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A novel method for preparation of bismuth(III) carbonate basic $(BiO)_2CO_3.3H_2O$ upon the reaction of urea with various bismuth(III) salts at high temperature

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ABSTRACT

Bismuth(III) carbonate basic, $(BiO)_2CO_3.3H_2O$, was prepared via novel simple synthetic route through the reaction of aqueous solutions of $BiCl_3$, $Bi(NO_3)_3$, $Bi(CH_3COO)_3$ or $Bi_2(SO_4)_3$ with a simple organic precursor like urea at ~ 90 °C for 72 hrs. The infrared spectra of the results indicate absence of the individual bands of urea, but exhibited of the characteristic band of ionic carbonate, CO_3^{2-}. A general reaction mechanisms describing the preparation of bismuth(III) carbonate basic compound was discussed.

Keywords: carbonate CO_3^{2-}, Infrared spectra, Elemental analyses, Urea.

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 1686 cm^{-1} band due to CO stretching vibration and the 1603 cm^{-1} band for NH_2 bending motion. The calculations studied by Yamaguchi showed that for the band at 1686 cm^{-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 1154 cm^{-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 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, FeO(OH) [20], $2ZnCO_3.3Zn(OH)_2$ [19], $SnOCl_2.2H_2O$ [18], (Cr_2O_3, MnO_2, MoO_3 and WO_3) oxides resulted from a novel oxidation reduction reaction between (K_2CrO_4 or $K_2Cr_2O_7$), $KMnO_4$, Na_2MoO_4 and Na_2WO_4, respectively, with urea in an aqueous solution at ~ 85 ^oC [27].

The bright side in this study was undertaken to identify the nature of the reaction mechanisms of the products resulted during the reaction of urea with $BiCl_3$, $Bi(NO_3)_3$, $Bi(CH_3COO)_3$ or $Bi_2(SO_4)_3$ at ~ 90 ^oC for 72 hrs in aqueous media. The reaction products were isolated as solids and characterized by elemental analysis, infrared spectroscopy.

MATERIALS AND METHODS

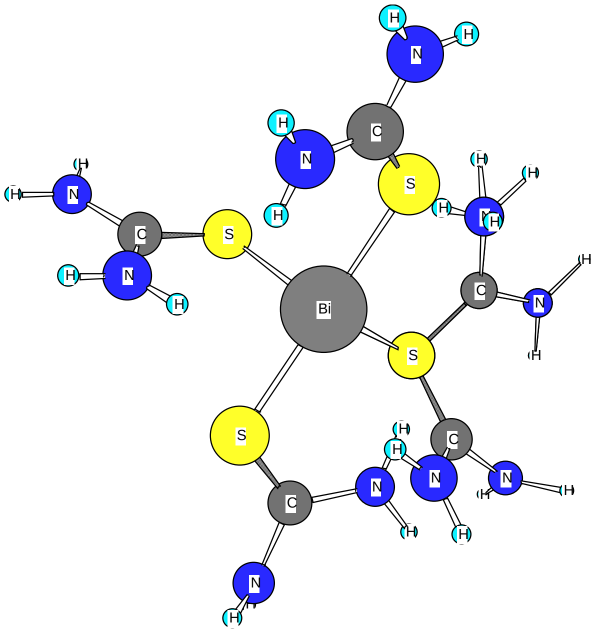
All chemicals used throughout this work were analytical pure. $(BiO)_2CO_3.3H_2O$ was prepared by mixing an aqueous solutions (75 ml) of 0.1M of urea with 0.01M of the respective $BiCl_3$, $Bi(NO_3)_3$, $Bi(CH_3COO)_3$ or $Bi_2(SO_4)_3$. The mixtures were heated at ~ 90 ^oC for 72 hrs in a hot plate. The solid products compounds were filtered off, washed several times with hot water, dried at 120 ^oC in an oven for 3 hours and then placed in *vacuo* over anhydrous calcium chloride. The yields of the obtained bismuth(III) carbonate basic were varied in the range 70-to-85% depending upon the type of metal ions as well as on the counter ions associated with the metal ion.

The elemental analysis for $(BiO)_2CO_3.3H_2O$ (Table 1) obtained during the reaction of urea with the respective $BiCl_3$, $Bi(NO_3)_3$, $Bi(CH_3COO)_3$ or $Bi_2(SO_4)_3$ salts almost the same and indicate the absence of nitrogen element.

Instruments

Carbonate content in the four salts of bismuth(III) 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 bismuth(III) in their compounds were determined gravimetrically method till constant weight and stable formula. The infrared spectra of urea, reactants and carbonate basic products were recorded in potassium bromide discs using a Shimadzu FT-IR Spectrophotometer.

RESULTS AND DISCUSSION



Formula 1: 3D structure of $[Bi(N_2H_4CS)_6](NO_3)_3$ complex

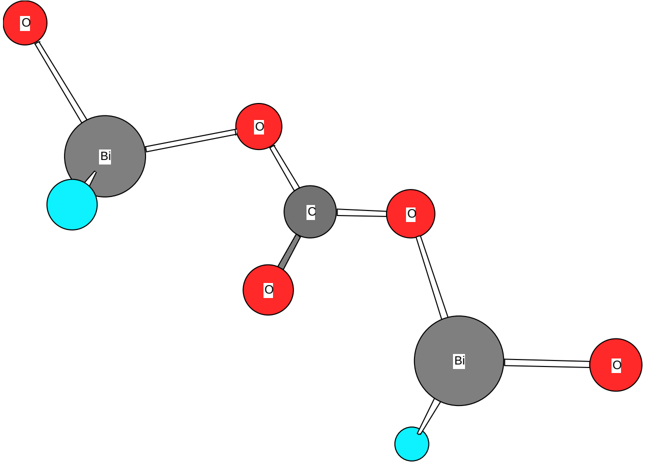
The reaction of aqueous solutions of urea with $BiCl_3$, $Bi(NO_3)_3$, $Bi(CH_3COO)_3$ or $Bi_2(SO_4)_3$ at ~ 90 ^oC produced a white solid crystalline products. The infrared spectra of urea as well as the reaction products of different bismuth(III) salts with urea at high temperature were obtained from potassium bromide discs. The spectra of free urea ligand [24], bismuth(III) chloride were comparison with Bismuth(III) carbonate basic, $(BiO)_2CO_3.3H_2O$ (Fig. 1). The band assignment for the product is given in Table 2. 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, $(CO_3)^{2-}$, is appeared [29]. Based on this fact, along with that obtained from elemental analysis data as well as the volumetric determination of $(CO_3)^{2-}$ group with standard solution of HCl and beside that the infrared spectra of the commercially obtained bismuth(III) carbonate basic, $(BiO)_2CO_3.3H_2O$, is the same as that of the reaction products. The products obtained were identified as Bismuth(III) carbonate basic $(BiO)_2CO_3.3H_2O$. The infrared assignments agree quite well with those known [29] for the ionic carbonate $(CO_3)^{2-}$. 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. At room temperature the coordination compounds of bismuth(III) ion with thiourea have been studied extensively [30-32] and it was found that, in these complexes thiourea coordinated through its sulfur atom forming the $[Bi(N_2H_4CS)_6](NO_3)_3$ complex [31] formula 1.

At high temperature the role of Bi(III) ions in decomposing the coordination urea in the form of $[Bi(N_2H_4CO)_6](X)_3$ could be understood as follows;

$$2[Bi(N_2H_4CO)_6](X)_3 + 18H_2O \xrightarrow{90^{o}C} (BiO)_2CO_3.3H_2O + 11CO_2 + 6NH_4X + 18NH_3$$

$$(X = Cl^-, NO_3^-, CH_3COO^-, \text{ or } ½SO_4^{2-})$$

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 $\nu_2$, $\nu_3$ and $\nu_4$ are infrared active. The stretching vibrations of the type; $\nu$(C-O); $\nu_3(E`)$ is observed as a very strong broad band at 1385 cm^{-1} while the stretching vibration ν(C-O); $\nu_1(A`_1)$ is observed in the region ~1070 $cm^{-1}$ 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 δ(OCO); $\nu_2(A``_2)$ is observed in the range of ~ 846 cm^{-1} as a very strong band while, the angle deformation bending vibration δ(OCO); $\nu_4(E`)$ appear in the range of 687 cm^{-1} as a medium weak. The infrared spectra of bismuth(III) carbonate basic, $(BiO)_2CO_3.3H_2O$ (formula 2), show that, some these products are hygroscopic and its clearly have moisture water. The band related to the stretching vibration ν(O-H) of uncoordinated H_2O is observed as expected in the range of ~ 3425 cm^{-1} Table 2.



Formula 2: 3D structure of bismuth(III) carbonate basic, $(BiO)_2CO_3$ compound

Table 1: Elemental analyses data of bismuth(III) carbonate basic, $(BiO)_2CO_3.3H_2O$ obtained using $BiCl_3$

Compounds	Mwt.	Elemental analyses/ Found (Calc.)							
		%C		%H		% bismuth		% CO_3^{2-}	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$(BiO)_2CO_3.3H_2O$	563.97	2.13	2.07	1.07	1.04	74.10	73.97	10.64	10.43

Table 2: Infrared frequencies (cm^{-1}) and assignments of the products obtained from the reaction of $BiCl_3$ with urea at 90 °C temperature.

$(cm^{-1})^a$	**Assignments ^{b}**
3426 ms, br	ν (O-H); H_2O
1385 vs, br, 1070 mw	ν (C-O); CO_3^{2-}
846 vs, 687 mw	δ(OCO); CO_3^{2-}

a: br, broad; m, medium; sh, shoulder; s, strong; w, weak *b: ν, stretching; δ, bending.*

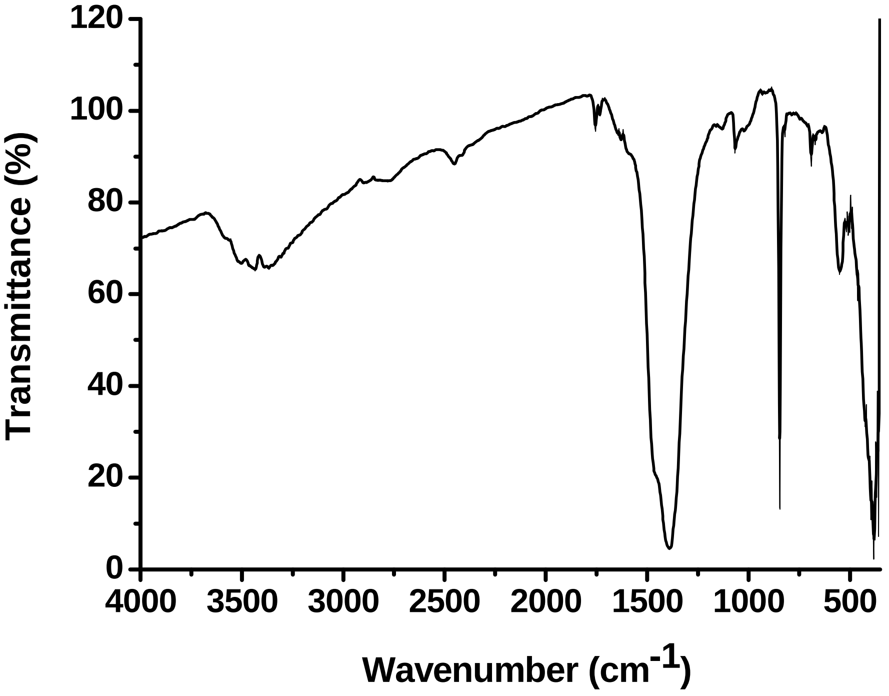


Fig. 1: Infrared spectra of bismuth(III) carbonate basic, $(BiO)_2CO_3.3H_2O$ obtained from the reaction of $BiCl_3$ with urea at 90 °C temperature.

REFERENCES

[1] Feldman D, Barbalata A, Synthetic Polymers, Chapman & Hall, London, **1996**.
[2] Finar IL, Organic Chemistry, Longman group limited, London, **1973**, pp460.
[3] Rahman MJ, Bozadjiev P, Polovski Y, fert Res, **1994**, 38(2) 89.
[4] George S, Chellapandian M, Sivasankar B, Jayaraman K, *Bioprocess Eng*, **1997**, 16(2), 83.
[5] Wang XJ, Douglas LA, *Agrochimica*, **1996**, 40(5-6), 209.
[6] Yerokun OA, Afr S, *J plant soil*, **1997**, 14(2), 63.
[7] Yadav YC, Srivastava DN, Saini V, Sighal S, Seth AK, Kumar S, Ghelani TK, *J Chem Pharm Res*, **2011**, 3(1) 621-627.
[8] Mistry MH, Parmar SJ, GC Desai, *J Chem Pharm Res*, **2011**, 3(4), 831-837.
[9] Patel KM, Patel HA, Sen DJ, Panigrahi BB, Badmanaban R, *J Chem Pharm Res*, **2010**, 2(3), 631-639.
[10] Kemasari P, Sangeetha S, Venkatalakshmi P, *J Chem Pharm Res*, **2011**, 3(5), 653-659.
[11] Yamaguchi A, Miyazawa T, Shimanouchi T, Mizushima S, *Spectrochim Acta*, **1957**, 10, 170.
[12] Stewart JE, *J Chem Phys*, **1957**, 26, 248.
[23] Srivastava PC, Aravindaksahn C, Z *Phys Chem Leipzig*, **1983**, 264, 61.
[14] Schafer M, Curran C, *Inorg Chem*, **1966**, 5, 256.
[15] Zarli B, Dall'Olio G, Sindellari L, *J Inorg Nucl Chem*, **1976**, 38, 491.
[16] Barbier JP, Hugel RP, *J Inorg Nucl, Chem*, **1977**, 39, 2283.
[17] Barbier JP, Hugel R, *Inorg Chimica Acta*, **1974**, 10, 93.
[18] Teleb SM, Refat MS, Sadeek SA, *J Ukrainian Chem*, **2004**, 68(5), 35.
[19] Sadeek SA, Refat MS, *J Coord Chem*, **2005**, 58(18), 1727.
[20] Sadeek SA, Refat MS, Teleb SM, *J Korea, Chem. Soc*, **2004**, 48(4), 358.
[21] Refat MS, Teleb SM, Sadeek SA, *Spectrochim Acta*, **2004**, A(60), 2803.
[22] MS Refat; SA Sadeek; SM Teleb, *J. Argen. Chem. Soc*., **2004**, 92(4-6), 23.
[23] Refat MS, *Synth React Inorg Met.-Org Chem*, **2004**, 34(9), 1605.
[24] Nour EM, Teleb SM, Al-Khososy NA, Refat MS, *Synth React Inorg Met-Org Chem*, **1997**, 27(4), 505.
[25] Refat MS, Sadeek SA, *Latvian J Chem*, **2005**, 4, 343.
[26] Refat MS, Sadeek SA, DE Nasr, *Bull Chem Technolog Maced*, **2005**, 24(2), 153.

[27] Teleb SM, Refat MS, *Bull Chem Technolog Maced*, **2006**, 25(1), 57.
[28] Vogel, “Qualitative Inorganic Analysis”, John wiely & Sans, Inc. New York, **1987**.
[29] Nakamoto K, "Infrared and Raman Spectra of inorganic and coordination compounds", 3rd edn, New York: Wiley Interscience, **1978**.
[30] Su X, Zhang G, Liu T, Liu Y, Qin J, Chen C, *Russian J Inorg Chem*, **2006**, 51(12), 1864.
[31] Semenov VN, Ostapenko OV, *Inorganic Materials*, **2000**, 36(3), 211.
[32] Golovnev NN, Leshok AA, Novikova GV, Petrov AI, *Russian J Inorg Chem*, **2010**, 55(1), 130.