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**New chemical procedures for preparation of
manganese(II), cobalt(II), zinc(II) and cadmium(II)
carbonates under the catalytic behavior of metal ions:
Discussion of infrared spectral bands**

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Abstract: Mn(II), Co(II), Zn(II) and Cd(II) carbonates, respectively, were achieved by a new chemical procedure under the reaction of aqueous solutions of metal ions (MnCl_2 , $\text{Co}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$ or CdCl_2), potassium iodide and urea with molar ratio 1:2:10, respectively, at $\sim 90^\circ\text{C}$ for 3 hrs. The infrared spectra of the results indicate absence of the essential bands of urea, but existed of the characteristic bands of ionic carbonate, CO_3^{2-} . An important chemical mechanisms discussed the preparation of Mn(II), Co(II), Zn(II) and Cd(II) carbonate compounds were suggested.

Keywords: carbonate CO_3^{2-} , infrared spectra, transition metals, potassium iodide, urea.

I. INTRODUCTION

Urea is physiologically very important. It is the chief nitrogenous product of protein metabolism. 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) [1], barbiturates [2], and fertilizers [3-6]. 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 biological and organic synthesis [7-10].

Yamaguchi and Stewart [11, 12] were assigned all of the observed frequencies in the spectra of urea and urea- d_4 . The two vibrations of the frequencies at 1686 and 1603cm^{-1} were assigned as the 1686cm^{-1} band due to CO stretching vibration and the 1603cm^{-1} band for 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 infrared bands of urea- d_4 observed at 1245 and 1154cm^{-1} are assigned to ND_2 bending vibrations. This assignment is consistent with the observed depolarization degrees of the Raman lines. The 1464cm^{-1} frequency of urea is assigned to the CN stretching vibration. The corresponding frequency of urea- d_4 is observed at 1490cm^{-1} . The 1150cm^{-1} band is assigned to NH_2 rocking vibrations. The reactions between transition metal ions and urea at room temperature have been studied extensively [13-17]. The infrared spectra of these complexes clearly indicated that urea molecule behaves as a mono dentate ligand and coordinates to the metal ions through the oxygen atom and not the nitrogen atom. The

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nature of the reaction products depend strongly on the type of metal ions and so the metal salt used. The novelty in our previously studies [18-27] were oriented to the reaction of urea ligand with different metals such as Co (II), pb(II), Sn(II), Cr(III), Fe(III), Au(III), Sn(IV), V(V) and Mo(IV) at high temperature which demonstrate that the types of metal ions beside their anions have a pronounced effect on the nature of the reaction products. The published papers were trended for the reaction of urea with different metal salts at elevated temperature lead to discovering a novel method for preparation pbCO_3 and CoCO_3 [21], lanthanide carbonates [23,27], limonite, $\text{FeO}(\text{OH})$ [20], $2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$ [19], $\text{SnOCl}_2 \cdot 2\text{H}_2\text{O}$ [18], (Cr_2O_3 , MnO_2 , MoO_3 and WO_3) oxides resulted from a novel oxidation reduction reaction between (K_2CrO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$), KMnO_4 , Na_2MoO_4 and Na_2WO_4 , respectively, with urea in an aqueous solution at $\sim 85^\circ\text{C}$ [27]. The main task in this paper was undertaken to identify the nature of the reaction mechanisms of the products resulted during the reaction of (MnCl_2 , $\text{Co}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$ or CdCl_2), potassium iodide and urea with molar ratio 1:2:10, respectively, at $\sim 90^\circ\text{C}$ for 3 hrs in aqueous media. The reaction products were isolated as solids and characterized by infrared spectroscopy technique.

II. EXPERIMENTAL

All chemicals used throughout this work were analytical pure. MCO_3 ($\text{M} = \text{Mn}(\text{II})$, $\text{Co}(\text{II})$, $\text{Zn}(\text{II})$ or $\text{Cd}(\text{II})$) were prepared by mixing an aqueous solutions (100 ml) of 0.1M of urea, 0.02 of potassium iodide with 0.01M of the respective MnCl_2 , $\text{Co}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$ or CdCl_2 . The mixtures were heated at 90°C for 3 hrs in a hot plate. The solid products compounds were filtered off, washed several times with hot water, dried at 80°C in an oven for 3 hours and then placed in *vacuo* over anhydrous calcium chloride. The yields of the obtained Mn(II), Co(II), Zn(II) and Cd(II) carbonates were varied in the range 70-to-80% depending upon the type of metal as well as on the counter ions associated with the metal ion.

Carbonate content in the four compounds were determined by dissolving a sample of each product in excess standard HCl and the excess of HCl was determined using standard sodium carbonate [28]. The percentage of manganese(II), cobalt(II), zinc(II) and cadmium(II) in their compounds were determined gravimetrically method till constant weight and stable formula. The infrared spectra of urea, all reactants and products were recorded using a Bruker FT-IR Spectrophotometer.

III. RESULTS AND DISCUSSION

The chemical reactions of 0.1M of urea, 0.02 of potassium iodide with 0.01M of the respective MnCl_2 , $\text{Co}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$ or CdCl_2 with molar ratio (10: 2: 1), respectively, at 90°C produces a buff, violet, white and white solid fine powders, respectively. The infrared spectra of urea as well as the reaction products of different manganese(II), cobalt(II), zinc(II) and cadmium(II) salts with urea at low temperature (90°C) were obtained. The spectra of free urea ligand, manganese(II), cobalt(II), zinc(II) and cadmium(II) carbonates are shown in Fig. 1-5, respectively. The band assignments for the products are given in Table 1. The infrared spectra show no bands due to any of the reactants and of coordinated urea, but instead, a group of bands characteristic for the ionic Carbonate, $(\text{CO}_3)^{2-}$, is appeared [29]. Based on this fact, along with that obtained data from the volumetric determination of $(\text{CO}_3)^{2-}$ group with standard solution of HCl and beside that the infrared spectra of the commercially obtained MnCO_3 , CoCO_3 , ZnCO_3 and CdCO_3 are the same as that of the reaction products. The products obtained were identified as MnCO_3 , CoCO_3 , ZnCO_3 and CdCO_3 . The infrared assignments agree quite well with those known [29] for the ionic carbonate $(\text{CO}_3)^{2-}$.

Previous studies [18-27] indicated that the nature of the reaction product obtained from the reaction of metal ions with urea at high temperature depends upon the type of metal ion and in some cases on the nature of the metal salts used. The manganese(II)-urea complexes have been studied extensively [30-33] and it was found that, these complexes are of high spin and possess octahedral structures. These investigation have also shown that, all of the studied Mn(II)-

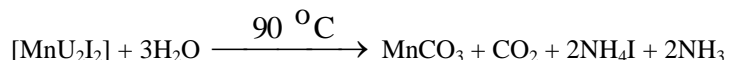
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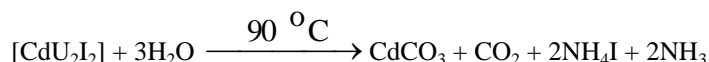
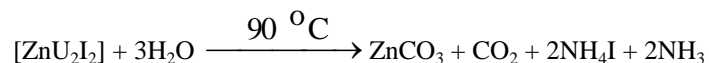
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urea complexes are of the general formula MnU_2X_2 ($X=Cl^-$ or Br^- , $U=Urea$). They have a chain like structure with halogen bridges. This structure is supported by electronic spectral measurements and the magnetic susceptibility data [34] but could not be checked by infrared spectroscopy because of the Mn-X-M bridging vibration frequency lying below 200 cm^{-1} . The trans-octahedral complex $[MnU_4(NCS)_2]$, ($U=urea$) has been prepared and investigated [35]. The ligand, urea is coordinated through its oxygen atom while the thiocyanate through the nitrogen atom. These results are supported by the crystallographic data of Tsintsadze et al [36] obtained on the $[MnU_4(NCS)_2]$ complex. The trifluorobis(urea)manganese(III) trihydrate, $[MnF_3(urea)_2] \cdot 3H_2O$ complex is prepared and its infrared spectrum is obtained [37]. The characteristic features of the infrared spectrum of this complex are the absorptions due to coordinated urea, coordinated fluoride and lattice water. The important bands of coordinated urea have been observed at 3425 and 1535 cm^{-1} , assignable to $\nu(NH_2)$ and $\nu(CO)$ modes, respectively. The unaltered position of $\nu(NH_2)$ and a significant lowering of $\nu(C=O)$ band frequencies compared with those for the free urea suggest that urea is coordinated with the metal in an unidentate manner through its oxygen atom. However, there is a shift to the lower frequency in the position of the $\nu(Mn-F)$ mode indicating that, the fluoro ligands are involved also in the formation of bridges among the contiguous Mn centers in the crystal lattice.

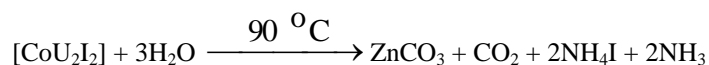
At high temperature the role of Mn(II) ions in decomposing the coordinated urea in the form of $[MnU_2I_2]$ could be understood according to the following reactions;



Adducts of $ZnX_2 \cdot 2urea$ ($X = Cl, Br, I$), $CdX_2 \cdot 2urea$ ($X = Br, I$), $CdX_2 \cdot urea$ ($X = Cl, Br, I$) and $HgX_2 \cdot urea$ ($X = Cl, Br$) have been characterized [38]. The shifts of the stretching vibrations to low frequency (νCO) and to high frequencies (νCN and νNH) indicated that urea is oxygen-bonded to the metals. At high temperature the role of Zn(II) and Cd(II) ions in decomposing the coordination urea in the form of $[Zn(urea)_2I_2]$ or $[Cd(urea)_2I_2]$ could be understood as follows;



The x-ray studies on cobalt(II) salt-urea complexes [39-41] have confirmed the existence of the double compounds $CoSO_4 \cdot 6CO(NH_2)_2$, $Co(NO_3)_2 \cdot CO(NH_2)_2$, $Co(NO_3)_2 \cdot 4CO(NH_2)_2$, $Co(NO_3)_2 \cdot 6CO(NH_2)_2$, and of the triple compound $Co(NO_3)_2 \cdot 4Co(SO_4)_2 \cdot 20CO(NH_2)_2 \cdot 2H_2O$ and $CoSO_4 \cdot 2CO(NH_2)_2 \cdot 6H_2O$. Complexes of N-allyl urea (NAU) with cobalt(II) and nickel(II) halides and perchlorates have prepared and characterized by electrical conductance, magnetic susceptibility [42]. The infrared spectra of N-allyl urea complexes with Ni(II) and Co(II) salts, $[Co(NAU)_2X_2]$; ($X = Cl, Br, \text{ and } I$), $[Ni(NAU)_4X_2]$; ($X = Cl, Br$), $[Ni(NAU)_4](ClO_4)_2$ and $[Ni(NAU)_6](ClO_4)_2$ are reported [43]. A negative shift in the frequencies of $\nu(C=O)$ and $\delta(NH_2)$ bands, and a positive shift in the frequency of $\nu(C-N)$ band, suggest that carbonyl oxygen is the donor site. Moreover, the negative shift of the N-H stretching frequency is arise from hydrogen bonding between N-H and halogen and not to coordination. A small negative shift of the double bond on coordination is probably due to drain of electrons towards oxygen. The role of Co(II) ions in decomposing of coordinated urea at high temperature may be understood as follows.



The $(CO_3)^{2-}$ ion is planar and therefore, it belongs to the D_{3h} symmetry. It is expected to display four modes of vibrations, $A_1^- + A_2^- + 2E^-$ (E^- is a doubly degenerate motion). The vibration A_1^- is only Raman active while the other

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ν_2 , ν_3 and ν_4 are infrared active. The stretching vibrations of the type; $\nu(\text{C-O})$; $\nu_3(\text{E}')$ is observed as a strong broad band in the range of $1550\text{-}1360\text{ cm}^{-1}$ while the stretching vibration $\nu(\text{C-O})$; $\nu_1(\text{A}'_1)$ is observed in the region $\sim 1030\text{ cm}^{-1}$ as a medium-to-weak band. It should be indicated here that this motion (A'_1) should be infrared inactive, its weak appearance in the spectrum of MCO_3 could be related to weak solid-solid interactions causes the symmetry of CO_3^{2-} to be lowered than D_{3h} . The out of plane of vibration $\delta(\text{OCO})$; $\nu_2(\text{A}''_2)$ is observed in the range of $\sim 800\text{ cm}^{-1}$ as a strong band while, the angle deformation bending vibration $\delta(\text{OCO})$; $\nu_4(\text{E}')$ appear in the range of 700 cm^{-1} as a medium strong. The infrared spectra of metal(II) carbonate, MCO_3 show that, some these products are hygroscopic and its clearly have moisture water. The band related to the stretching vibration $\nu(\text{O-H})$ of uncoordinated H_2O is observed as expected in the range of $\sim 3000\text{ cm}^{-1}$ Table 1.

Table 1: Infrared frequencies (cm^{-1}) and assignments of the products obtained from the reaction of (a): MnCl_2 , (b): $\text{Co}(\text{NO}_3)_2$, (c): $\text{Zn}(\text{NO}_3)_2$ or (d): CdCl_2 with potassium iodide and urea at 90°C temperature.

Frequencies*, cm^{-1}				Assignments
a	b	c	d	
3341	3321	3331	3331	$\nu(\text{O-H}); \text{H}_2\text{O}$
3190	3198	3198	3187	
1570	1570	1560	1570	$\nu(\text{C-O}); \text{CO}_3^{2-}$
1368	1366	1366	1377	
1039	1060	1029	1060	
862	763	773	855	$\delta(\text{OCO}); \text{CO}_3^{2-}$
773			722	

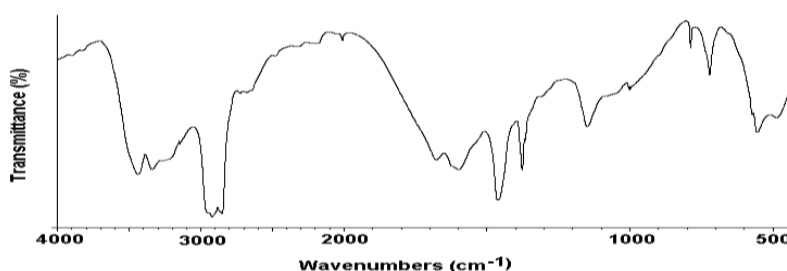


Fig. 1: Infrared spectrum of urea free ligand

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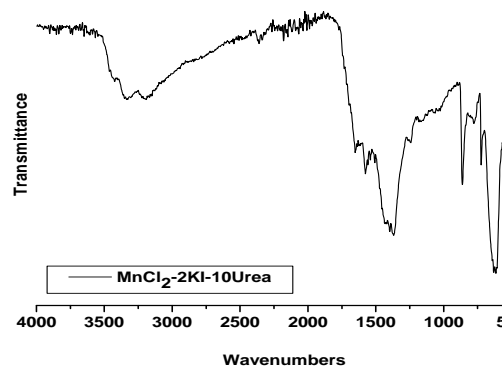


Fig. 2: Infrared spectrum of MnCO₃.xH₂O compound

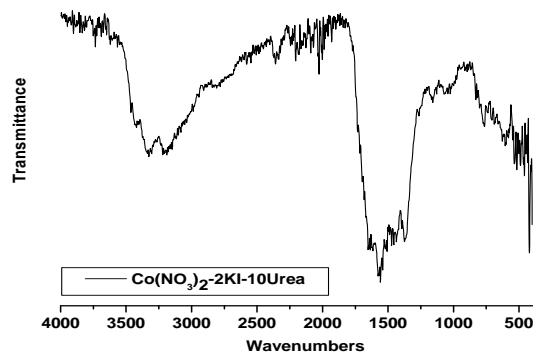


Fig. 3: Infrared spectrum of CoCO₃.xH₂O compound

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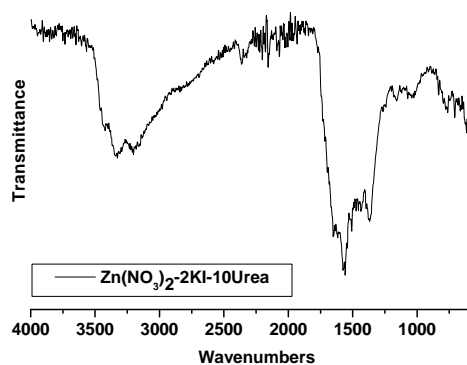


Fig. 4: Infrared spectrum of $ZnCO_3 \cdot xH_2O$ compound

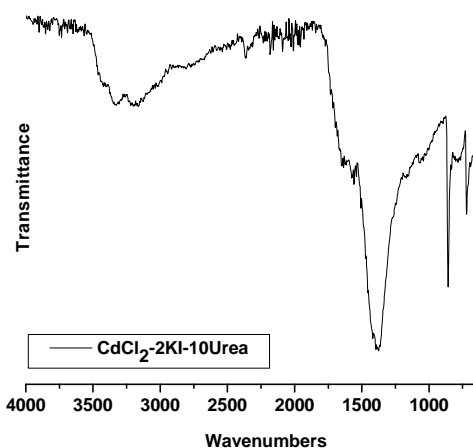


Fig. 5: Infrared spectrum of $CdCO_3 \cdot xH_2O$ compound

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