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A Novel Method for Synthesis of Co^{II}, Ni^{II}, Zn^{II} and Ag^{I} Transition Metal Carbonates using Methylurea Precursor

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Abstract: Co^{II}, Ni^{II}, Zn^{II} and Ag^{I} carbonates; $M(CO_3)_2$ (M = Co^{II}, Ni^{II}, and Zn^{II}) and Ag_2CO_3 were obtained during the reaction of aqueous solutions of $Co(NO_3)_2$, $Ni(NO_3)_2$, $Zn(NO_3)_2$ and $AgNO_3$ with methylurea at ~ 90 ^oC for twelve hours. The reaction products were characterized through their elemental analysis and infrared spectroscopy. The infrared spectra clearly show the characteristic bands due to carbonate ions. General reaction equations describing the formation of some transition carbonates were proposed.

Keywords: $M(CO_3)_2$, methylurea, Infrared spectra.

Introduction

Stable compounds have been isolated during the reaction of urea as a neutral oxygen-containing molecule with uranyl ions and these compounds were well characterized [1-3]. The reactions of rare earth metal ions with urea and some of its related complexes have been carried out [4-9] and solid metal-urea complexes were isolated and characterized using elemental analysis, electronic and IR spectra as well as thermal analysis. Lanthanide (Y, La, Ce, Pr, Nd, Sm, Gd and Dy) complexes using substituted ureas and thioureas as ligands and lanthanide mixed complexes using urea and phenylthioureas have been prepared and characterized [10]. The infrared spectra of all of these complexes showed that urea molecule behaves as a monodentate ligand and coordinates to the metal ions through the oxygen atom and not the nitrogen atom. The common features of all of this investigation are the synthesis and studying the properties of the isolated metal-urea complexes obtained during the reaction of urea with these metal ions at room or lower temperature. But none of them were designated to investigate the nature of the reaction of urea with these metal ions at high temperature. In general, studies on the nature of the reaction of urea with metal ions at high temperature are very rare in literature and the available publications describe interesting features: the reaction products depend not only on the type of metal ions but also on the metal salt used in these reactions [11-16]. The present investigation was undertaken to investigate the nature of the reaction products obtained during the reaction of methylurea with $Co(NO_3)_2$, $Ni(NO_3)_2$, $Zn(NO_3)_2$ and $AgNO_3$ salts in aqueous solution at ~ 90 ^oC. The reaction products were isolated as solids and characterized by elemental analysis, infrared spectra as well as gravimetric analysis to determine the water content.

Experimental

Reagent grade chemical were used throughout. $M(CO_3)_2$ (M = Co^{II}, Ni^{II}, and Zn^{II}) and Ag_2CO_3 were prepared by mixing aqueous solutions (50 ml) of 1 mmol of the $Co(NO_3)_2$, $Ni(NO_3)_2$, $Zn(NO_3)_2$ and $AgNO_3$ salts with a volume of 50 ml of 10 mmol of methylurea. The mixtures were heated at ~ 90 ^oC for 12 h in a water bath. The colored precipitated were filtered out, washed several times with hot water, dried at 90 ^oC in an oven for 3 h and then in vacuo over anhydrous calcium(II) chloride. The yields of the obtained $M(CO_3)_2$ (M = Co^{II}, Ni^{II}, and Zn^{II}) and Ag_2CO_3 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 contents in $M(CO_3)_2$ (M = Co^{II}, Ni^{II}, and Zn^{II}) and Ag_2CO_3 were determined by dissolving a weighted sample of the products in excess standard HCl and the excess of HCl was determined by titration with standard sodium carbonate. Co^{II}, Ni^{II}, Zn^{II} and Ag^{II} metal ions were determined gravimetrically as dioxides, MO. The infrared spectra of methyurea and $M(CO_3)_2$ (M = Co^{II}, Ni^{II}, and Zn^{II}) and Ag_2CO_3 carbonates were recorded in KBr discs using a Bruker Infrared Spectrophotometer FT-IR.

Results and discussion

The elemental analysis for $M(CO_3)_2$ (M = Co^{II}, Ni^{II}, and Zn^{II}) and Ag_2CO_3 carbonates obtained during the reaction of methylurea with the respective metal nitrate were almost the same and indicate the absence

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of nitrogen. Analysis of the products obtained using metal nitrates is as follows (Table 1): The reactions of aqueous solutions of methylurea and $Co(NO_3)_2$, $Ni(NO_3)_2$, $Zn(NO_3)_2$ and $AgNO_3$ produce colored solid products of Co^{II} (pink), Ni^{II} (green), Zn^{II} (white) and Ag^{I} (grayish) carbonates. The infrared spectra of methylurea and the carbonates of $M(CO_3)_2$ (M = Co^{II}, Ni^{II}, and Zn^{II}) and Ag_2CO_3 are shown in Fig. 1. Band assignments of all of infrared bands observed in the spectra of carbonates are given in Table 2. The infrared spectra of the all obtained products show no bands due to coordinated methylurea, but instead a group of bands characteristic for ionic carbonate [17]. These bands are observed above 1550-1350 cm^{-1} and around 1050 cm^{-1} due to the stretching vibrations, □(C-O) and around 800 and 730 cm^{-1} due to the bending motions, □(OCO) associated with carbonate ions. The assignment of these bands to these frequencies agrees quite well with those generally known for the ionic carbonate. The infrared spectrum obtained for the ionic carbonate (CO_3^{2-}) is almost the same as those of the reaction products. Based on these facts along with the obtained from elemental analysis data as well as the determination of (CO_3^{2-}) with HCl, the reaction products obtained were identified as $M(CO_3)_2$ (M = Co^{II}, Ni^{II}, and Zn^{II}) and Ag_2CO_3. Literature survey [11-16] indicates that the nature of the reaction products obtained from the reaction of metal ions with urea at high temperature depends upon the type of metal ions and the metal salt used. In this investigation, the role of metal ions (II)/(I) in decomposition of the coordinated methylurea at high temperature may be understood as follows: At room temperature, $Co(NO_3)_2$, $Ni(NO_3)_2$, $Zn(NO_3)_2$ and $AgNO_3$ salts react with methylurea to form the $[Co(CH_3NHCONH_2)_6](NO_3)_2$, $[Ni(CH_3NHCONH_2)_6](NO_3)_3$, $[Zn(CH_3NHCONH_2)_4](NO_3)_3$ and $[Ag(CH_3NHCONH_2)_2]NO_3$, complexes. At high temperature, the following reactions may take place:

$$M(NO_3)_2+10CH_3NHCONH_2 \xrightarrow{90^oC} MCO_3+NH_4NO_3+7CO+6C_2H_4+4NH_3+7.5N_2+10H_2$$

(M^{II} = Co, Ni and Zn)

$$2AgNO_3+20CH_3NHCONH_2 \xrightarrow{90^oC} Ag_2CO_3+NH_4NO_3+16CO+23CH_4+2NH_4OH+2H_2+19N_2+7.5H_2$$

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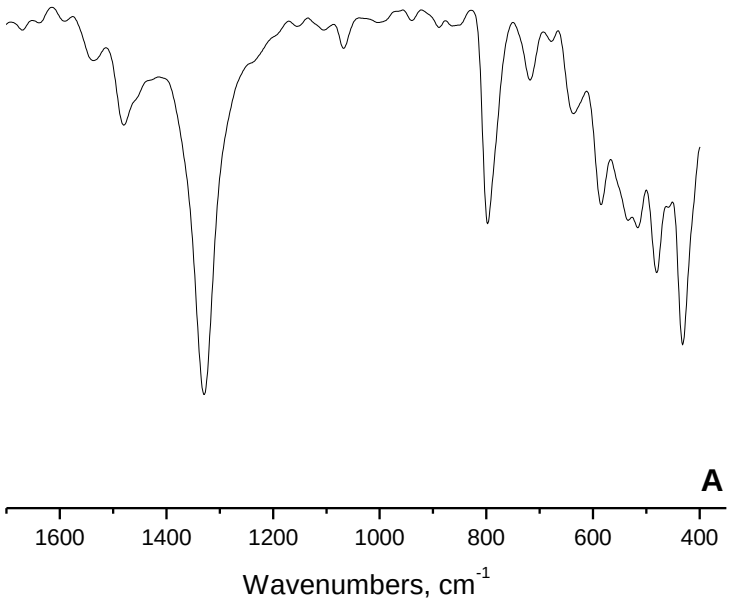
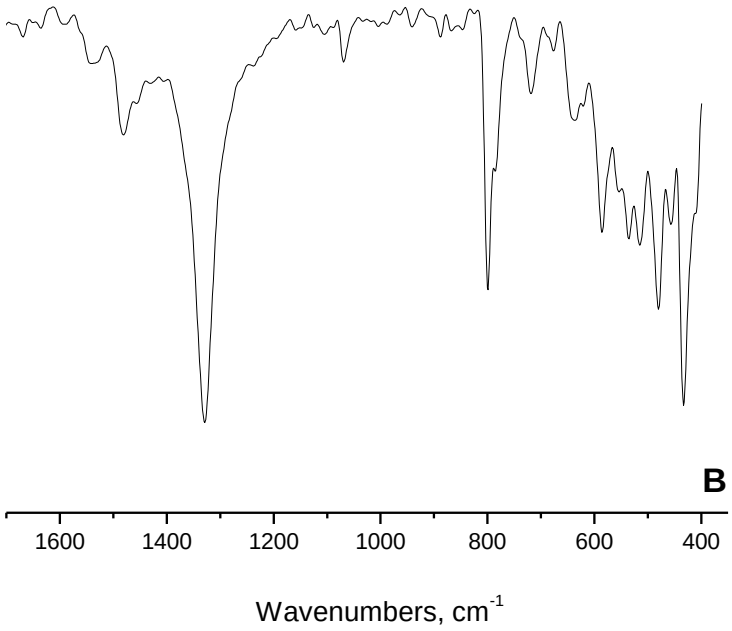
Table 1: Elemental analysis data of $M(CO_3)_2$ (M = Co^{II}, Ni^{II}, and Zn^{II}) and Ag_2CO_3

Compunds	% C		% M		% CO_3	
	Calc.	Found	Calc.	Found	Calc.	Found
$CoCO_3$	10.10	9.98	49.55	49.12	50.44	50.19
$NiCO_3$	10.12	10.04	49.45	49.09	50.55	50.31
$ZnCO_3$	9.58	9.32	52.15	52.08	47.85	47.32
Ag_2CO_3	4.36	4.30	78.24	78.21	21.76	21.44

Table 2: Infrared frequencies (cm^{-1}) and assignments of $M(CO_3)_2$ (M = Co^{II}, Ni^{II}, and Zn^{II}) and Ag_2CO_3 obtained from the reaction of $Co(NO_3)_2$, $Ni(NO_3)_2$, $Zn(NO_3)_2$ and $AgNO_3$ with methylurea at ~ 90 ^oC for 12 h.

Assignments	Frequencies, cm^{-1}				
	$CoCO_3$	$NiCO_3$	$ZnCO_3$	Ag_2CO_3	$CaCO_3$
□(C-O); CO_3^{2-}	1479, 1329	1482, 1332	1482, 1329	1486, 1329	1492, 1429
	1068	1068	1071	1070	1080
□(OCO); CO_3^{2-}	800	800	797	797	879
	717	718	718	717	706

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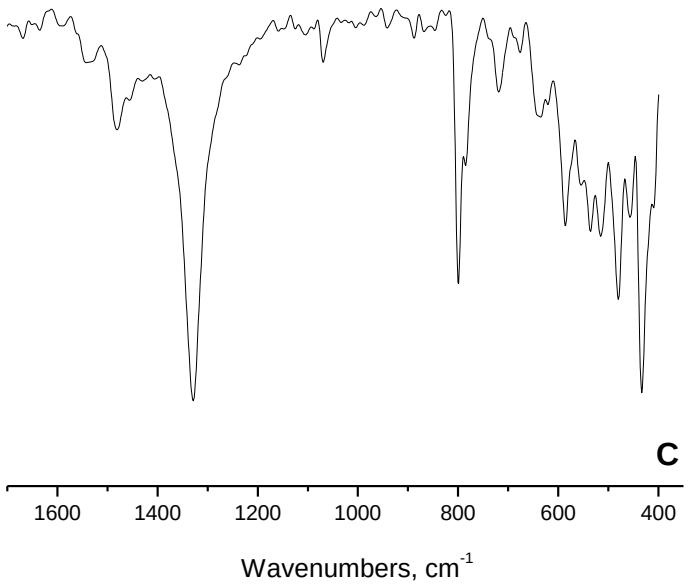
Wavenumbers, cm-1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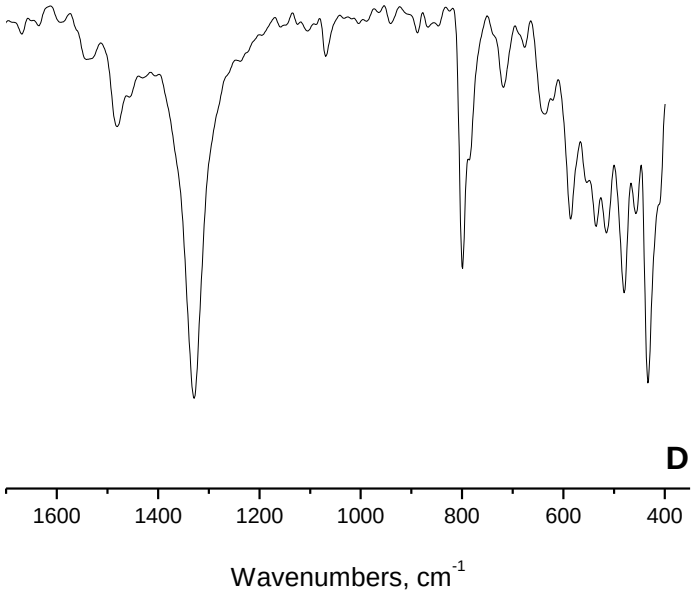

Fig. 1: Infrared spectra of (A): $Co(NO_3)_2$, (B): $Ni(NO_3)_2$, (C): $Zn(NO_3)_2$ and (D): $AgNO_3$.