Spectral and Kinetic Studies of Thermal Decomposition of Ni^{II} hexanoate Complex Ni$_2$(cap)$_4$

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Abstract: Nickel(II) hexanoate complex, Ni$_2$(cap)$_4$, (where cap is the hexanoate anion = CH$_3$(CH$_2$)$_4$COO$^-$) was prepared and discussed using elemental analysis, infrared spectra, thermogravimetric analysis (TGA), differential thermal analysis (DTA), UV-vis spectra, and X-ray powder diffraction (XRD) studies. Using the non-isothermal, Horowitz-Metzger (HM) and Coats-Redfern methods, and the kinetic parameters for the non-isothermal degradation of the respective complex was calculated by using TG data. The infrared data are in agreement with coordination through carboxylate-to-metal, with cap acting as a bridging bidentate ligand. Thermogravimetric analysis of the Ni^{II} complex shows that the first degradation step is associated with the release of terminal methyl groups followed by the decomposition of the hexanoate molecules to form nickel carbonate salt and then give nickel(II) oxide as residual product.
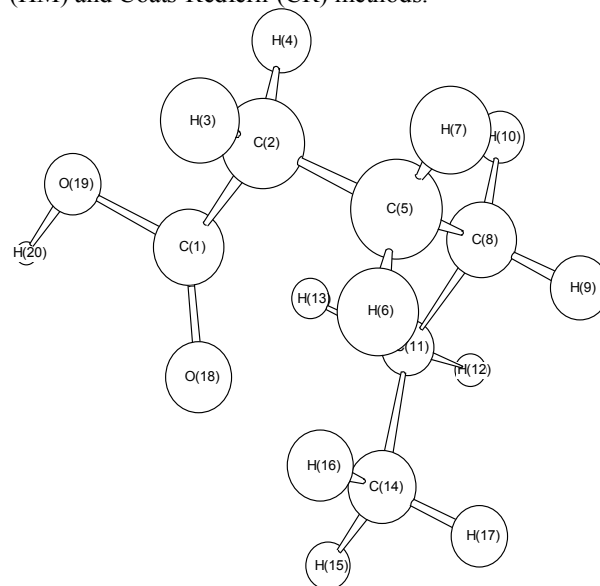[Mohamed Y. El-Sayed and Samy M. El-Megharbel **Spectral And Kinetic Studies of Thermal Decomposition of Ni^{ii} Hexanoate Complex Ni$_2$(Cap)$_4$.** *Life Sci J* 2012;9(3):1143-1151]. (ISSN: 1097-8135). http://www.lifesciencesite.com. 159

Keyword: Infrared spectra, Hexanoic acid, Thermal analysis, Nickel oxide.

1. Introduction

n- Hexanoic acid (n- hexanoic acid) Scheme 1, C$_6$H$_{12}$O$_2$, occurs in milk fats (about 2%), in coconut oil (< 1%). Such fatty acid is employed in the manufacture of pharmaceuticals and flavorings [1]. It is slightly soluble in water and readily soluble in ethanol and ether [2]. The binding of metal ions to carboxylic acids has been a subject of intense research investigation in view of its diverse applications, such as from the relevance of metal-carboxylate complexes as model systems for the metalloactive sites in bioinorganic chemistry [3, 4]. The structural diversity encountered in metal-carboxylate complexes can be attributed to the versatile bonding behavior of the carboxylate group which can act as a bidentate ligand or a bridging ligand [5, 6]. Compounds of transition and non-transition elements with hexanoic acid are not so common. A literature survey reveals that there are some papers on the preparation of hexanoates of some rare earth elements [7, 8] and the preparation of anhydrous copper(II) hexanoate from cuprous and cupric oxides [9]. Pietsch [10] extracted hexanoates of thorium, lead and iron hexanoates into CHCl$_3$. From the point of view of analytical chemistry, hexanoic acid is a good extracting agent for many elements [11-13] such as rare earths, zirconium, chromium, manganese, iron, gallium as well as aluminum with catechol violet by a mixture containing CHCl$_3$, hexanoic and propionic acids. The aim of the present work is to enhance the knowledge about metal-fatty acid (mono carboxylate) compounds. For such purpose, the synthesis, characterization and TG-DTA analysis of Ni(II)-hexanoate are reported. By using non-isothermal TG data, kinetic parameters for the thermal degradation processes were calculated, through Horowitz Metzger (HM) and Coats-Redfern (CR) methods.

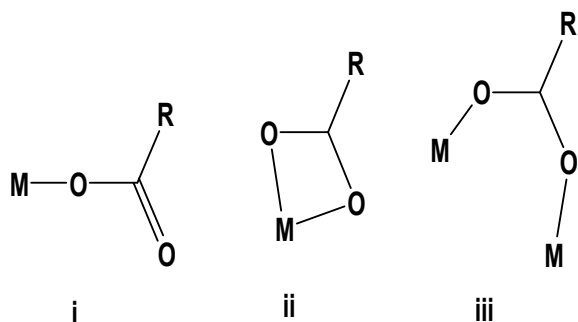**Scheme 1**: Structure of hexanoic acid

2- Experimental

All used reagents were of analytical grade and were employed without further purifications. Nickel(II) chloride anhydrous (1 mmol, Aldrich Company) were dissolved in 25 cm^3 of methanol and then the prepared solutions were slowly added to 25 cm^3 of an methanolic solution with 1 mmol of hexanoic acid (Fluka) under magnetic stirring. The

pH of each solution was adjusted to 8-9 by addition of ammonium hydroxide. The resulting mixture was heated at 60°C and left to evaporate slowly at room temperature overnight. The Turquoise precipitate was filtered off, washes with hot methanol and dried at 60°C. The elemental analysis data of carbon and hydrogen were performed in a CHN 2400 Perkin Elmer analyzer. The metal content was found gravimetrically by converting the resulted complex into its corresponding stable oxide. FTIR spectra were recorded on a Genesis II FT IR spectrometer in the 4000-400 cm^{-1} range with 40 scans in KBr discs. The electronic spectra were recorded in dimethylsulphoxide (DMSO) using a Shimadzu model 1601 PC UV spectrophotometer with quartz cells of 1 cm path length. The X-ray diffraction patterns (XRD) were obtained on a Rikagu diffractometer using Cu/K$_α$ radiation. The thermal studies TG/DTA–50H were carried out on a Shimadzu thermogravimetric analyzer under nitrogen till 800 °C.

3- Results and Discussion

Nickel hexanoate complex was obtained as green solid product. The elemental analysis results summarized as: Calc. %C= 54.42; %H= 8.52; %Ni= 17.73, Found %C= 53.95; %H= 8.47; %Ni= 17.75, these data are compatible with TGA and in a good agreement with the proposed formulas. The main infrared spectral data are summarized in Table 1. The carboxylate group is able to coordinate to metal ions by three different modes, as shown in Scheme 2 [14].

Scheme 2: Mode of carboxylate chelation

Type I: When the carboxylate group coordinates the metal ion in a monodentate manner, the difference between the wave numbers of the asymmetric and symmetric carboxylate stretching bands, $\Delta v = v_{as}COO^- - v_sCOO^-$), is larger than that observed for ionic compounds. Type II: When the ligand chelates, Δv is considerably smaller than that for ionic compounds, while on the asymmetric bidentate coordination, the values is in the range characteristic of monodentate coordination [15].

Type III: The characteristic wave numbers difference, Δv, is larger than that for chelated ions and nearly the same as observed for ionic compounds. Based on these facts it is possible to distinguish the coordination mode of the – COO$^-$ group.

Table 1a: Main infrared data for Ni$_2$(cap)$_4$ (values in cm^{-1}).

Ni$_2$(cap)$_4$	Assignments
3410 br	v (OH); H$_2$O
3135 br	v CH; CH$_3$
2952 m	v_{as} (CH)
2922 m	
2864 ms	v_s (CH)
1580 vs	v_{as} (OCO)
1510 m	
1440 w	δ(CH$_2$)
1412 ms	v_s (OCO)
1366 s	
1340 s	
1312 w	
1253 mw	$^\rho_w$ (CH$_2$)
1223 mw	v_{as} (CC)
1202 s	
1110 ms	
965 vw	v_s (CC)
902 mw	
849 mw	δ (CC)
804 w	
729 s	δ (OCO)
674 s	$^\rho_r$ (H$_2$O)
543 w	δ (CCO)
	$^\rho_w$ (OCO)
454 mw	v (M-O)
427 mw	

vs: very strong, s: strong, m: medium, w: weak, vw: very weak, br: broad. v_{as}: asymmetric stretching; v_s : symmetric stretching; δ: angle deformation; $^\rho_w$: wagging mode; $^\rho_r$: rocking mode.

Table 1b: Asymmetric and symmetric stretching vibrations of the carboxylate group, and their difference (in cm^{-1}) [$\Delta v = v_{as} - v_s$].

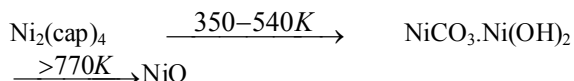| Compounds	v_{as} (COO)	v_s (COO)	$\Delta v = v_{as} - v_s$	Bonding mode
Ni$_2$(cap)$_4$	1580	1366	214	Bridge Bidentate

The hexanoic acid exhibits a strong absorption band around 1700 cm^{-1} due to the C=O group. For the prepared complexes, the difference between the asymmetrical and symmetrical vibrations, summarized in Table 1b, when compared with those data for sodium hexanoates (the (v_{as}-v_s) values of the

COO$^-$ groups are smaller than the value of sodium salt), strongly, suggest that COO$^-$ groups are acting as bridge bidentate chelating ligand (type III) [16]. Synthesized nickel hexanoate compound exhibit a strong absorption band around 260 nm, furthermore, the Ni(II) hexanoate exhibits a peak at 660 nm which assigned to d-d transition. The molar absorptivities (ε_{max}) of the nickel(II) hexanoate is 9783 l.mol^{-1}.cm^{-1}. These values are almost twice the value found for hexanoic acid (5068), in agreement with the fact that two ligand molecules of the ligand are present. The TG and DTA results are summarized in Table 2. The final product of thermal decompositions is the respective NiO.

Table 2: Main TGA and DTA data for the nickel (II) hexanoate complex

Compounds	DTA results T/K peak		TG results	
		T range (K)	Losses	Residue
Ni$_2$(cap)$_4$	375 endo 550 exo 570 exo 665 exo	353-538 538-550 563-870	4C$_2$H$_4$ Organic matter 2CO$_2$	NiO

The TGA and DTA curves of the compound Ni$_2$(cap)$_4$ shown that this compound is thermally stable up to 350 K, when the slow decomposition to NiO begins. The TG curve shows that the first mass loss between 350-540 K corresponds to the release of terminal four ethylene molecules, followed by the release of organic moiety. Hence the hexanoate of Ni(II) decompose to oxide (NiO) with intermediate formation of basic carbonate, NiCO$_3$.Ni(OH)$_2$, at 665 K. The most probable thermal decomposition Scheme can be shown as below:

Ni$_2$(cap)$_4$ $\xrightarrow{350-540K}$ NiCO$_3$.Ni(OH)$_2$
$\xrightarrow{>770K}$ NiO

The DTA curve for Ni(II)-hexanoate displays two spaced endothermic and exothermic peaks, respectively at 375 and 550 K. The inflexion points at 375 and 550 K can be attributed to the loss water molecules. The exothermic signal at 665 K can be attributed to the decomposition reaction of the intermediate formed: NiCO$_3$.Cu(OH)$_2$, involving the loss of CO$_2$ and hydroxyl group with simultaneous formation of NiO.

The previous studies showed an increase in the use of non-isothermal TG data to the calculation of rate-dependent parameters of solid-state decomposition has occurred, and several equations [19-26] have been employed for such purpose. Many authors [19-23] have discussed the advantages of the non-isothermal methods in comparison with the isothermal ones. The rate of a decomposition process can be described as the product of two separate functions of temperature and conversion rate [20]:

$$d\alpha/dt = k(T)f(\alpha) \qquad (1)$$

Where α is the fraction decomposed at time t, k(T) is the temperature dependent function and f(α) is the conversion function dependent on the mechanism of decomposition. It has been established that the temperature dependent function k(T) is of the Arrhenius type and can be considered as the rate constant k.

$$k = A\,e^{-E*/RT} \qquad (2)$$

Where, R is the gas constant in (Jmol^{-1}K^{-1}). Substituting equation (2) into equation (1), we get,

$$d\alpha/dT = (A/\varphi\,e^{-E*/RT})f(\alpha)$$

Where φ is the linear heating rate dT/dt. On integration and approximation, this equation can be obtained in the following form

$$\ln g(\alpha) = -E*/RT + \ln[AR/\varphi E*]$$

Where g(α) is a function of α dependent on the reaction mechanism. Several techniques have been used for the evaluation of temperature integral. Most commonly used methods for this purpose are the differential method of Freeman and Carroll [19] integral method of Coat and Redfern [21] and the approximation method of Horowitz and Metzger [24]. The thermodynamic parameters obtained for the nickel hexanoate complex are summarized in Table 3, in terms of stability ranges, peak temperatures and values of kinetic parameters.

The Coats-Redfern equation, which is a typical integral method, can be represented as:

$$\int_0^\infty d\alpha/(1-\alpha)^n = (A/\varphi)\int_{T1}^{T2} e^{-E*/RT}\,dT$$

For convenience of integration the lower limit T$_1$ is usually taken as zero. This equation on integration gives;

$$\mathrm{Ln}[-\ln(1-\alpha)/T^2] = -E*/RT + \ln[AR/\varphi E*]$$

A plot of left-hand side (LHS) against 1/T was drawn. E* is the energy of activation in kJ mol^{-1} and calculated from the slop and A in (s^{-1}) from the intercept value. The entropy of activation ΔS^* in (JK^{-1}mol^{-1}) was calculated by using the equation:

$$\Delta S^* = R\ln(Ah/k_B T_s) \qquad (3)$$

where k$_B$ is the Boltzmann constant, h is the Plank's constant and T$_s$ is the DTG peak temperature [27].

The Horowitz-Metzger equation is a good illustration of the approximation methods. These authors derived the relation:

$$\log[\{1-(1-\alpha)^{1-n}\}/(1-n)] = E*\theta/2.303RT_s^2 \quad \text{for } n\neq1 \quad (4)$$

Where $\theta = T - T_s$, $w_\gamma = w_\alpha - w$, w_α = mass loss at the completion of the reaction; w = mass loss up to time t. The plot of $\log[\log(w_\alpha / w_\gamma)]$ vs θ was drawn and found to be linear from the slope of which E^* was calculated. The pre-exponential factor, A, was calculated from the equation:
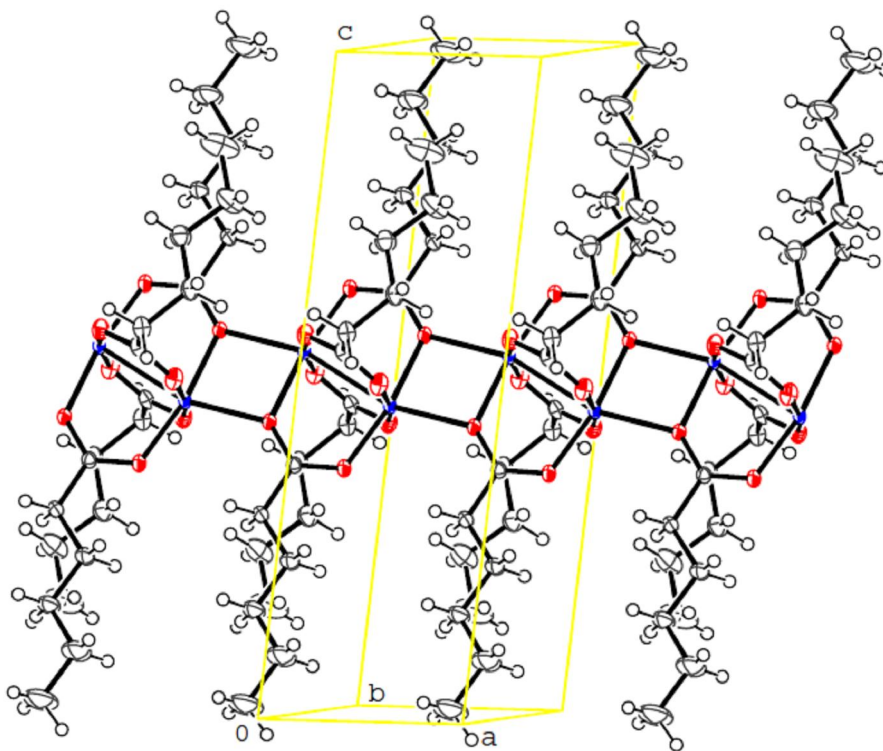
$$E^* / RT_s^2 = A / [\varphi \exp(-E^*/RT_s)]$$

The entropy of activation, ΔS^*, was calculated from equation 3. The enthalpy of activation, ΔH^*, and Gibbs free energy, ΔG^*, were calculated from $\Delta H^* = E^* - RT$ and $\Delta G^* = \Delta H^* - T \Delta S^*$, respectively.

Table 3: Kinetic parameters of the studied nickel hexanoate complex from Coats-Redfern (CR) and Horowitz-Metzger (HM)

Parameters	$E/$ kJmol^{-1}	$Z/$ s^{-1}	$\Delta S/$ Jmol^{-1}K^{-1}	$\Delta H/$ kJmol^{-1}	$\Delta G/$ kJmol^{-1}	r
Horowitz-Metzer	250	3.20E+21	162	245	155	0.99
Coats-Redfen	226	1.30E+19	116	222	160	0.97

From the point of view of TG analysis, the most important and reliable kinetic parameter is the activation energy, which can be related with the thermal stability of the compounds and, in some cases, with some IR data. As can be verified by inspection of Table 3 data, the nickel compound is the one with the higher value of E_a, suggesting a stronger metal-to-ligand interaction for this compound. Since Ni(II) exhibits a [Ar] $3d^8$ configuration, it is possible to suppose that the interaction with the ligand molecules has promoted a higher stabilization to this cation. Significantly, the Ni(II) complex is the only one to exhibits a positive ΔS for the thermal degradation process. This fact is probably related with the fact that this compound exhibits the higher ΔH value. We mean, if it is most difficult to remove the ligands from this compound, the degree of disorder introduced into the system by such process could be positive. In this kind of process it is always necessary to take into account that under heating a solid (the compound) is producing a new solid and a gaseous product. So, the ΔS value is for this "large system", and not only to the main decomposition process product. Hence, the overall ΔS value can be positive, as consequence of the entropy changes in the gaseous and solid products (in this last case, the formation of a new crystalline lattice) [28]. X-ray powder diffraction study of nickel hexanoate complex was carried in order to obtain an idea about the lattice dynamics of the compound. The obtained X-ray powder diffraction patterns exhibit a diffraction peak in the range 11-13º. On the basis of above physiochemical data in conjunction with consideration we can suggest the pentadentate geometry Fig. 1.

Fig. 1: Suggested structure of nickel (II) hexanoate complex

Molecular modeling had been successfully used to detect three dimensional arrangements of atoms in free hexanoic acid ligand and its nickel (II) complex. The bond lengths and bond angles values of the chelation complex were summarized and refereed in Table 4 and Fig. 1. This calculation for $Ni_2(cap)_4$ complex was obtained by using the commercial available molecular modeling software Chem Office Ultra–7. These statistical data have a good agreement with Fig. 1 confirmed the place of coordination towards cobalt(II) ions.

Table 4: The values of bond lengths and bond angles of hexanoic acid and its nickel complex

Atoms	Actual	Optimal
C(1)-C(2)	1.509	1.509
C(1)-O(18)	1.208	1.208
C(1)-O(19)	1.338	1.338
C(2)-C(5)	1.523	1.523
C(2)-H(3)	1.113	1.113
C(2)-H(4)	1.113	1.113
C(5)-C(8)	1.523	1.523
C(5)-H(6)	1.113	1.113
C(5)-H(7)	1.113	1.113
C(8)-C(11)	1.523	1.523
C(8)-H(9)	1.113	1.113
C(8)-H(10)	1.113	1.113
C(11)-C(14)	1.523	1.523
C(11)-H(12)	1.113	1.113
C(11)-H(13)	1.113	1.113
C(14)-H(15)	1.113	1.113
C(14)-H(16)	1.113	1.113
C(14)-H(17)	1.113	1.113
O(19)-H(20)	0.972	0.972
C(2)-C(1)-O(18)	122.5	122.5
C(2)-C(1)-O(19)	107.099	107.1
O(18)-C(1)-O(19)	122.002	122
C(1)-C(2)-C(5)	109.998	110
C(1)-C(2)-H(3)	108.8	108.8
C(1)-C(2)-H(4)	108.8	108.8
H(3)-C(2)-C(5)	109.409	109.41
H(3)-C(2)-H(4)	110.411	109.4
H(4)-C(2)-C(5)	109.409	109.41
C(2)-C(5)-C(8)	109.5	109.5
C(2)-C(5)-H(6)	109.411	109.41
C(2)-C(5)-H(7)	109.411	109.41
H(6)-C(5)-C(8)	109.409	109.41
H(6)-C(5)-H(7)	109.687	109.4
H(7)-C(5)-C(8)	109.409	109.41
C(5)-C(8)-C(11)	109.5	109.5
C(5)-C(8)-H(9)	109.409	109.41
C(5)-C(8)-H(10)	109.411	109.41
H(9)-C(8)-C(11)	109.411	109.41
H(9)-C(8)-H(10)	109.689	109.4
H(10)-C(8)-C(11)	109.409	109.41
C(8)-C(11)-C(14)	109.498	109.5
C(8)-C(11)-H(12)	109.409	109.41
C(8)-C(11)-H(13)	109.411	109.41
H(12)-C(11)-C(14)	109.409	109.41
H(12)-C(11)-H(13)	109.69	109.4
H(13)-C(11)-C(14)	109.409	109.41
C(11)-C(14)-H(15)	109.998	110
C(11)-C(14)-H(16)	110	110
C(11)-C(14)-H(17)	110	110
H(15)-C(14)-H(16)	108.998	109
H(15)-C(14)-H(17)	109.002	109
H(16)-C(14)-H(17)	108.811	109
C(1)-O(19)-H(20)	106.099	106.1
Ni(1)-Ni(2)	2.3	
Ni(1)-O(3)	1.79	
Ni(1)-O(6)	1.79	

Ni(1)-C(7)	1.92	
Ni(1)-C(12)	1.92	
Ni(2)-O(4)	1.79	
Ni(2)-O(5)	1.79	
Ni(2)-C(9)	1.92	
Ni(2)-C(10)	1.92	
O(3)-C(44)	1.355	1.355
O(4)-C(44)	1.694	1.421
O(5)-C(35)	1.664	1.421
O(6)-C(35)	1.355	1.355
C(7)-C(8)	1.514	1.514
C(7)-H(95)	1.113	1.113
C(7)-H(96)	1.113	1.113
C(8)-O(15)	1.402	1.402
C(8)-H(87)	1.111	1.111
C(8)-H(88)	1.111	1.111
C(9)-O(16)	1.402	1.402
C(9)-H(91)	1.111	1.111
C(9)-H(92)	1.111	1.111
C(10)-C(11)	1.514	1.514
C(10)-H(89)	1.113	1.113
C(10)-H(90)	1.113	1.113
C(11)-O(14)	1.402	1.402
C(11)-H(85)	1.111	1.111
C(11)-H(86)	1.111	1.111
C(12)-O(13)	1.402	1.402
C(12)-H(93)	1.111	1.111
C(12)-H(94)	1.111	1.111
O(13)-C(18)	1.502	1.355
O(14)-C(18)	1.355	1.355
O(15)-C(17)	1.355	1.355
O(16)-C(17)	1.353	1.355
C(17)-C(19)	1.497	1.497
C(18)-C(27)	1.497	1.497
C(19)-C(20)	1.523	1.523
C(19)-H(83)	1.113	1.113
C(19)-H(84)	1.113	1.113
C(20)-C(21)	1.523	1.523
C(20)-H(73)	1.113	1.113
C(20)-H(74)	1.113	1.113
C(21)-C(22)	1.523	1.523
C(21)-H(71)	1.113	1.113
C(21)-H(72)	1.113	1.113
C(22)-C(23)	1.523	1.523
C(22)-H(69)	1.113	1.113
C(22)-H(70)	1.113	1.113
C(23)-H(24)	1.113	1.113
C(23)-H(25)	1.113	1.113
C(23)-H(26)	1.113	1.113
C(27)-C(28)	1.523	1.523
C(27)-H(81)	1.113	1.113
C(27)-H(82)	1.113	1.113
C(28)-C(29)	1.523	1.523
C(28)-H(67)	1.113	1.113
C(28)-H(68)	1.113	1.113
C(29)-C(30)	1.523	1.523
C(29)-H(65)	1.113	1.113
C(29)-H(66)	1.113	1.113
C(30)-C(31)	1.523	1.523

C(30)-H(63)	1.113	1.113	Ni(2)-O(5)-C(35)	87.692	
C(30)-H(64)	1.113	1.113	Ni(1)-O(6)-C(35)	104.499	
C(31)-H(32)	1.113	1.113	Ni(1)-C(7)-C(8)	109.468	
C(31)-H(33)	1.113	1.113	Ni(1)-C(7)-H(95)	109.474	
C(31)-H(34)	1.113	1.113	Ni(1)-C(7)-H(96)	109.468	
C(35)-C(36)	1.497	1.497	C(8)-C(7)-H(95)	109.409	109.41
C(36)-C(37)	1.523	1.523	C(8)-C(7)-H(96)	109.409	109.41
C(36)-H(79)	1.113	1.113	H(95)-C(7)-H(96)	109.596	109.4
C(36)-H(80)	1.113	1.113	C(7)-C(8)-O(15)	107.398	107.4
C(37)-C(38)	1.523	1.523	C(7)-C(8)-H(87)	109.409	109.41
C(37)-H(75)	1.113	1.113	C(7)-C(8)-H(88)	109.411	109.41
C(37)-H(76)	1.113	1.113	O(15)-C(8)-H(87)	106.697	106.7
C(38)-C(39)	1.523	1.523	O(15)-C(8)-H(88)	106.704	106.7
C(38)-H(61)	1.113	1.113	H(87)-C(8)-H(88)	116.784	109.4
C(38)-H(62)	1.113	1.113	Ni(2)-C(9)-O(16)	109.47	
C(39)-C(40)	1.523	1.523	Ni(2)-C(9)-H(91)	109.468	
C(39)-H(59)	1.113	1.113	Ni(2)-C(9)-H(92)	109.472	
C(39)-H(60)	1.113	1.113	O(16)-C(9)-H(91)	106.702	106.7
C(40)-H(41)	1.113	1.113	O(16)-C(9)-H(92)	106.702	106.7
C(40)-H(42)	1.113	1.113	H(91)-C(9)-H(92)	114.866	109.4
C(40)-H(43)	1.113	1.113	Ni(2)-C(10)-C(11)	109.47	
C(44)-C(45)	1.497	1.497	Ni(2)-C(10)-H(89)	109.47	
C(45)-C(46)	1.523	1.523	Ni(2)-C(10)-H(90)	109.47	
C(45)-H(77)	1.113	1.113	C(11)-C(10)-H(89)	109.412	109.41
C(45)-H(78)	1.113	1.113	C(11)-C(10)-H(90)	109.407	109.41
C(46)-C(47)	1.523	1.523	H(89)-C(10)-H(90)	109.594	109.4
C(46)-H(57)	1.113	1.113	C(10)-C(11)-O(14)	107.398	107.4
C(46)-H(58)	1.113	1.113	C(10)-C(11)-H(85)	109.409	109.41
C(47)-C(48)	1.523	1.523	C(10)-C(11)-H(86)	109.409	109.41
C(47)-H(55)	1.113	1.113	O(14)-C(11)-H(85)	106.697	106.7
C(47)-H(56)	1.113	1.113	O(14)-C(11)-H(86)	106.699	106.7
C(48)-C(49)	1.523	1.523	H(85)-C(11)-H(86)	116.789	109.4
C(48)-H(53)	1.113	1.113	Ni(1)-C(12)-O(13)	109.472	
C(48)-H(54)	1.113	1.113	Ni(1)-C(12)-H(93)	109.474	
C(49)-H(50)	1.113	1.113	Ni(1)-C(12)-H(94)	109.47	
C(49)-H(51)	1.113	1.113	O(13)-C(12)-H(93)	106.7	106.7
C(49)-H(52)	1.113	1.113	O(13)-C(12)-H(94)	106.697	106.7
Ni(2)-Ni(1)-O(3)	104.503		H(93)-C(12)-H(94)	114.868	109.4
Ni(2)-Ni(1)-O(6)	90		C(12)-O(13)-C(18)	112.035	110.8
Ni(2)-Ni(1)-C(7)	119.998		C(11)-O(14)-C(18)	110.799	110.8
Ni(2)-Ni(1)-C(12)	119.998		C(8)-O(15)-C(17)	110.799	110.8
O(3)-Ni(1)-O(6)	149.999		C(9)-O(16)-C(17)	110.608	110.8
O(3)-Ni(1)-C(7)	120		O(15)-C(17)-O(16)	120.241	
O(3)-Ni(1)-C(12)	120		O(15)-C(17)-C(19)	133.047	120
O(6)-Ni(1)-C(7)	33.32		O(16)-C(17)-C(19)	106.707	120
O(6)-Ni(1)-C(12)	33.32		O(13)-C(18)-O(14)	124.245	
C(7)-Ni(1)-C(12)	0		O(13)-C(18)-C(27)	103.663	120
Ni(1)-Ni(2)-O(4)	89.997		O(14)-C(18)-C(27)	103.667	120
Ni(1)-Ni(2)-O(5)	104.501		C(17)-C(19)-C(20)	109.5	109.5
Ni(1)-Ni(2)-C(9)	120.001		C(17)-C(19)-H(83)	109.407	109.41
Ni(1)-Ni(2)-C(10)	120.001		C(17)-C(19)-H(84)	109.411	109.41
O(4)-Ni(2)-O(5)	149.999		C(20)-C(19)-H(83)	109.411	109.41
O(4)-Ni(2)-C(9)	120.001		C(20)-C(19)-H(84)	109.409	109.41
O(4)-Ni(2)-C(10)	119.998		H(83)-C(19)-H(84)	109.69	109.4
O(5)-Ni(2)-C(9)	30.204		C(19)-C(20)-C(21)	109.5	109.5
O(5)-Ni(2)-C(10)	75.398		C(19)-C(20)-H(73)	109.409	109.41
C(9)-Ni(2)-C(10)	90.002		C(19)-C(20)-H(74)	109.409	109.41
Ni(1)-O(3)-C(44)	104.499		C(21)-C(20)-H(73)	109.409	109.41
Ni(2)-O(4)-C(44)	110.329		C(21)-C(20)-H(74)	109.412	109.41

H(73)-C(20)-H(74)	109.689	109.4
C(20)-C(21)-C(22)	109.498	109.5
C(20)-C(21)-H(71)	109.405	109.41
C(20)-C(21)-H(72)	109.411	109.41
C(22)-C(21)-H(71)	109.407	109.41
C(22)-C(21)-H(72)	109.412	109.41
H(71)-C(21)-H(72)	109.69	109.4
C(21)-C(22)-C(23)	109.5	109.5
C(21)-C(22)-H(69)	109.407	109.41
C(21)-C(22)-H(70)	109.414	109.41
C(23)-C(22)-H(69)	109.409	109.41
C(23)-C(22)-H(70)	109.409	109.41
H(69)-C(22)-H(70)	109.687	109.4
C(22)-C(23)-H(24)	109.998	110
C(22)-C(23)-H(25)	110	110
C(22)-C(23)-H(26)	110	110
H(24)-C(23)-H(25)	109	109
H(24)-C(23)-H(26)	109.002	109
H(25)-C(23)-H(26)	108.813	109
C(18)-C(27)-C(28)	109.498	109.5
C(18)-C(27)-H(81)	109.409	109.41
C(18)-C(27)-H(82)	109.411	109.41
C(28)-C(27)-H(81)	109.412	109.41
C(28)-C(27)-H(82)	109.411	109.41
H(81)-C(27)-H(82)	109.687	109.4
C(27)-C(28)-C(29)	109.5	109.5
C(27)-C(28)-H(67)	109.409	109.41
C(27)-C(28)-H(68)	109.412	109.41
C(29)-C(28)-H(67)	109.412	109.41
C(29)-C(28)-H(68)	109.407	109.41
H(67)-C(28)-H(68)	109.687	109.4
C(28)-C(29)-C(30)	109.5	109.5
C(28)-C(29)-H(65)	109.412	109.41
C(28)-C(29)-H(66)	109.407	109.41
C(30)-C(29)-H(65)	109.409	109.41
C(30)-C(29)-H(66)	109.412	109.41
H(65)-C(29)-H(66)	109.687	109.4
C(29)-C(30)-C(31)	109.498	109.5
C(29)-C(30)-H(63)	109.407	109.41
C(29)-C(30)-H(64)	109.407	109.41
C(31)-C(30)-H(63)	109.412	109.41
C(31)-C(30)-H(64)	109.414	109.41
H(63)-C(30)-H(64)	109.687	109.4
C(30)-C(31)-H(32)	110.002	110
C(30)-C(31)-H(33)	110	110
C(30)-C(31)-H(34)	110.003	110
H(32)-C(31)-H(33)	108.998	109
H(32)-C(31)-H(34)	109	109
H(33)-C(31)-H(34)	108.809	109
O(5)-C(35)-O(6)	132.126	
O(5)-C(35)-C(36)	110.976	120
O(6)-C(35)-C(36)	110.977	120
C(35)-C(36)-C(37)	109.498	109.5
C(35)-C(36)-H(79)	109.412	109.41
C(35)-C(36)-H(80)	109.411	109.41
C(37)-C(36)-H(79)	109.412	109.41
C(37)-C(36)-H(80)	109.412	109.41
H(79)-C(36)-H(80)	109.685	109.4
C(36)-C(37)-C(38)	109.498	109.5
C(36)-C(37)-H(75)	109.409	109.41
C(36)-C(37)-H(76)	109.407	109.41
C(38)-C(37)-H(75)	109.411	109.41
C(38)-C(37)-H(76)	109.411	109.41
H(75)-C(37)-H(76)	109.689	109.4
C(37)-C(38)-C(39)	109.498	109.5
C(37)-C(38)-H(61)	109.411	109.41
C(37)-C(38)-H(62)	109.407	109.41
C(39)-C(38)-H(61)	109.412	109.41
C(39)-C(38)-H(62)	109.411	109.41
H(61)-C(38)-H(62)	109.687	109.4
C(38)-C(39)-C(40)	109.498	109.5
C(38)-C(39)-H(59)	109.409	109.41
C(38)-C(39)-H(60)	109.407	109.41
C(40)-C(39)-H(59)	109.412	109.41
C(40)-C(39)-H(60)	109.409	109.41
H(59)-C(39)-H(60)	109.69	109.4
C(39)-C(40)-H(41)	109.996	110
C(39)-C(40)-H(42)	109.998	110
C(39)-C(40)-H(43)	110	110
H(41)-C(40)-H(42)	109.003	109
H(41)-C(40)-H(43)	109.003	109
H(42)-C(40)-H(43)	108.814	109
O(3)-C(44)-O(4)	129.589	
O(3)-C(44)-C(45)	118.372	120
O(4)-C(44)-C(45)	112.04	120
C(44)-C(45)-C(46)	109.5	109.5
C(44)-C(45)-H(77)	109.405	109.41
C(44)-C(45)-H(78)	109.412	109.41
C(46)-C(45)-H(77)	109.407	109.41
C(46)-C(45)-H(78)	109.409	109.41
H(77)-C(45)-H(78)	109.692	109.4
C(45)-C(46)-C(47)	109.498	109.5
C(45)-C(46)-H(57)	109.411	109.41
C(45)-C(46)-H(58)	109.409	109.41
C(47)-C(46)-H(57)	109.409	109.41
C(47)-C(46)-H(58)	109.411	109.41
H(57)-C(46)-H(58)	109.69	109.4
C(46)-C(47)-C(48)	109.498	109.5
C(46)-C(47)-H(55)	109.409	109.41
C(46)-C(47)-H(56)	109.409	109.41
C(48)-C(47)-H(55)	109.412	109.41
C(48)-C(47)-H(56)	109.412	109.41
H(55)-C(47)-H(56)	109.689	109.4
C(47)-C(48)-C(49)	109.5	109.5
C(47)-C(48)-H(53)	109.407	109.41
C(47)-C(48)-H(54)	109.409	109.41
C(49)-C(48)-H(53)	109.412	109.41
C(49)-C(48)-H(54)	109.412	109.41
H(53)-C(48)-H(54)	109.687	109.4
C(48)-C(49)-H(50)	109.998	110
C(48)-C(49)-H(51)	110	110
C(48)-C(49)-H(52)	109.996	110
H(50)-C(49)-H(51)	109.002	109
H(50)-C(49)-H(52)	108.998	109
H(51)-C(49)-H(52)	108.814	109

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References
1. The Merck Index Text Book, Twelfth Edition, 1998.
2. Beilstein F., Handbuch der Organischem Chemie, Bd. IX, Springer Verlag, Berlin 1926.
3. Zell A., H. Einspahr and C. E. Bugg, Model for calcium binding to γ – carboxyglutamic acid residues of proteins. (Crystal structure of calcium α-ethyl malonate) .Biochem., 1985, 24: 533.
4. Pecoraro, V. L., Gelasco, A., Baldwin, M., "A Modelling Approach for Understanding the Reactivity and Mechanism of Manganese Enzymes". InMechanistic Bioinorganic Chemistry, Advances in Chemistry Series; H. H. Thorp and V. L. Pecoraro, Ed(s); ACS Books: New York, (1995), pp 265-301.
5. Mehrotra R. C. and R. Bohra, Metal Carboxylates, Academic Press, London, 1983.
6. Brusau E. V., J. C, Pedregosa, G. E. Narda, E. P. Ayala and E. A. Oliveira, A parallel implementation of exact euclidean distance transform based on exact dilations. Microprocessors and Microsystems J. Arg. Chem. Soc., 2004, 92(1/3): 43.
7. Gushchina T. N. and G. A. Kotenko, Transcranial electric pulse therapy in combination with mexidol premedication for the management of cerebrovascular complications in the patients presenting with type 2 diabetes mellitus Koord. Khim., 1986, 12(3), 325.
8. Brzyska W. and B. Paszkowska, The complexes of rare earth elements with 2,5-dihydroxybenzoic acidpreparation, properties and thermal decomposition. J. Thermal Anal., 1998, 51, 561.
9. Doyle A., J. Felcman, M. Gambardella, C. N. Verani and M. L. B. Tristao, Anhydrous copper(II) hexanoate from cuprous and cupric oxides. Crystal and molecular strucutre of [Cu2(O2CC5H11)4]Polyhedron, 2000, 19(26/27), 2621.
10. Pietsch R., Untersuchungen über die extraktion von thorium, blei und eisen (III) als verbindungen der capronsäure Anal. Chim. Acta, 1971, 53(2), 287.
11. Kolomiets L. L., O. V. Lysenko and I. V. Pyatnitskii, Z. Photoelectric counter of disperse particles. Anal. Khim., 1988, 43(10), 1773.
12. Pyatnitskii I. V., L. L. Kolomeits, O. V. Lysenko and M. G. Sobko, Z., Gradient method of constructing functions in problems of absolute stability. Anal. Khim., 1990, 45(1), 56.
13. Kopacz S., J. Szantula and T. Pardela, Z., Effect of ropivacaine on cutaneous capillary blood flow in pigs.Prikladoni Khim, 1989, 62(11), 2535.
14. Deacon G. B. and R. J. Phillips, Relationships between thae carbon –oxygen stretching frequencies of carboxylato complexes and the types of carboxylate coordination.Coord. Chem. Rev., 1980, 33, 227.
15. Alcock N. W., J. Culver and S. M. Roe, The Effects of Cations and Anions on the Ionic of the development of organic substitution methods. J. Chem. Soc. Dalton Trans., 1992, 1447.
16. Nakamoto K., Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1997.
17. Srinivasan B. R. and S. C. Sawant, Thermal and spectroscopic characterization of Mg (II) complexes of nitro-substituted benzoic acids. Thermochim. Acta, 2003, 402, 45.
18. Murugavel R., V. V. Karambelkar, G. Anantharaman and M. G. Walawalkar, Synthetic, spectroscopic, and structural studies on 4-aminobenzoate complexes of divalent alkaline earth metals: X-ray crystal structures of [{$Mg(H_2O)_6$}(4-aba)$_2$].2H_2O and [Ca(4-aba)$_2$(H_2O)$_2$]. Inorg. Chem., 2000, 39, 1381.
19. Freeman E.S. and B. Carroll, The Application of Thermoanalytical Techniques to Reaction Kinetics: The Thermogravimetric Evaluation of the Kinetics of the Decomposition of Calcium Oxalate Monohydrate. J. Phys. Chem., 1958, 62, 394.
20. Sestak J., V. Satava and W.W. Wendlandt, Kinetic analysis of thermogravimetric measurements. Thermochim. Acta, 1973, 7, 333.
21. Coats A.W. and J.P. Redfern, Kinetics Parameters from Thermogravimetric Data. Nature, 1964, 201, 68.
22. Ozawa T., kinetic Analysis of Derivative Curves in thermal Analysis Bull. Chem. Sot. Jpn., 1965, 38, 1881.
23. Wendlandt W.W., Thermal Methods of Analysis, Wiley, New York, 1974**.**
24. Horowitz H.W. and G. Metzger, A New Analysis of Thermogravimetric Traces.Anal. Chem., 1963, 35, 1464.
25. Flynn J.H. and L.A. Wall, AQuick, Direct Method for the Determination of Activation energy from thermogravimetric Data Polym. Lett., 1966, 4, 323.
26. Kofstad P., Nature, High Temperature Corrosion, 1957, 179, 1362.
27. Flynn J. H. F., L. A. Wall, the Isoconversional Method for Determination of energy of Activation at Constant Heating rates J. Res. Natl. Bur. Stand., 1996, 70A, 487.
28. Madusudanan P.M., Yasuff K.K.M., C.G.R. Nair, Thermal methods of Analysis .J. Therm. Anal. 1975, 8, 31.

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