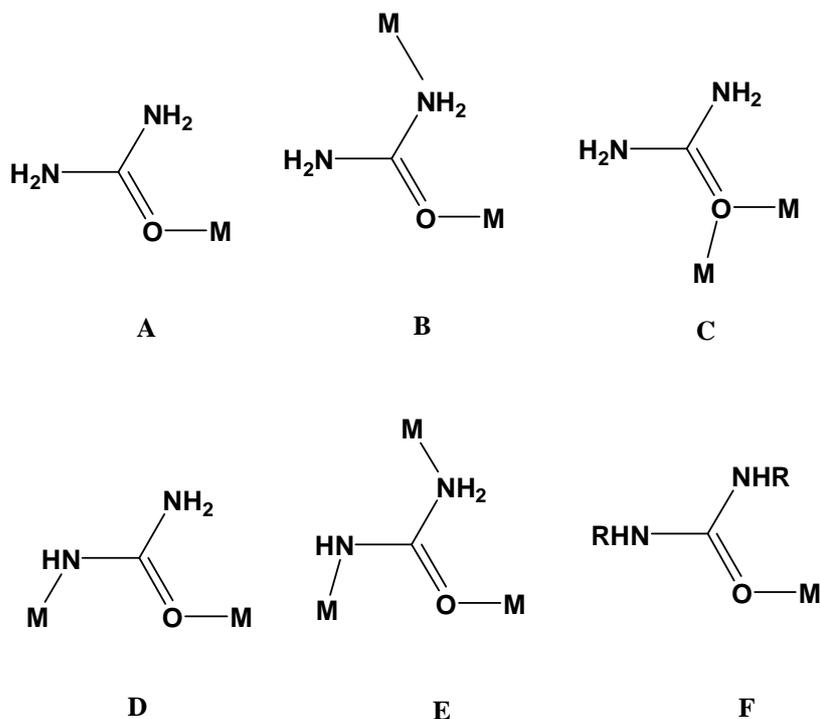
Urea is physiologically very important. It is the chief nitrogenous product of protein metabolism. Adults excrete about 30g of urea per day in the urine, from which it can be extracted by evaporating the urine to small volume and adding nitric acid, to give the slightly soluble urea nitrate, $CO(NH_2)_2.HNO_3$. Urea has a melting point of 132°C, soluble in water and ethanol, but insoluble in ether. Urea is used for preparing formaldehyde-Urea resin (plastics) [5], barbiturates [6], and fertilizers [7-10]. Urea is also extensively used in the paper industry to soften cellulose and has been used to promote healing in infected wounds and many other applications in the field of medicine [11-13]. Recently, urea is used for the manufacture of hydrazine in which urea is treated with alkaline sodium hypochlorite [6] e.g.,



Scheme 1: Structure of urea

Urea is used in reactive dyeing [14] which has an effect on the formation and cleavage of covalent bond between the reactive dye and cellulose. The overall effect of urea on reactive dyeing depends on the solvolytic stability of the dye-fiber bond under specific dyeing conditions.

Complexes of urea with some metal ions are used as fertilizers [15-18]. Complexes of urea with zinc sulphate and nitrate, $[\text{Zn}(\text{CON}_2\text{H}_4)_6]\text{SO}_4 \cdot \text{H}_2\text{O}$ and $[\text{Zn}(\text{CON}_2\text{H}_4)_4](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ have very important application in this field [19]. These complexes were found to increase the yield of rice more than a dry mixture of urea-zinc salt does. Calcium nitrate-urea complex, $[\text{Ca}(\text{urea})_4](\text{NO}_3)_2$, [20,21] was used also as an adduct fertilizer. Some metal-urea complexes have pharmaceutical application, e.g., the platinum-urea complex which is used as antitumor [22].



Scheme 2: The coordination modes of urea towards metal ions

Crystal structure studies have shown that in solid urea, both nitrogen atoms are identical. Bond length measurements [6] in urea give the C-N distance as 1.37\AA , while, in aliphatic amines the C-N bond length is 1.47\AA . This indicates that the C-N bond in urea has some double bond character (about 28%).

Urea usually coordinates as a monodentate ligand through the oxygen atom, forming a $\text{C}=\text{O} \cdots \text{M}$ angle considerably smaller than 180° , in accordance with the sp^2 hybridization of the O atom (**A** in Scheme 2). The rare N,O-bidentate coordination mode (**B** in Scheme 2) has been found in a very limited number of cases [23, 24], while in $[\text{Hg}_2\text{Cl}_4\text{U}_2]$ each U molecule bridges the two Hg^{II} atoms through the oxygen atom [25] (**C** in Scheme 2). Of particular chemical/biological interest is the ability of U to undergo metal-promoted deprotonation [26]; the monoanionic ligand H_2NCONH^- adopts the μ_2 (**D** in Scheme 2) and μ_3 (**E** in Scheme 2) coordination modes. The urea and its derivatives such as the N,N'-dimethylurea and N,N'-diethylurea (Scheme 2) have only been found to coordinate as monodentate ligands through the oxygen atom (**F** in Scheme 2).

Raman and infrared spectra of urea have been observed by several investigators [27-32]. The normal vibrations of the urea molecule were calculated by Kellner [33] on the assumption of the non-planar model. However, on the basis of the dichronic measurement of the infrared band arising from the N-H stretching vibration by Waldron and Badger [34] and the proton magnetic resonance absorption measurement made by Andrew and Hyndman [35], it is concluded that urea molecule has a planar structure. Yamaguchi *et al.* [36] calculated the normal vibrations of the C_{2v} model of urea molecule as an eight-body problem using a potential function of the Urey-Bradley force field and obtained the force constants which have been refined by the least-squares method. Based on the result of these calculations, Yamaguchi [36], assigned all of the observed frequencies in the spectra of urea and urea- d_4 . To the two vibrations of the frequencies 1686 and 1603cm^{-1} , there are considerable contributions of both CO stretching and NH_2 bending motions, whereas Stewart [37] assigned the 1686cm^{-1} band to CO stretching vibration and the 1603cm^{-1} band to NH_2 bending motion. The calculations studied by Yamaguchi showed that for the band at 1686cm^{-1} , the contribution of the NH_2 bending motion is greater than that of CO stretching motion. The band at 1629cm^{-1} corresponds to almost pure NH_2 bending vibration. The NH_2 bending motion of A_1 type is equal to that of B_2 type. The A_1 type band should have a frequency of about 1630cm^{-1} , if there is no coupling between NH_2 bending and CO stretching motions. On the other hand, the observed frequency of 1610cm^{-1} of urea- d_4 is assigned to almost pure skeletal vibration. Therefore, the interaction between the 1630 and 1610cm^{-1} vibration gives rise to the two observed bands at 1686 and 1603cm^{-1} . The infrared bands of urea- d_4 observed at 1245 and 1154cm^{-1} are assigned, respectively, to A_1 type and B_2 type, ND_2 bending vibrations. This assignment is consistent with the observed depolarization degrees of the Raman lines. The large frequency difference between the A_1 and B_2 vibrations is due to the fact that in the A_1 vibration, the cross term related to the CN stretching vibration is large.

The 1464cm^{-1} frequency of urea is assigned to the CN stretching vibration of B_2 type. The corresponding frequency of urea- d_4 is observed at 1490cm^{-1} . The 1150cm^{-1} band is assigned to NH_2 rocking vibrations of both A_1 and B_2 types. The normal vibration calculation yields almost the same values for these frequencies.

Urea possesses two types of potential donor atoms, the carbonyl oxygen and amide nitrogens. Penland *et al.* [38] studied the infrared spectra of urea complexes to determine whether coordination occurs through oxygen or nitrogen atoms. The electronic structure of urea may be represented by a resonance hybrid of structures **A-F** as shown in scheme 1 with each contributing roughly an equal amount. If coordination occurs through nitrogen, contributions of structure **B** will decrease. This results in an increase of the CO stretching frequency with a decrease of CN stretching frequency. The N-H stretching frequency in this case may fall in the same range as those of the amido complexes. If coordination occurs through oxygen, the contribution of structure (**A**) will decrease. This may result in a decrease of the CO stretching frequency but no appreciable change in NH stretching frequency. Since the vibrational spectrum of urea itself has been analyzed completely [36], band shifts caused by coordination can be checked immediately. For example, the effect of the coordination on the spectra of the complexes of urea with $\text{Pt}(\text{II})$ and $\text{Cr}(\text{III})$ in which the coordination occurs through nitrogen and oxygen atoms, respectively [38]. The mode of coordination of urea with metal ions seems to be dependent upon the type and nature of metal. $\text{Pd}(\text{II})$ coordinates to the nitrogen, whereas $\text{Fe}(\text{III})$, $\text{Zn}(\text{II})$, and $\text{Cu}(\text{II})$ coordinate to the oxygen of urea [38].

In urea-metal complexes, if a nitrogen-to-metal bond is present, the vibrational spectrum of this complex differs significantly from that of the free urea molecule. The N-H stretching frequencies would be shifted to lower values, and the $\text{C}=\text{O}$ bond stretching vibration, ($\nu(\text{C}=\text{O})$) would be shifted to higher frequency at about 1700cm^{-1} [39].

Recently, urea represents not only an important molecule in biology [40] but also an important raw material in chemical industry [41]. The present paper of this publication is to report the synthesis, infrared characterization, and conductance behavior of the resulting compounds formed from the reactions of urea with cobalt(II), copper(II), ferric(III), manganese(II), nickel(II), and zinc(II) phosphate salts at 85°C temperature with 3-5 hrs.

EXPERIMENTAL SECTION

2-1- Materials

Urea, $\text{Co}_3(\text{PO}_4)_2$, $\text{Cu}_3(\text{PO}_4)_2$, FePO_4 , $\text{Mn}_3(\text{PO}_4)_2$, $\text{Ni}_3(\text{PO}_4)_2$, and $\text{Zn}_3(\text{PO}_4)_2$ were obtained from Aldrich Company. Urea was received from Fluka chemical company. All chemicals used in this study were of analytically reagent grade and used without further purification.

2-2- Synthesis of transition metal phosphate urea complexes

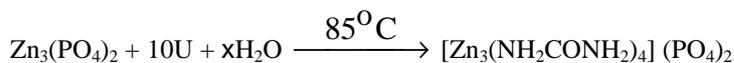
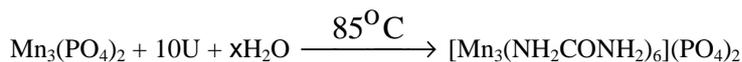
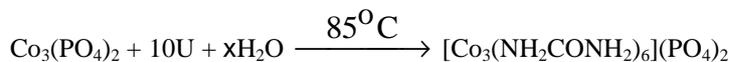
The urea complexes, $[\text{Co}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, $[\text{Cu}_3(\text{NH}_2\text{CONH}_2)_4](\text{PO}_4)_2$, $[\text{Fe}(\text{NH}_2\text{CONH}_2)_6]\text{PO}_4$, $[\text{Mn}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, $[\text{Ni}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, and $[\text{Zn}_3(\text{NH}_2\text{CONH}_2)_4](\text{PO}_4)_2$ were prepared as a 50 mL volume of urea solution (0.1 mole) was mixed with an equal volume of (0.01 mole) $\text{Co}_3(\text{PO}_4)_2$, $\text{Cu}_3(\text{PO}_4)_2$, FePO_4 , $\text{Mn}_3(\text{PO}_4)_2$, $\text{Ni}_3(\text{PO}_4)_2$, and $\text{Zn}_3(\text{PO}_4)_2$ in 50 mL distilled water. The mixtures were stirred for about 2 hr then heated to 85 °C for 3-5 hours on a water bath under refluxed system. The precipitated products were filtered off, dried at 60 °C in an oven for 3 hours and then dried under *vacuo* over anhydrous calcium chloride.

2-3- Measurements

The molar conductivities of freshly prepared 1.0×10^{-3} mol/cm³ dimethylsulfoxide (DMSO) solutions were measured for the soluble urea complexes using Jenway 4010 conductivity meter. The infrared spectra with KBr discs were recorded on a Shimadzu FT-IR Spectrophotometer (4000–400 cm⁻¹). The X-ray diffraction patterns for the urea phosphate complexes at 800 °C were recorded on X'Pert PRO PANalytical X-ray powder diffraction, target copper with secondary monochromate.

RESULTS AND DISCUSSION

The color, physical characteristic, molecular weight data, formula weight, and molar conductance measurements of Co(II), Cu(II), Fe(III), Mn(II), Ni(II), and Zn(II) phosphate urea complexes are given in Table 1. The formula weight data of the prepared complexes revealed 1:6 molar ratio (M: urea) except for Cu(II) and Zn(II) complexes are 1:4 (M: urea) and good agreement with the general formulas $[\text{Co}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, $[\text{Cu}_3(\text{NH}_2\text{CONH}_2)_4](\text{PO}_4)_2$, $[\text{Fe}(\text{NH}_2\text{CONH}_2)_6]\text{PO}_4$, $[\text{Mn}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, $[\text{Ni}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, and $[\text{Zn}_3(\text{NH}_2\text{CONH}_2)_4](\text{PO}_4)_2$ complexes. The reactions can be represented by the stoichiometric equations:



The complexes are stable, high melting points, soluble in dimethylsulfoxide, DMSO. The molar conductivities of 10^{-3} mol dm⁻³ solutions of the prepared complexes in DMSO (Table 1) indicate that the complexes have an electrolytic nature.

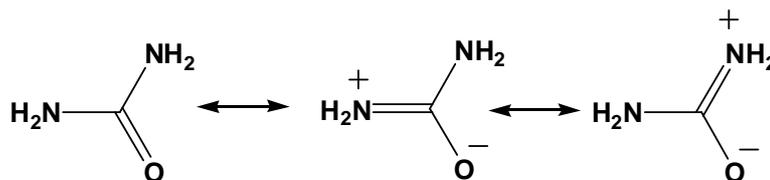
3-1- Molar conductance measurements

The molar conductivity values for the urea complexes in DMSO solvent (10^{-3} mol dm⁻³) are exhibited in the range of (65–93) Ω⁻¹cm²mol⁻¹, suggesting them to be electrolytes (Table 1). Conductivity measurements have frequently been used in structural of metal complexes (mode of coordination) within the limits of their solubility. They provide a method of testing the degree of ionization of the complexes, the molar ions that a complex liberates in solution (in case of presence anions outside the coordination sphere), the higher will be its molar conductivity and vice versa. It is clear from the conductivity data that the complexes present seem to be electrolytes. Also the molar conductance values indicate that the anions present outside the coordination sphere. This result was confirmed from the elemental analysis data where PO_4^{3-} ions are precipitated with colored solution by adding of respective reagents solutions, this experimental test is a good matched with CHN data. All these complexes have electrolytic properties. This fact

elucidated that the anions are present. These results establish the stoichiometry of these complexes, which are in agreement with the general formulas were suggested.

3-2- Infrared spectra

The infrared spectra of the Co(II), Cu(II), Fe(III), Mn(II), Ni(II), and Zn(II) phosphate urea complexes at room 85 °C and 800 °C temperature are shown in Figs. 1 and 2, respectively. The band locations were measured for the mentioned transition metal-urea phosphate complexes, together with the proposed assignments for the most characteristic vibrations are presented in Table 2. In order to facilitate the spectroscopic analysis and to put our hand on proper structure of the prepared complexes, the spectra of the transition metal-urea-phosphate complexes were accurately compared with those of the urea and similar complexes in literature survey. The infrared spectra in the wide frequency range (4000–400 cm^{-1}) are shown in Fig. 1, whereas the region between 1500–to–400 cm^{-1} is focused to Co(II), Cu(II), Fe(III), Mn(II), Ni(II), and Zn(II) phosphate urea complexes at 800 °C temperatures (Fig. 2). The discussion of the spectra will be addressed on the basis of the most characteristic vibrations. The assignments of full vibrational analysis of crystalline urea have been published [38]. Table 2 gives diagnostic infrared peaks of the free urea ligand, published work and six transition metal-urea-phosphate complexes. Assignments have been given in comparison with the data obtained for the free urea, that is, coordinated, U [38] and its $[\text{Pt}(\text{urea})_2\text{Cl}_2]$ and $[\text{Cr}(\text{urea})_6]\text{Cl}_3$ complexes [38]. The effect of the coordination on the spectra of the complexes of urea with $[\text{Pt}(\text{urea})_2\text{Cl}_2]$ and $[\text{Cr}(\text{urea})_6]\text{Cl}_3$ complexes in which the coordination occurs through nitrogen and oxygen atoms, respectively [38]. The mode of coordination of urea with metal ions seems to be dependent upon the type and nature of metal. Pd(II) ions in $[\text{Pt}(\text{urea})_2\text{Cl}_2]$ coordinate to the nitrogen, whereas Fe(III), Zn(II), and Cu(II) coordinate to the oxygen of urea [38]. The distinguished bands of $\nu(\text{C}-\text{N})$ are exhibited at same or higher wavenumbers in the spectra of $[\text{Co}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, $[\text{Cu}_3(\text{NH}_2\text{CONH}_2)_4](\text{PO}_4)_2$, $[\text{Fe}(\text{NH}_2\text{CONH}_2)_6]\text{PO}_4$, $[\text{Mn}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, $[\text{Ni}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, and $[\text{Zn}_3(\text{NH}_2\text{CONH}_2)_4](\text{PO}_4)_2$ complexes than for free urea, whereas the $\nu(\text{C}=\text{O})$ band shows a lower frequency wavenumber than free urea. These shifts are consistent with oxygen coordination, suggesting the presence of $(\text{NH}_2)_2-\text{C}=\text{O}-\text{M}$ resonance features [42], see Scheme 3.



Scheme 3: Resonance types of urea

Table 1: Physical characterization, micro-analytical and molar conductance data of transition metal urea phosphate complexes

Complexes Molecular formula	Color	Molar ratio M: urea	Molecular weight g/mol	Λ_m ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
$[\text{Co}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$	Violet	1:2	727.07	77
$[\text{Cu}_3(\text{NH}_2\text{CONH}_2)_4](\text{PO}_4)_2$	Blue	3:4	620.80	68
$[\text{Fe}(\text{NH}_2\text{CONH}_2)_6]\text{PO}_4$	Brown	1:6	511.15	65
$[\text{Mn}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$	Light brown	1:2	715.09	93
$[\text{Ni}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$	Green	1:2	726.91	87
$[\text{Zn}_3(\text{NH}_2\text{CONH}_2)_4](\text{PO}_4)_2$	White	3:4	626.33	81

Table 2: Characteristic infrared frequencies (cm^{-1}) and tentative assignments of urea (U), $[\text{Pt}(\text{urea})_2\text{Cl}_2]$ (A), $[\text{Cr}(\text{urea})_6]\text{Cl}_3$ (B), $[\text{Co}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, $[\text{Cu}_3(\text{NH}_2\text{CONH}_2)_4](\text{PO}_4)_2$, $[\text{Fe}(\text{NH}_2\text{CONH}_2)_6]\text{PO}_4$, $[\text{Mn}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, $[\text{Ni}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, and $[\text{Zn}_3(\text{NH}_2\text{CONH}_2)_4](\text{PO}_4)_2$ complexes

U	A	B	Co(II)	Cu(II)	Fe(III)	Mn(II)	Ni(II)	Zn(II)	Assignments ^(b)
3450	3390 3290	3440 3330	3392	3400	3385	3410	3387	3396	$\nu_{\text{as}}(\text{NH}_2)$
3350	3130 3030	3190	3121	3128	3132	3120	3130	3132	$\nu_{\text{s}}(\text{NH}_2)$
1683	1725	1505	1588	1590	1593	1590	1584	1580	$\delta(\text{C}=\text{O})$
1471	1395	1505	1478	1483	1480	1484	1493	1490	$\nu(\text{C}-\text{N})$
---	---	---	1031	1032	1031	1035	1035	1037	$\nu(\text{P}-\text{O})$
---	---	---	585	593	594	588	590	582	$\delta(\text{O}-\text{P}-\text{O})$

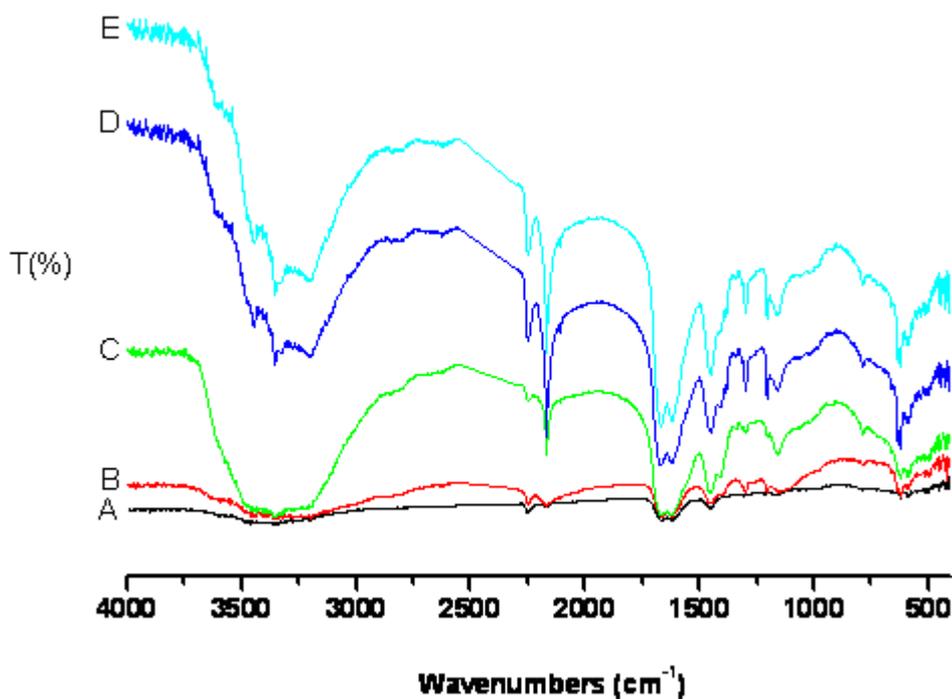


Fig. 1: Infrared spectra of $[\text{Co}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, $[\text{Cu}_3(\text{NH}_2\text{CONH}_2)_4](\text{PO}_4)_2$, $[\text{Fe}(\text{NH}_2\text{CONH}_2)_6]\text{PO}_4$, $[\text{Mn}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, $[\text{Ni}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, and $[\text{Zn}_3(\text{NH}_2\text{CONH}_2)_4](\text{PO}_4)_2$ complexes

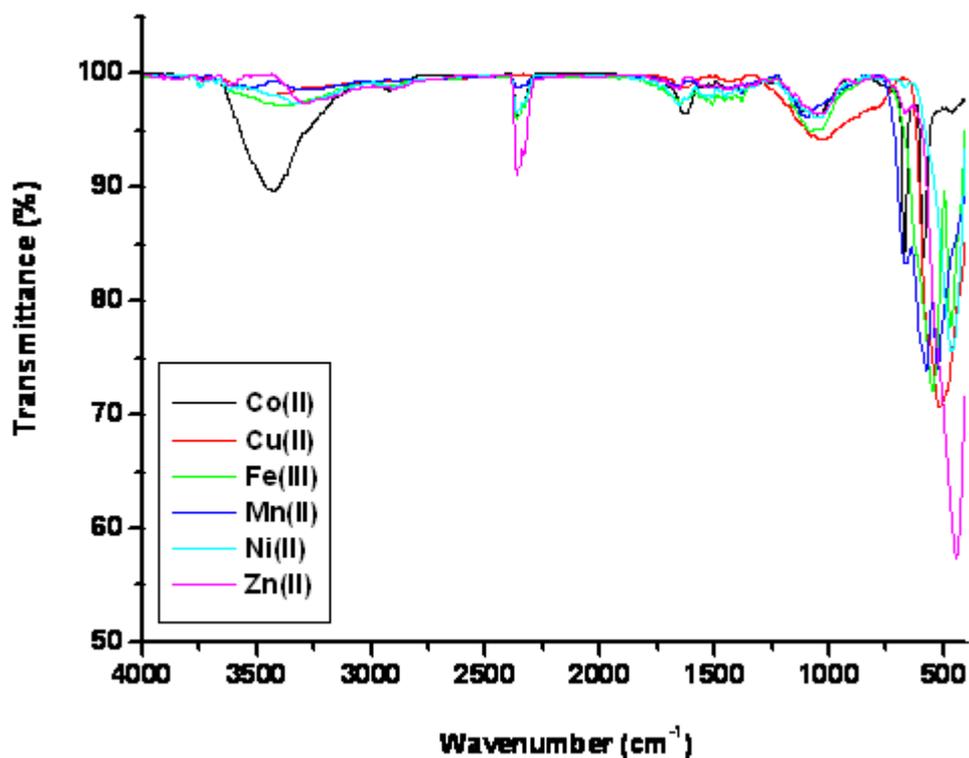


Fig. 2: Infrared spectra of $[\text{Co}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, $[\text{Cu}_3(\text{NH}_2\text{CONH}_2)_4](\text{PO}_4)_2$, $[\text{Fe}(\text{NH}_2\text{CONH}_2)_6]\text{PO}_4$, $[\text{Mn}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, $[\text{Ni}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, and $[\text{Zn}_3(\text{NH}_2\text{CONH}_2)_4](\text{PO}_4)_2$ complexes at 800 °C.

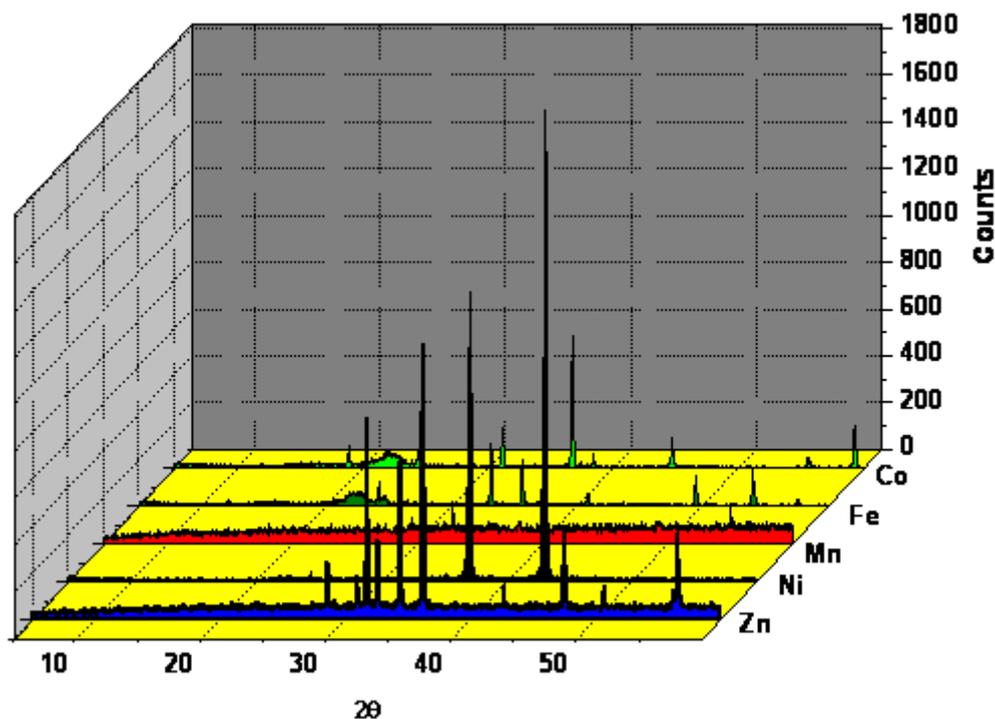


Fig. 3: XRD spectra of the $[\text{Co}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, $[\text{Cu}_3(\text{NH}_2\text{CONH}_2)_4](\text{PO}_4)_2$, $[\text{Fe}(\text{NH}_2\text{CONH}_2)_6]\text{PO}_4$, $[\text{Mn}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, $[\text{Ni}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, and $[\text{Zn}_3(\text{NH}_2\text{CONH}_2)_4](\text{PO}_4)_2$ complexes at 800 °C.

The band related to the stretching vibration $\nu(\text{O-H})$ of uncoordinated H_2O is observed as expected in the range of $(3400\text{-}3450)\text{ cm}^{-1}$, while the corresponding bending motion of the uncoordinated water, $\delta(\text{H}_2\text{O})$, is observed in the range of $(1630\text{-}1638)\text{ cm}^{-1}$. The infrared spectra of the transition metal-urea-phosphate products, Fig. 1, clearly indicate the formation of the (PO_4^{3-}) group with its characteristic $\delta(\text{O-P-O})$ at $650\text{-}400\text{ cm}^{-1}$ [43], while the different symmetric and antisymmetric bond vibrations, $\nu(\text{P-O})$ of $(\text{PO}_4)^{3-}$ intensities exhibited at $1200\text{-}900\text{ cm}^{-1}$. The one IR-active $\nu(\text{M-O})$ vibration of transition urea phosphate complexes presence at around $495\text{-}500$ [44].

3-3- X- ray powder diffraction studies

The x-ray powder diffraction patterns for the $[\text{Co}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, $[\text{Cu}_3(\text{NH}_2\text{CONH}_2)_4](\text{PO}_4)_2$, $[\text{Fe}(\text{NH}_2\text{CONH}_2)_6]\text{PO}_4$, $[\text{Mn}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, $[\text{Ni}_3(\text{NH}_2\text{CONH}_2)_6](\text{PO}_4)_2$, and $[\text{Zn}_3(\text{NH}_2\text{CONH}_2)_4](\text{PO}_4)_2$ complexes after ignited at 800 °C are depicted in Fig. 3. Inspecting these patterns, it notice that Co(II), Cu(II), Fe(III), Mn(II), Ni(II), and Zn(II) phosphate urea complexes at 800 °C temperatures system are well crystalline. The crystallite size of these complexes could be estimated from XRD patterns by applying FWHM of the characteristic peaks using Deby-Scherrer equation 1 [45]. Where D is the particle size of the crystal gain, K is a constant (0.94 for Cu grid), λ is the x-ray wavelength (1.5406 \AA), θ is the Bragg diffraction angle and β is the integral peak width. The particle size was estimated according to the highest value of intensity compared with the other peaks. These data gave an impression that the particle size located within nano scale range.

$$D = K\lambda/\beta\cos\theta \quad (\text{Deby-Scherrer equation})$$

REFERENCES

- [1] Wöhler, *Ann. Physik*, **1828**, 12, 253.
- [2] Jr. Tonn, *Chem. Eng.*, **1955**, 62, 186.
- [3] P. Moore, *Chem. & Eng. News*, **1959**, 37, 84.
- [4] A. Franz, *J. Org. Chem.*, **1961**, 26, 3304.
- [5] D. Feldman, A. Barbalata. *Synthetic Polymers*, Chapman & Hall, London, **1996**.
- [6] I. L. Finar. *Organic Chemistry*, Longman group limited, London , **1973**, 460.
- [7] M. J. Rahman; P. Bozadjiev; Y. Polovski, *fert. Res.*, **1994**, 38(2) ,89.
- [8] S. George; M. Chellapandian; B. Sivasankar; K. Jayaraman, *Bioprocess Eng.*, **1997**, 16(2), 83.
- [9] X. J. Wang; L.A. Douglas; *J. Agrochimica*, **1996**, 40(5-6), 209.
- [10] O. A. Yerokun; S. Afr, *J. plant soil*, **1997**,14(2) ,63.
- [11] R. Heinig, *SOFW J.*, **1996**, 122(14), 998.

- [12] C. T. Gnewuch; G. Sosnovsky, *Chem. Rev.*, **1997**, 97(3), 829.
- [13] C. I. Miyagawa, *Drug Intell. & Clin. Pharma.*, **1986**, 20, 527.
- [14] E. Kissa, *Text. Res. J.*, **1969**, 39(8), 734.
- [15] I. Srinivasa; K. Vishivanathapuram; M. B. Mishra; S. K. Ghosh, *Technology*, **1970**, 7(12), 27.
- [16] I. M. Kaganskii; A. M. Babenko, *Zh. Prikl. Khim.*, **1970**, 43(11), 2390.
- [17] Y. Zhang; J. Bai; T. Wei; A. Lu; *Huaxue Shijie*, **1996**, 37(4), 178.
- [18] Y.K. Kim; J.W. Williard; A.W. Frazier, *J. Chem. Eng. Data*, **1988**, 33(3), 306.
- [19] Hu. Chuncong, *Chem. Abs.*, **1990**, 113, 888.
- [20] A.D. Pandey; L. Singh; R. Yadav; K. M. Varma, *Chem. Abs.*, **1993**, 118, 607.
- [21] A. Crispoldi, *Chem. Abs.*, **1993**, 119, 831.
- [22] M. Sugimura; Y. Kameyama; T. Hashimoto; T. Kobayashi; S. Muramatsu, *Chem. Abs.*, **1990**, 112, 63.
- [23] P. S. Gentile; P. Carfagno; S. Haddad; L. Campisi, *Inorg. Chim. Acta*, **1972**, 6(C), 296.
- [24] D. S. Sagatys; R. C. Bott; G. Smith; K. A. Byriell, C. H. L. Kennard, *Polyhedron*, **1992**, 11(1), 49.
- [25] K. Lewinski; J. Sliwinski; L. Lebioda, *Inorg. Chem.*, **1983**, 22(16), 2339.
- [26] S. V. Kryatov; A. Y. Nazarenko; P. D. Robinson; E. V. Rybak-Akimova, *Chemical Communications*, **2000**, 11, 921.
- [27] T. J. Bhoopathy; M. Baskaran; S. Mohan, *Indian J. Phys.*, **1988**, 62 B (1), 47.
- [28] A. Yamaguchi; R. B. Penland; S. Mizushima; T. J. Lane; Columba Curran; J. V. Quagliano, *J. Amer. Chem. Soc.*, **1958**, 80, 527.
- [29] J. L. Duncan, *Spectrochim. Acta, Part A*, **1970**, 27, 1197.
- [30] G. B. Aitken; J. L. Duncan; G. P. Mc Quillan, *J. Chem. Soc. A*, **1971**, 2695.
- [31] D. Hadzi; J. Kidric; Z. V. Knezevic; B. Barlic, *Spectrochim. Acta, Part A*, **1976**, 32, 693.
- [32] Sib Sankar Bala; Pradip N. Ghosh, *J. Mol. Str.*, **1983**, 101, 69.
- [33] L. Kellner; *Proc. Roy. Soc. A*, **1941**, 177, 456.
- [34] R. D. Waldron; R. M. Badger, *J. Chem. Phys.*, **1950**, 18, 566.
- [35] E. R. Andrew; D. Hyndman, *Proc. Phys. Soc. A*, **1953**, 66, 1187.
- [36] A. Yamaguchi; T. Miyazawa; T. Shimanouchi; S. Mizushima, *Spectrochim. Acta*, **1957**, 10, 170.
- [37] J. E. Stewart, *J. Chem. Phys.*, **1957**, 26, 248.
- [38] R. B. Penland; S. Mizushima; C. Curran, J. V. Quagliano, *J. Amer. Chem. Soc.*, **1957**, 79, 1575.
- [39] G. F. Svatos; C. Curran, J. V. Quagliano, *This Journal*, **1965**, 77, 6159.
- [40] W. F. Boron and E. L. Boulpaep, *Medical Physiology*, Updated Edition, Saunders, Philadelphia, Pa, USA, **2004**.
- [41] J. H. Meessen and H. Petersen, "Urea," in Ullmann's Encyclopedia of Industrial Chemistry, Electronic Release, Wiley-VCH, Weinheim, Germany, 6th edition, **2002**.
- [42] R. Keuleers; H.O. Dessey; B. Rousseau; C. Van Alsenoy, *J. Phys. Chem. A*, **1999**, 103(24), 4621.
- [43] D. Forster and W.D. Harrocks., *Inorg. Chem.*, **1967**, 6, 339.
- [44] K. Nakamoto "Infrared and Raman Spectra of Inorganic and Coordination Compounds", Wiley, New York, **1978**.
- [45] C.X. Quan; L.H. Bin; G.G. Bang, *Mater. Chem. Phys.* **2005**, 91, 317.