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Synthesis, Structural Visualization, Spectroscopic, and Thermal Studies of Charge Transfer Cu(II), Ni(II) and Zn(II) Bromides-carbamide Complexes at Elevated Temperature

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ABSTRACT

In the present study, the composition and structure of Cu(II), Ni(II) and Zn(II) compounds resulted from the chemical reactions of copper(II), nickel(II) and zinc(II) bromide salts with carbamide in aqueous media at 95 °C have been investigated, using IR, electron spin resonance ESR and x-ray powder diffraction spectroscopy as well as thermal analysis TG/DTG/DSC. The $Cu_2(OH)_3Br$, $[Ni_2(NCO)_2(H_2O)_2(Br)_2]$, and $ZnCO_3.xH_2O$ compounds were achieved by a novel synthetic route through with a low cost precursor like carbamide. The infrared spectra of the results indicate absence of the individual bands of carbamide, but exhibited of the distinguished bands of hydroxyl, isocyanate, NCO, and ionic carbonate, CO_3^{2-} for Cu(II), Ni(II) and Zn(II) compounds, respectively. Visualized investigations were performed to confirm crystal structure, validity and stability of the product compounds. A general reaction mechanisms describing the preparation of Cu(II), Ni(II), and Zn(II) compounds were discussed.

Key words: carbonate CO_3^{2-}, Isocyanate ion, Infrared spectra, X-ray, carbamide.

INTRODUCTION

Carbamide is physiologically very important. It is the chief nitrogenous product of protein metabolism. Carbamide has a melting point of 132 °C, soluble in water and ethanol, but insoluble in ether. Carbamide is used for preparing formaldehyde-Carbamide resin (plastics)[1], barbiturates[2], and fertilizers[3-6]. Carbamide 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[7-9]. Some metal-carbamide complexes have pharmaceutical application, e.g., the platinum-carbamide complex which is used as antitumor[10].

Yamaguchi and Stewart[11, 12] were assigned all of the observed frequencies in the spectra of carbamide and carbamide-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 carbamide-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 carbamide is assigned to the CN stretching vibration. The corresponding frequency of carbamide-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 carbamide at room temperature have been studied extensively[13-17]. The infrared spectra of these complexes clearly indicated that carbamide 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 carbamide 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 carbamide 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 carbamide in an aqueous solution at ~ 85 °C[27].

The sunshine side in this study was undertaken to identify the nature of the reaction mechanisms of the products resulted during the reaction of carbamide with $CuBr_2$, $NiBr_2$ or $ZnBr_2$ at 95 °C for 16 hrs in aqueous media. The reaction products were isolated as solids and characterized well by X-ray diffraction reinforced and supported with visualization studies as well as spectroscopic and thermal analyses tools.

EXPERIMENTAL

Materials and synthesis

All chemicals used throughout this work were analytical pure. The $Cu_2(OH)_3Br$, $[Ni_2(NCO)_2(H_2O)_2(Br)_2]$, and $ZnCO_3.xH_2O$ compounds were prepared by mixing an aqueous solutions (100 ml) of 0.1M of carbamide with 0.01M of the respective $CuBr_2$, $NiBr_2$ or $ZnBr_2$ salts. The mixtures were heated at 95 °C for 16 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 Cu(II), Ni(II), and Zn(II) compounds were varied in the range 63-to-77% depending upon the type of metal as well as on the counter ions associated with the metal ion. The elemental analyses for $Cu_2(OH)_3Br$, $[Ni_2(NCO)_2(H_2O)_2(Br)_2]$, and $ZnCO_3.xH_2O$ compounds (Table 1) obtained during the reaction of carbamide with the respective metal bromide salts almost the same and indicate the absence of nitrogen element.

Instruments

The elemental analyses of carbon, hydrogen and nitrogen contents were performed by the microanalysis unit at Cairo University, Egypt, using a Perkin Elmer CHN 2400 (USA). The infrared spectra with KBr discs were recorded on a Shimadzu FT-IR Spectrophotometer (4000–400 cm^{-1}) in Taif University. The electron spin resonance (ESR) spectrum for copper(II) compound was performed on Jeol, JES-FE2XG, ESR-spectrometer, Frequency 9.44 GHz with Jeol Microwave unit. The thermal studies TG/DTG/DSC were carried out on a SCINCO DSC 1500 STA in Taif University, which was calibrated with indium metal. The X-ray diffraction patterns for the selected charge-transfer complexes were recorded on X 'Pert PRO PANanalytical X-ray powder diffraction, target copper with secondary monochromate. Carbonate content in the zinc(II) compound was 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 Cu(II), Ni(II), and Zn(II) within their compounds were determined gravimetrically method till constant weight and stable formula.

RESULTS AND DISCUSSION

Infrared spectra

The reaction of aqueous solutions of carbamide with bromide salts of copper(II), nickel(II), and zinc(II) at 95 °C produces a green, light green, and white solid crystalline products, respectively. The infrared spectra of carbamide as well as the reaction products of different Cu(II), Ni(II) and Zn(II) salts with carbamide at elevated temperature were obtained from potassium bromide discs. The spectra of free carbamide ligand,

Table 1: Elemental analyses data of Mn(II), Cd(II), Mg(II) and Ca(II) carbonate compounds

Compounds	Color.	Elemental analyses/ Found (Calc.)							
		%C		%H		%Metal		$\%CO_3^{2-}$	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$Cu_2(OH)_3Br$	green	-	-	1.17	1.12	49.26	48.97	-	-
$[Ni_2(NCO)_2(H_2O)_2(Br)_2]$	Light green	6.05	5.99	1.01	1.00	29.55	29.43	-	-
$ZnCO_3.H_2O$	white	8.37	8.21	1.41	1.32	45.60	45.33	41.84	40.47

Table 2: Selective bond lengths and angles inside unit cell of $Cu_2(OH)_3Br$ compound

atom1	atom2	d1-2	atom3	d1-3	angle^ 213°
Cu1	O3	1.9899	O3	1.9899	180.000
	O3	1.9899	O1	2.3297	107.925
	O3	1.9899	O1	2.3297	72.075
	O3	1.9899	O1	2.3297	107.925
	O1	2.3297	O1	2.3297	180.000
Cu2	Cu1	0.0000	O3	1.9899	0.000
	Cu1	0.0000	O3	1.9899	0.000
	Cu1	0.0000	O1	2.3297	0.000
	Cu1	0.0000	O1	2.3297	0.000
	O3	1.9899	O3	1.9899	180.000
	O3	1.9899	O1	2.3297	72.075
	O3	1.9899	O1	2.3297	107.925
	O3	1.9899	O1	2.3297	107.925
	O3	1.9899	O1	2.3297	72.075
	O1	2.3297	O1	2.3297	180.000
	O1	1.9004	O2	1.9173	105.366
	O1	1.9004	Br1	2.1175	96.010
	O2	1.9173	Br1	2.1175	156.476

copper(II), nickel(II), and zinc(II) compounds are shown in Fig. 1a-d, respectively. The infrared spectra show no bands due to any of the reactants and of coordinated carbamide.

In case of zinc carbonate hydrated compound, 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 spectrum of the commercially obtained $ZnCO_3$ is the same as that of the product resulted from the reaction between zinc(II) bromide and carbamide at 95 °C. The infrared assignments agree quite well with those known[29] for the ionic carbonate $(CO_3)^{2-}$. 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 ν_2, ν_3 and ν_4 are infrared active. The stretching vibrations of the type; ν(C-O); $\nu_3(E')$ is observed as a medium band in the range of 1500-1370 cm^{-1} while the stretching vibration (C-O); $\nu_1(A'_1)$ is observed in the region ~1050 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

Table 3: Some selected visualized XRD-data inside Ni-complex lattice

No	2q	d Å	F	h	k	l	Multi
1	40.014	2.2515	174.46	3	4	1	8
2	40.041	2.2500	86.34	0	0	4	2
3	40.262	2.2381	174.29	8	1	1	8
4	40.333	2.2344	53.53	1	0	4	4
5	40.418	2.2299	127.87	0	3	3	4
6	40.518	2.2246	193.46	6	3	1	8
7	40.707	2.2147	125.94	1	3	3	8
8	40.753	2.2123	199.69	4	4	0	4
9	41.087	2.1951	339.81	0	1	4	4
10	41.198	2.1894	99.15	2	0	4	4
11	41.201	2.1893	128.27	5	3	2	8
12	41.278	2.1854	113.48	0	4	2	4
13	41.372	2.1806	39.05	1	1	4	8
14	41.427	2.1779	150.34	6	0	3	4
15	41.562	2.1711	209.58	1	4	2	8
16	41.566	2.1709	135.72	2	3	3	8
17	42.023	2.1483	83.48	4	4	1	8
18	42.086	2.1453	162.63	8	2	0	4
19	42.220	2.1388	288.17	2	1	4	8
20	42.397	2.1302	112.82	5	2	3	8
21	42.407	2.1298	65.14	2	4	2	8
22	42.445	2.1280	90.79	6	1	3	8
23	42.608	2.1202	10.56	3	0	4	4
24	42.874	2.1076	88.29	7	2	2	8
25	42.936	2.1048	162.07	7	3	0	4
26	42.967	2.1033	178.51	3	3	3	8
27	43.029	2.1004	14.73	8	0	2	4
28	43.286	2.0885	85.98	5	4	0	4
29	43.324	2.0868	98.15	8	2	1	8
30	43.603	2.0741	30.88	3	1	4	8

symmetry of CO_3^{2-} to be lowered than D_{3h}. The out of plane of vibration d(OCO); ν_2(A“$_2$) is observed in the range of ~830 cm^{-1} as a medium strong band while, the angle deformation bending vibration δ(OCO); ν_4(E‘) appear in the range of 690 cm^{-1} as a medium strong. The infrared spectra of zinc(II) carbonate hydrate, $ZnCO_3.xH_2O$ (Fig. 1d) show that, some these products are hygroscopic and its clearly have moisture water. The band related to the stretching vibration ν_{as}(O-H) and ν_s(O-H) of H_2O are observed as expected at 3441 and 3353 cm^{-1}, respectively. At room temperature the coordination compounds of Zinc(II) ion with urea have been studied extensively [30,31] and it was found that, in these complexes, urea coordinated through its oxygen atom forming the $[Zn(urea)_2X_2]$ where (X = Cl^-, NO_3^- or CH_3COO^-). At high temperature the role of Zn(II) ions in decomposing the coordination urea

Table 4a: Selective bond lengths and angles for Nickel-type one inside crystal lattice of $[Ni_2(NCO)_2(H_2O)_2(Br)_2]$ complex

Atom1	Atom2	d_{1-2}	Atom3	d_{1-3}	Angle^ 213°
Ni1	O2	2.2163	O1	2.3540	85.828
	O2	2.2163	O3	2.3788	95.915
	O2	2.2163	O4	2.3805	81.709
	O1	2.3540	O3	2.3788	99.428
	O1	2.3540	O4	2.3805	89.254
	O1	2.3540	O5	2.5380	166.246
	O1	2.3540	O6	2.7991	124.131
	O3	2.3788	O4	2.3805	170.837
	O3	2.3788	O5	2.5380	80.488
	O3	2.3788	O6	2.7991	82.229
	O4	2.3805	O5	2.5380	91.781
	O4	2.3805	O6	2.7991	95.371
	O4	2.3805	C2	3.2780	95.466
	O4	2.3805	C1	3.3074	107.172
	O5	2.5380	O6	2.7991	42.121
	O5	2.5380	C2	3.2780	82.690
	O5	2.5380	N2	3.3262	121.033
	O6	2.7991	C2	3.2780	123.912
	O6	2.7991	C1	3.3074	102.946
	O6	2.7991	N2	3.3262	82.627
	C2	3.2780	C1	3.3074	125.474
	C2	3.2780	N2	3.3262	136.858
	C2	3.2780	Br2	3.5118	66.637
	C1	3.3074	N2	3.3262	21.681
	C1	3.3074	N3	3.4102	127.934
	C1	3.3074	C3	3.4375	72.827
	N2	3.3262	N3	3.4102	129.667
	N2	3.3262	C3	3.4375	71.802
	N2	3.3262	Br3	3.4409	69.972
	N3	3.4102	C3	3.4375	58.067
	N3	3.4102	Br3	3.4409	64.749
	C3	3.4375	Br3	3.4409	20.550
	C3	3.4375	C4	3.4695	169.096
	C3	3.4375	Br2	3.5118	19.615

in the form of $[Zn(urea)_2X_2]$ could be understood as follows;

$$[Zn(urea)_2Br_2] + 3H_2O \xrightarrow{95^oC} ZnCO_3.xH_2O + CO_2 + 2NH_4Br + 2NH_3$$

Metallic hydroxy salts with the composition $M_2(OH)_3X$ (M = Cu, Co; X = organic anion) [32-34] have been extensively studied because of their interesting magnetic properties, that are strongly dependent on the structure and molecular ordering of intercalated anions, as well as, the interlayer distance determined by them. Accordingly, the properties of those materials can be easily manipulated, such that can be considered tunable magnetic materials[34]. So, it is reported in this paper a new cheap and simple method for preparation of copper hydroxybromide, an interesting member of this class of layered materials. The infrared spectrum of copper hydroxyl bromide, $Cu_2(OH)_3Br$, compound has some characteristic vibrational modes which are expected in the IR spectrum. In the specific case of the metal-oxygen bond, medium peaks are expected between 496 and 407 cm^{1}. Medium intensity vibrational modes associated to the Cu–O–H bond should appear in the interval at 815, 844 and 1110 cm^{-1}[35]. The narrow bands at 3523 and 3405 cm^{-1} corresponds to stretching symmetric and asymmetric OH groups. The frequency of the vibrational modes attributed to Cu–O–H bonds are depend on the degree of hydrogen bonding and were found at 777, 681 and 534 cm^{-1}[34]. In this study, the decomposition of coordinated carbamide in aqueous media at ~ 95 °C forming the new

Table 4b: Selective bond lengths and angles for Nickel-type two inside crystal lattice of $[Ni_2(NCO)_2(H_2O)_2(Br)_2]$ complex

Atom1	Atom2	d_{1-2}	Atom3	d_{1-3}	Angle^ 213°
Ni2	O2	2.2163	O1	2.3540	85.828
	O2	2.2163	O3	2.3788	95.915
	O2	2.2163	O4	2.3805	81.709
	O1	2.3540	O3	2.3788	99.428
	O1	2.3540	O4	2.3805	89.254
	O1	2.3540	O5	2.5380	166.246
	O3	2.3788	O4	2.3805	170.837
	O3	2.3788	O5	2.5380	80.488
	O3	2.3788	O6	2.7991	82.229
	O4	2.3805	O6	2.7991	95.371
	O4	2.3805	C2	3.2780	95.466
	O5	2.5380	O6	2.7991	42.121
	O5	2.5380	C2	3.2780	82.690
	O5	2.5380	C1	3.3074	142.688
	O6	2.7991	C2	3.2780	123.912
	O6	2.7991	C1	3.3074	102.946
	O6	2.7991	N2	3.3262	82.627
	C2	3.2780	C1	3.3074	125.474
	C2	3.2780	N2	3.3262	136.858
	C2	3.2780	N3	3.4102	20.883
	C1	3.3074	N2	3.3262	21.681
	N2	3.3262	Br3	3.4409	69.972
	N3	3.4102	C3	3.4375	58.067
	C3	3.4375	Br2	3.5118	19.615
	Br3	3.4409	C4	3.4695	151.929
	Br3	3.4409	Br2	3.5118	0.965
	C4	3.4695	Br2	3.5118	152.889

compound, $[Cu_2(OH)_3Br$ may be understood as follows. It is well known [30, 36] that Cu(II) forms with urea the complex ion $[Cu(urea)_4]^{2+}$ at room temperature. Accordingly, in our case the parent complex $[Cu(urea)_4](Br)_2$ is formed. This parent complex may decompose at high temperature according to the following equation;

$$2[Cu(urea)_4](Br)_2 + 11\ H_2O \xrightarrow{95^{o}C} Cu_2(OH)_3Br + 3NH_4Br + 8CO_2 + 13NH_3$$

The reaction of nickel nitrate with urea in water was studied at 40° by the isothermal method[37]. The ternary solubility diagram of the $Ni(NO_3)_2$-Urea-H_2O system is presented. The solid phases in the system have the compounds of $Ni(NO_3)_2.2(NH_2)_2CO.2H_2O$, $Ni(NO_3)_2.4(NH_2)_2CO$, and $Ni(NO_3)_2.10(NH_2)_2CO$. All solubility of solid phases were determined at 30° and confirmed by an X-ray structural method. Complexes of N-ally urea (NAU) with cobalt(II) and nickel(II) halides and perchlorates have prepared and characterized by electrical conductance, magnetic susceptibility[38]. The infrared spectra of N-allyl urea complexes with Ni(II) and Co(II) salts, $[Co(NAU)_2X_2]$; (X= Cl^-, Br^-, and I^-), $[Ni(NAU)_4X_2]$; (X=Cl^-, Br^-), $[Ni(NAU)_4](ClO_4)_2$ and $[Ni(NAU)_6](ClO_4)_2$ are reported [39]. A negative shift in the frequencies of n(C=O) and d(NH_2) bands, and a positive shift in the frequency of n(C-N) band, suggest that carbonyl oxygen is the donor site.

Table 5(a): Selective bond lengths and angles for oxygen-type one and two inside crystal lattice of $[Ni_2(NCO)_2(H_2O)_2(Br)_2]$ complex

Atom1	Atom2	d1-2	Atom3	d1-3	Angle^ 213°
O1	C1	1.5699	Ni1	2.3540	113.381
	C1	1.5699	N2	2.4450	26.238
	Ni1	2.3540	N2	2.4450	87.732
	Ni1	2.3540	N1	2.5670	138.350
	N2	2.4450	N1	2.5670	52.545
	N1	2.5670	O2	3.1136	147.959
	N1	2.5670	Br3	3.2513	88.778
	O2	3.1136	Br3	3.2513	60.344
	O2	3.1136	O4	3.3260	55.607
	Br3	3.2513	Br2	3.3401	0.415
	O4	3.3260	Br1	3.7856	68.950
	O4	3.3260	C3	3.8837	104.240
	Br2	3.3401	O3	3.6104	41.659
	O3	3.6104	C3	3.8837	25.148
	N2	3.7160	Br1	3.7856	55.508
	N2	3.7160	C3	3.8837	124.003
	Br1	3.7856	C3	3.8837	172.426
O2	C2	1.6985	Ni1	2.2163	113.050
	C2	1.6985	N3	2.5538	24.073
	C2	1.6985	N2	3.7713	144.904
	C2	1.6985	O5	3.8485	78.412
	Ni1	2.2163	N3	2.5538	90.987
	Ni1	2.2163	N4	2.5826	137.048
	Ni1	2.2163	O5	3.8485	38.872
	N3	2.5538	N4	2.5826	49.096
	N3	2.5538	O4	3.0096	119.498
	N3	2.5538	O5	3.8485	61.597

The infrared spectrum of $[Ni_2(NCO)_2(H_2O)_2(Br)_2]$ complex clearly indicates the absence of bands due to the coordinated carbamide and the presence of very strong bands characteristic for isocyanate ions at 2220 $\nu(NCO^-)$ cm^{-1} and 644 $\sigma(NCO^-)$ cm^{-1} [40] and for coordinated water at the 1629, 3642 and 3434 cm^{-1} respectively, for $\delta(H_2O)$, $\nu_{as}(O\text{-}H)$ and $\nu_s(O\text{-}H)$ of H_2O. At room temperature the nickel(II)-urea complex is formulated as $[Ni(urea)_4]^{2+}$ [37, 38]. At high temperature this complex may undergo the following reaction; where (X =Br^-).

$$2[Ni(urea)_4]Br_2+8H_2O \xrightarrow{95^oC} [Ni_2(NCO)_2(H_2O)_2(Br)_2]+2HBr+14NH_3+6CO_2.$$

Electron spin resonance

The ESR tool of analysis is useful in discuss the geometry and state of electrons in metal ion of

Table 5b: Selective bond lengths and angles for oxygen-type three (O3) and four (O4) inside crystal lattice of $[Ni_2(NCO)_2(H_2O)_2(Br)_2]$ complex

Atom1	Atom2	d1-2	Atom3	d1-3	Angle^ 213°
O3	C3	1.6531	Ni1	2.3788	115.812
	C3	1.6531	Br3	2.4697	26.193
	Ni1	2.3788	Br3	2.4697	90.396
	Ni1	2.3788	Br2	2.4844	92.434
	Br3	2.4697	Br2	2.4844	2.101
	Br3	2.4697	Br1	2.5914	53.881
	Br2	2.4844	Br1	2.5914	51.780
	Br2	2.4844	N3	3.0939	81.686
	Br1	2.5914	N3	3.0939	85.186
	N3	3.0939	O5	3.1788	66.971
	N3	3.0939	O2	3.4143	45.881
	O5	3.1788	O2	3.4143	71.321
	O5	3.1788	O6	3.4195	33.825
	O6	3.4195	N2	3.4224	72.863
	O6	3.4195	Br2	3.4545	77.670
	N2	3.4224	Br2	3.4545	79.334
	Br2	3.4545	Br3	3.4892	1.406
	Br3	3.4892	C1	3.7954	98.048
	O1	3.6104	C2	3.6560	79.927
	O1	3.6104	C1	3.7954	24.311
	C2	3.6560	C1	3.7954	103.535
O4	C4	1.6867	Ni1	2.3805	116.044
	Ni1	2.3805	O2	3.0096	46.781
	Ni1	2.3805	N2	3.3206	104.291
	O2	3.0096	N2	3.3206	72.947
	O2	3.0096	O1	3.3260	58.617
	O2	3.0096	O5	3.5333	71.549
	O2	3.0096	O5	3.6483	109.215
	O2	3.0096	N3	3.7248	112.789
	N2	3.3206	O1	3.3260	67.984
	O1	3.3260	O5	3.5333	90.105
	O5	3.5333	O5	3.6483	112.165
	N3	3.7248	N1	3.8015	107.084
	N3	3.7248	O6	3.8405	73.985

the compounds. In this paper, the ESR spectrum of the Cu(II) compound (Fig. 2). The solid-state ESR spectra of some of the compounds exhibit axially symmetric g-tensor parameters with $g_{II} > g_{4\%} >$ 2.0023, indicating that the copper site has a $d_{x^{2}-y^{2}}$ ground-state characteristic of tetrahedral, square-planar, or octahedral stereochemistry. The $g_{II} > g_{4\%}$ for synthesized copper(II) hydroxylbromide, $Cu_2(OH)_3Br$, indicates a distorted octahedral. In axial symmetry, the G-values are given by Eq. 1.

$$G = (g_{II}-2)/(g_{4\%}-2) = 4 \rightarrow (1)$$

Where G is the exchange interaction parameter, according to literature, for the considerable exchange interaction process between Cu(II) centers in the solid state the value of $G \geq 4$. The G_{iso}. Value obtained for Cu(II) compound is estimated to be 2.3850 which satisfy the above mentioned parameter. The g_{iso} value was evaluated by using the relation g_{iso} = 1/3 g_{II} + 2/3 $g_{4\%}$, and these calculated values are in agreement with an orbital non-degenerate state**.**

The values of g_{II} were calculated for assigned arrows peaks in Fig.2 and found to be 1.934, 2.2512 and 3.0016 respectively.

This trend of increasing in g_{II} values was observed with V. P. Singh[41] who was studying the electronic and ESR spectra of Cu(II) halo-hydrazones complexes and indicated that each complex exhibits a six-coordinate tetragonally distorted octahedral geometry in the solid state and in DMSO solution. The ESR spectra of most of the Cu-complexes reported in[41] are typically isotropic

Table 5(c): Selective bond lengths and angles for oxygen-type five (O5) and six (O6) inside crystal lattice of $[Ni_2(NCO)_2(H_2O)_2(Br)_2]$ complex

Atom1	Atom2	d1-2	Atom3	d1-3	Angle ^213°
O5	O6	1.9333	Ni1	2.5380	76.180
	O6	1.9333	O3	3.1788	79.928
	Ni1	2.5380	O3	3.1788	47.565
	O3	3.1788	N3	3.4616	55.343
	N3	3.4616	O4	3.5333	86.911
	O4	3.5333	N1	3.6039	140.302
	O4	3.5333	O4	3.6483	110.280
	N1	3.6039	C2	3.8820	129.654
	N1	3.6039	C4	3.9892	82.932
	O4	3.6483	N3	3.7458	74.220
	O2	3.8485	C2	3.8820	25.380
	O2	3.8485	C4	3.9892	72.740
	C2	3.8820	C4	3.9892	55.599
O6	O5	1.9333	Ni1	2.7991	61.700
	O5	1.9333	O3	3.4195	66.246
	Ni1	2.7991	O3	3.4195	43.573
	Ni1	2.7991	O4	3.8405	38.107
	O3	3.4195	O4	3.8405	81.382
	O3	3.4195	C4	3.8459	103.848
	O3	3.4195	Br1	3.8722	71.947
	O3	3.4195	N1	3.9880	140.086
	O4	3.8405	C4	3.8459	25.352
	C4	3.8459	Br1	3.8722	125.685
	C4	3.8459	N1	3.9880	81.126
	Br1	3.8722	N1	3.9880	73.355

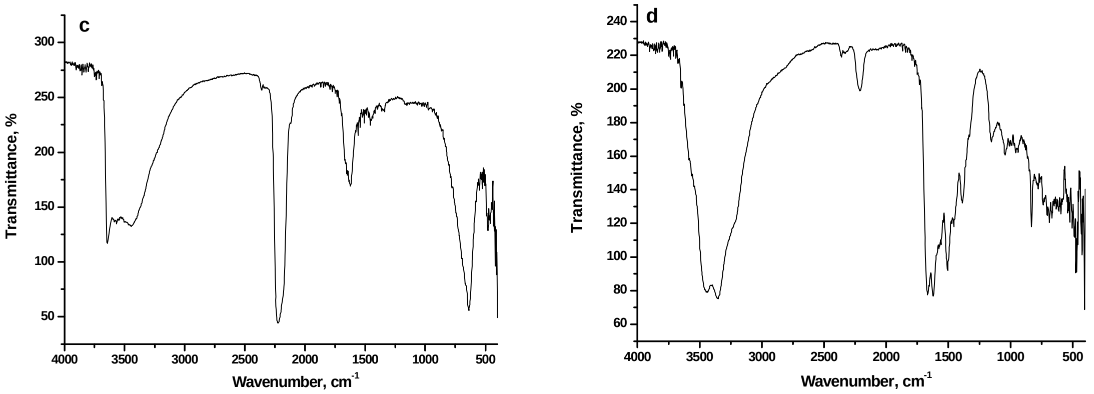


Fig. 1: Infrared spectra of a- Urea, b- $Cu_2(OH)_3Br$, c- $[Ni_2(NCO)_2(H_2O)_2(Br)_2]$ and d- $ZnCO_3.H_2O$ compounds

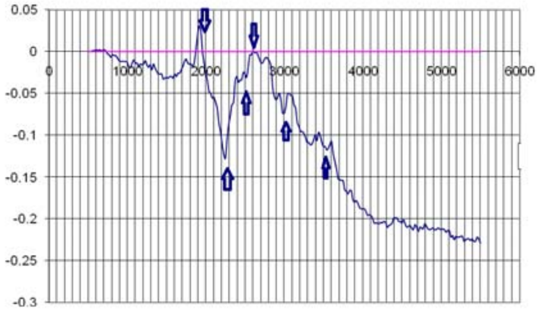


Fig. 2: ESR spectrum of $Cu_2(OH)_3Br$ compound

type at room temperature (300 K) in solid state as well as in DMSO solution. However, all the Cu-complexes have the trend $g_{||} > g_{4\%}$, observed in all the complexes measured. The same trend was observed in Fig.2 all values of $g_{||} > g_{4\%}$ which reflect that all axial position in the monoclinic crystal form of $Cu_2(OH)_3Br$ are effectively by the magnetic field by ratio higher than those of perpendicular positions ($g_{4\%}$). The unusual behavior of isocyanate and halide complexes of copper (II) was repored by Chughtai *et al.*[42] were investigated the magnetic

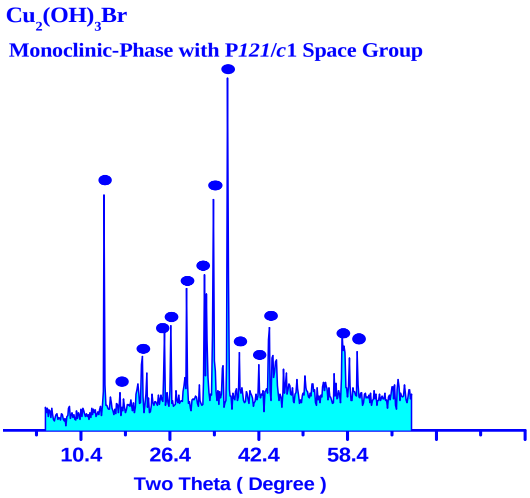


Fig. 3: Experimental X-ray diffractogram of the $Cu_2Br(OH)_3$ with A2XY3 type structure and P*121/c*1 space group

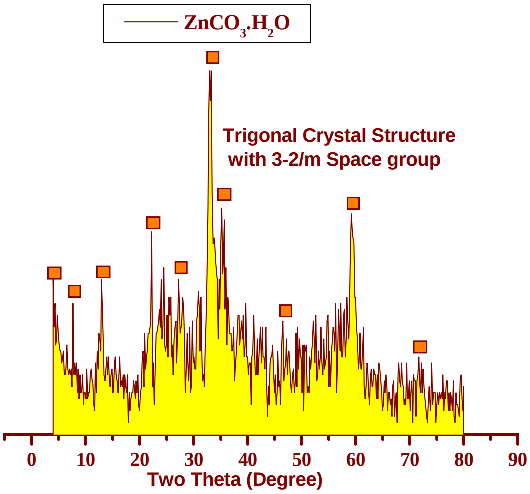


Fig. 3(a): Experimental X-ray diffractogram of the $ZnCO_3.H_2O$ with trigonal structure and 3-*2/m* space group

effects on the geometry of some salts of the isocyanato and halo-cuprate(II) anion involving tetraethylammonium and other bulky cations .

They proposed that the -N=C=O isocyanate and halo cuprate (II) entities are arrayed about the copper in a square planar (or pseudo octahedral) manner in the blue isomer and in a tetrahedral (though probably distorted tetrahedral) crystal form.

X-Ray diffraction (XRD) and structural analysis measurements

The X-ray diffraction measurements (XRD) were carried out at room temperature on the fine ground powders of pure products resulted from reaction of metal bromide with urea in the range (2è =2-70º) using Cu-Ká radiation source and a computerized X-ray diffractometer with two theta scan technique. The accurate analysis of XRD indicated that the first compound is $Cu_2(OH)_3Br$ which has A_2XY_3 structure type with monoclinic crystal form as clear in Fig. 3. The lattice parameters were calculated and found to be *a* = 6.154, *b* = 6.813 and *c* = 9.114 Å for monoclinic structure of P*121*/*c*1 space group respectively. By the same technique the analysis of XRD of compound II resulted from reaction of zinc bromide with urea was found $ZnCO_3.H_2O$ trigonal crystal structure with 32/m space group and lattice parameters *a* = 4.672 and *c* = 15.0199Å respectively as clear in assigned figure Fig. 3a.

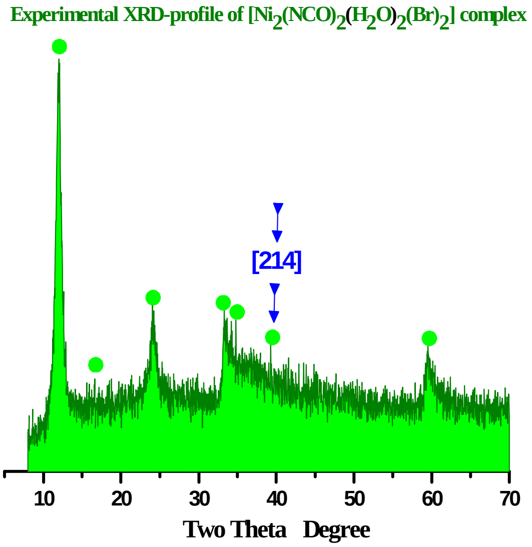


Fig. 3(b): Experimental X-ray diffractogram of the $[Ni_2(NCO)_2(H_2O)_2(Br)_2]$ complex

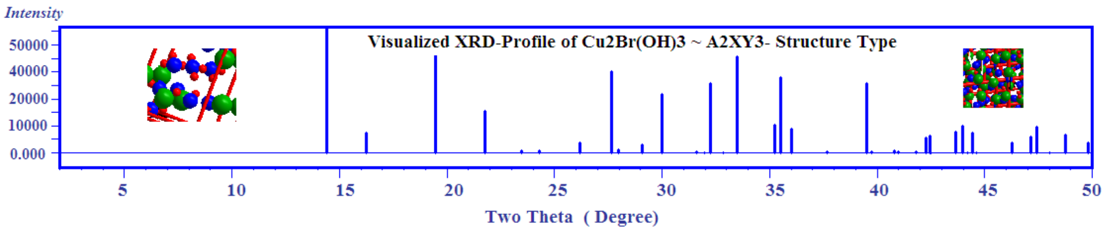
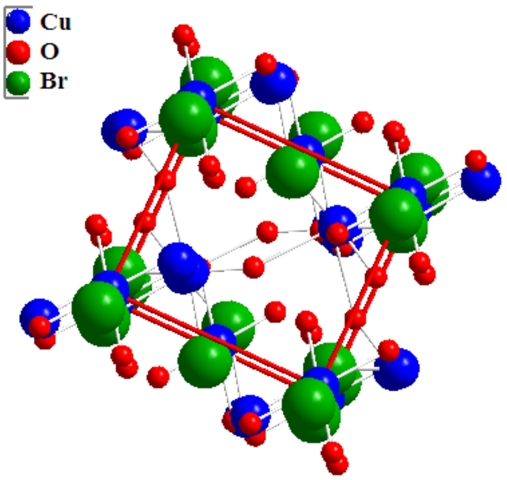


Fig. 4: Visualized XRD-profile of $Cu_2Br(OH)_3$ with monoclinic crystal form



Monoclinic Cu2Br(OH)3 with P121/c1

Fig. 5: Unit cell of $Cu_2Br(OH)_3$ compound

The analysis of Fig.3b which describes experimental XRD-profile of polycrystalline phases exist together with nickel-complex proved that the highest figure of merit (*F*) was for monoclinic phase with P_{212121} space group. The last product produced from nickel bromide with urea reaction was

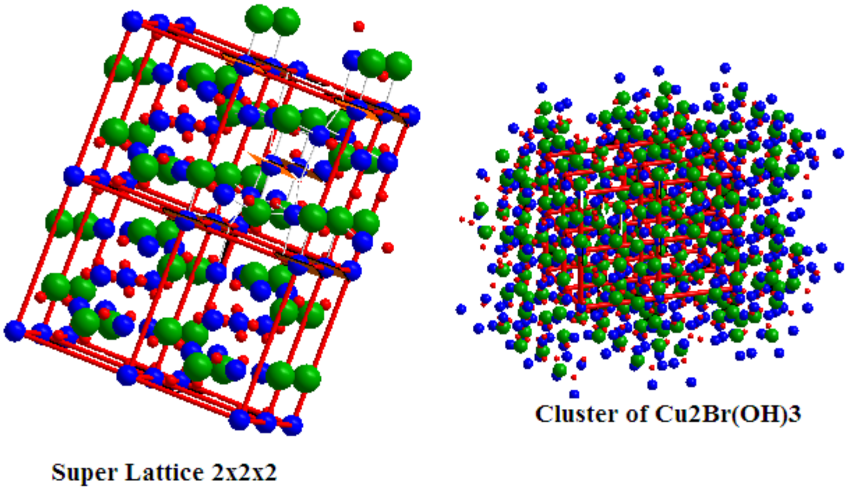


Fig. 6: Side view of super-lattice of $Cu_2Br(OH)_3$ and cluster formed with minimum 500 atoms

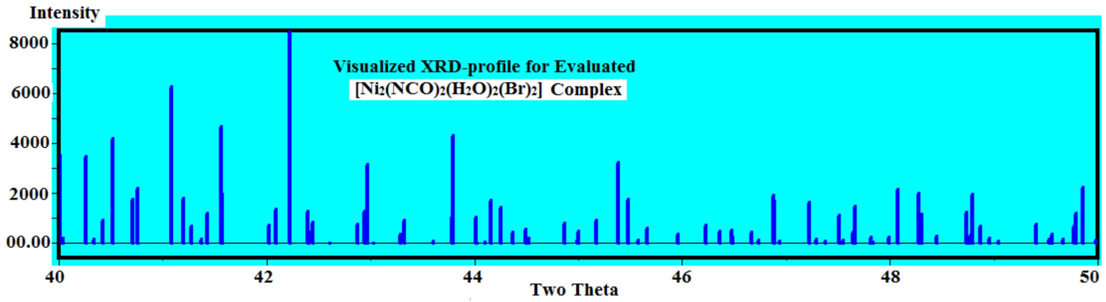


Fig. 7: Rhomboheral visualized structure pattern for Nickel-complex

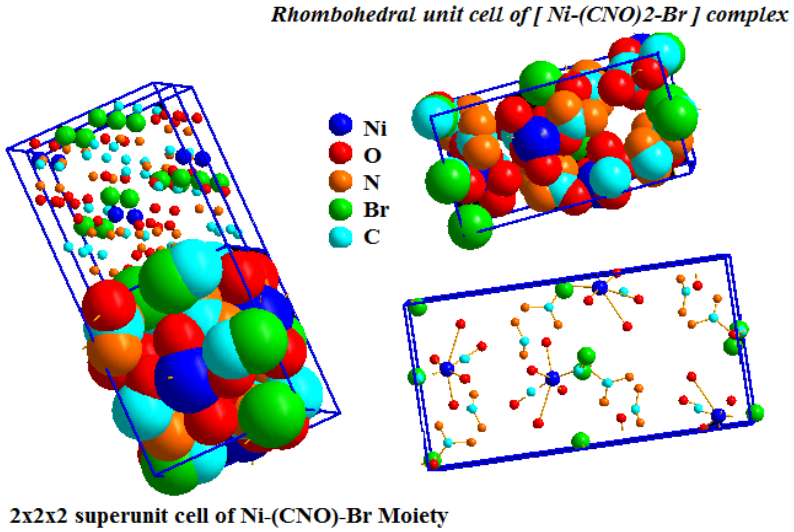


Fig. 8: Ball-stick and space filling models for rhommohedral Nickel-Complex

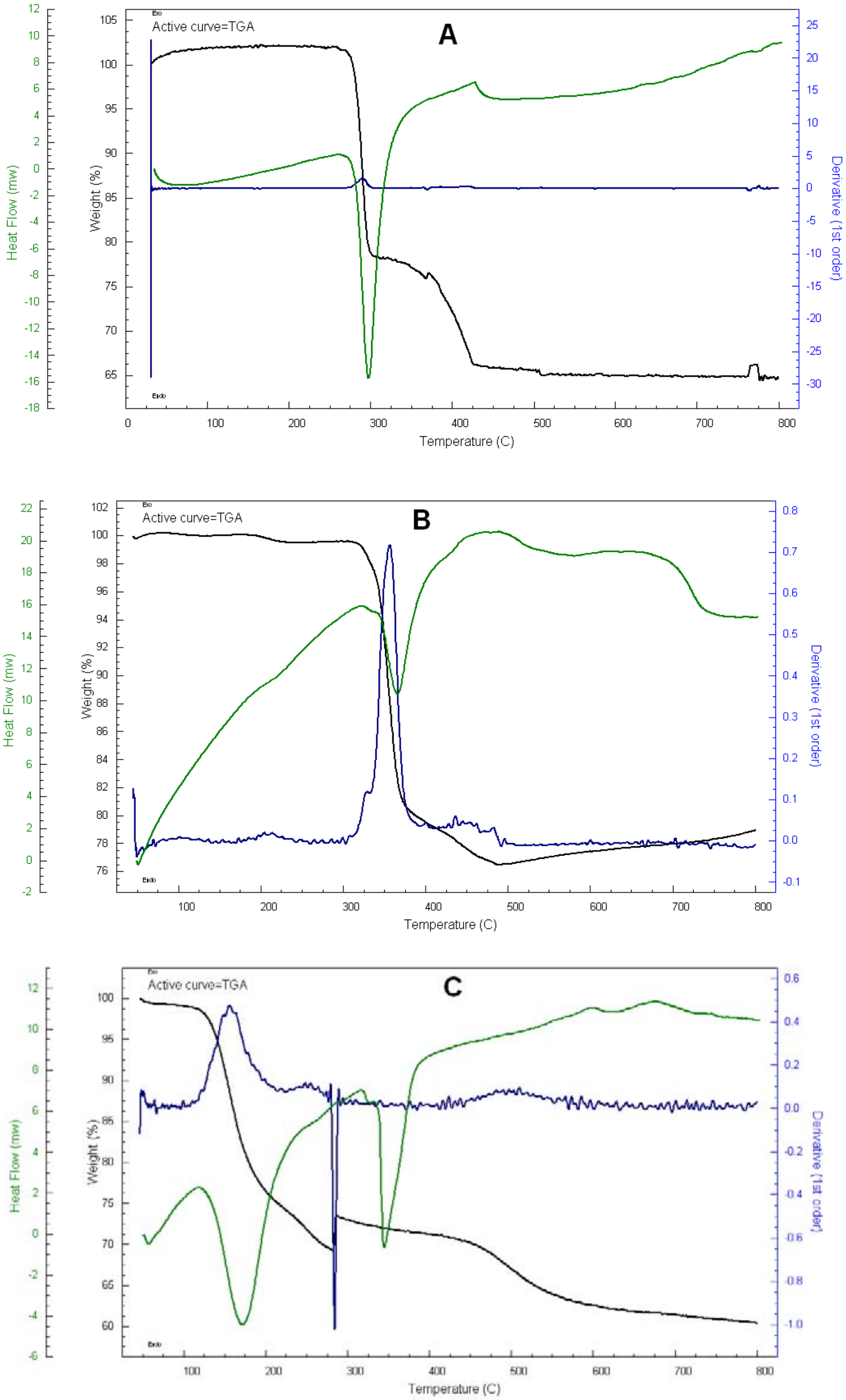


Fig. 9: TG/DTG/DSC curves of a- $Cu_2(OH)_3Br$, b- $[Ni_2(NCO)_2(H_2O)_2(Br)_2]$ and c- $ZnCO_3.H_2O$ compounds

formulated and confirmed to be $[Ni_2(NCO)_2(H_2O)_2(Br)_2]$ complex with rhombohedra unit cell with lattice parameters *a* =19.0711, *b*=10.4231 and *c* = 8.9876 Å respectively and P_{212121} space group.

Structural visualization

Visualized studies of crystal structure were made by using Diamond Molecular Structure version 3.2 packages, Germany and Mercury 2.3-BUILD RC4-UK. A visualization study made is concerned by matching and comparison of experimental and theoretical data of atomic positions, bond distances, oxidation states and bond torsion on the crystal structure formed. The visualized studies for compound I ($Cu_2(OH)_3Br$) as model of urea precursor reactions confirmed that there are very good fitting between experimental XRD of $Cu_2(OH)_3Br$ see Fig. 3a and visualized XRD-pattern Fig. 4.

Table 2 displays some selective bond distances and angles inside unit cell of ($Cu_2(OH)_3Br$) compound as it cleat there is two different types of copper atoms nominated as Cu1 and Cu2 ,three types of oxygen atoms symbolized as O1,O2 and O3 respectively .And finally only one type of bromide .One can observe that copper linked with oxygen recording 1.98 ,2.3297 ,1.91 Å for Cu1-O3,Cu2-O1 and Cu2-O1 respectively .These observations confirmed that there are more one oxidation state for copper which consistent and support ESR-data reported in the present manuscript .

Furthermore Figs. 5, 6 together with Table 2 confirm that the obtained compound I is hundred percent $Cu_2(OH)_3Br$ with A_2XY_3 structure type and monoclinic crystal form.

Fig. 3b shows experimental polycrystalline XRD-profile recorded for $[Ni_2(NCO)_2(H_2O)_2(Br)_2]$ complex. It was notified that the most intense reflection peak is located at two theta ~ 42.22 with [214] Muller index. This peak has highest figure of merit (F) ~288.17 accompanied with maximum multiplicities = 8 respectively as shown and tabulated in Table.3 which shows also some visualized selected XRD-diffraction data with its d-spacing inside unit cell of Ni-Isocyanate-Bromide complex.

Fig.7 shows the visualized XRD-profile of evaluated rhombohedra nickel-complex with intense diffraction peak lies at two theta value ~ 42.15° which is nearly identical to that induced in the experimental XRD-profile Fig.3b .

Fig.8 displays ball-stick and fill-space models for Ni-NCO-Br complex with minimum 78 atoms inside visualized unit cell of nickel-isocyanate-bromide complex .Furthermore 2x2x2 super unit cell was built up to confirm validity of rhombohedral structure of nickel complex $[Ni_2(NCO)_2(H_2O)_2(Br)_2]$ as stable valid structure form .

To complete visualization investigations with good fitting between theoretical and experimental studies many of structural parameters were analyzed carefully such as bond lengths, torsion on angles and symmetry operations.

Tables 4a,4b describe some selected bond distances and structural parameters of visualized $[Ni_2(NCO)_2(H_2O)_2(Br)_2]$ complex concerned by the two different types of nickel atoms inside unit cell of Ni-isocyanate- bromide complex symbolized as Ni1 and Ni2 .

As it clear from table.4a Ni1 linked with six different types of oxygen atoms nominated as (O1,O2,O3,O4,O5 and O6) recording bond lengths equal to 2.35 ,2.21 ,2.37 ,2.38,2.53 and 2.7 Å respectively . These data confirmed that the average density of positively charge focused on the nickel atoms (Ni1 ,Ni2) are varying as environmental neighboring atoms is changed[43-48] . Similar behavior was observed with nickel type two (Ni2) as reported and tabulated in Table.4b.

Tables 5a,b,c are describing the bonding between different six oxygen atoms symbolized as O1,O2,O3,O4,O5 and O6 with other neighboring atoms .

Accurate analysis of these tabulated data enhance to understand why $[Ni_2(NCO)_2(H_2O)_2(Br)_2]$ complex is stable and valid specially at the point of view in which torsion on angles inside unit cell still within normal ranges[44,46, 47] recording minimum torsion (2.1°) for angle Br2-O3-Br3 which is nearly linear and maximum is for C3-O1-Br1 which equal 172.4° , which is also very close to (180°) linear angle . As reported in[44,47] if the torsion on angle inside unit cell of crystal lattice within the normal range (5-10 %) of the angle value whatever the angle, is enhancing stability of the proposed structure .

Thermal analysis studies

The thermogravimetric analyses (TG/DTG/DSC) curves for the copper hydroxybromide, $[Ni_2(NCO)_2(H_2O)_2(Br)_2]$ and $ZnCO_3.xH_2O$ in nitrogen atmosphere are illustrated in Figs 9. There is one step event leading to a total weight loss of 38% at 300 °C which attributed to the removal of hydrogen bromide and one water molecules. The final decomposition product was detected as copper(II) oxide. Also, The $[Ni_2(NCO)_2(H_2O)_2(Br)_2]$ complex has a sharp decomposition peak at 375 °C with weight loss about 24% due to the loss of the two coordinated water molecules, one nitrogen and on carbon monoxide molecules. The residual moieties consists of mixture from nickel(II) oxide and nickel(II) bromide contaminated with few carbon atoms. Additionally, Fig. 9 shows typical curves for thermogravimetric (TG), differential scanning calorimetry (DSC) and differential thermogravimetric analysis (DTG) of the decomposition of the zinc carbonated hydrate together with the mass spectra of the evolved gases at various temperatures. The thermal decomposition of the sample takes place in temperature ranges of 100-to-200 °C and 200-to-800 °C with mass loss corresponding to hydrated water molecules and carbon dioxide gas. Only the fragment ions of H_2O and CO_2 can be detected in the mass spectra during the course of the thermal decomposition.

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