HACETTEPE JOURNAL OF BIOLOGY AND CHEMISTRY
Volume 35, Issue 2, June 2007

Research Article

Hacettepe J. Biol. & Chem., 2007, 35 (2), 123-128

Synthesis and Characterization of the Nicotinamide-Acetylsalicylato Complexes of Co(II), Ni(II), Cu(II), and Zn(II)

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Abstract

Nicotinamide-acetylsalicylato complexes of Co(II), Ni(II), Cu(II), and Zn(II) were synthesised and their structural properties were investigated by employing elemental analysis, magnetic susceptibilitiy, solid state UV-vis, direct injection probe mass, FTIR and thermoanalytic TG-DTG methods. It was found that ratio of metal:ligand:ligand is 1:2:2 and the decomposition of each complex starts with dehydration and follows by decomposition of the nicotinamide and acetylsalicylato, respectively. The thermal dehydration of the complexes takes place in steps from one to two. The decomposition mechanism and thermal stability of the investigated complexes are interpreted in terms of their structures. The final decomposition products are found to be the respective metal oxides

Key Words: Nicotinamide; N,N-diethylnicotinamide, acetylsalicylato; thermal decomposition; metal complexes.

Introduction

Acetylsalicylic acid or aspirin (asp, $C_9H_8O_4$) was first synthesised by the German Chemist Felix Hoffmann in 1897 and tested pharmacologically by H. Dreser in 1899. Among the others, Wohlgemuth and Witthauer have undertaken the clinical studies and well documented the anti-rheumatic, anti-pyretic and analgesic properties of salicylic acid free of undesirable side effects [1]. Not only acetylsalicylic acid, but also its derivatives are well known as anti-pyretic, anti-septic and anti-inflammatory agent and have long been found a widespread application in medical practices. It has also been stated in several sources that the metal complexes of inactive ligands and anti-inflammatory organic drugs are generally more active than those of free ligands or organic drugs. Investigations revealed that the biological activity of the laboratory synthesised $[Cu_2(asp)_4]$ is more effective as an anti-inflammatory agent than that of aspirin alone. In addition to this, the copper complex is of an anti-ulcer activity while aspirin is accepted having ulcerogenic properties. The $[Cu_2(asp)_2(py)_2]$ adduct has also been reported to be an effective anti-inflammatory, anti-cancer and anti-convulsant agent [2-4]. On the other hand, zinc salicylate and a number of substituted salicylates have been employed in the paper coating to produce carbonless copying paper, and as an antioxidant or stabiliser in polymer industry [5].

Nicotinamide is known as a component of the vitamin B complex as well as a component of the coenzyme, nicotinamide adenine dinucleotide (NAD). It is documented that heterocyclic compounds play a significant role in many biological systems, especially N-donor ligand systems being a component of several vitamins and drugs such as nicotinamide [6-8]. Nicotinamide itself plays an important role in the metabolism of living cells and some of its metal complexes are biologically active as antibacterial or insulin-mimetic agents [9]. Therefore, the structure of nicotinamide has been the subject of many studies [10-13].

The studies on mixed-ligand complex formation have also a great deal of importance in the field of biological and environmental chemistry. A special interest of mixed-ligand complex formation is focused on complexes between copper(II) ion, salicylate ion and a nitrogen base. Various studies on the mixed-ligand metal complexes of the salicylate and nicotinamide ($C_6H_6N_2O$) have been reported [14-17]. The structures of the mixed-ligand metal-nicotinamide-nitrobenzoat complexes and their derivatives have also been extensively studied by Hökelek and Necefoglu [18-20].

In this work, Co(II), Ni(II), Cu(II), and Zn(II) with aspirin-nicotinamide complexes have been synthesised and their thermal decomposition results have been presented. The decomposition pathways of the investigated complexes are discussed in connection with the available spectroscopic data.

Experimental

Materials and instrumentation

All chemicals used were analytical reagent products. $CoSO_4.6H_2O$, $NiSO_4.6H_2O$, $CuSO_4.5H_2O$, $ZnSO_4.7H_2O$, m-hydroxybenzoic acid and nicotinamide were ob-

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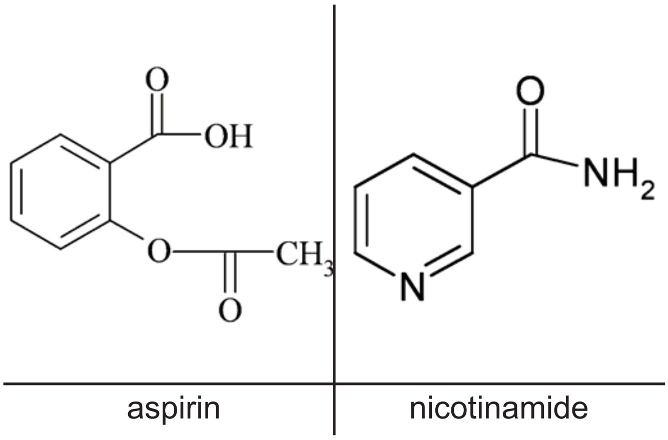
tained from Merck (Darmstadt, Germany). Elemental analyses (C, H, N) were carried out by standard methods (Tubitak Marmara Research Center). Magnetic susceptibility measurements were performed at room temperatures using a Sherwood Scientific MXI model Gouy magnetic balance. IR spectra were recorded in the 4000-400 cm^{-1} region with a Perkin Elmer 1000 FT-IR spectrophotometer using KBr pellets. A Rigaku TG 8110 thermal analyser combined with a TAS 100 thermogravimetric analyser was used to record simultaneous TG, TDG and DTA curves. The experiments were performed in static air atmosphere with a heating rate of 10 $Kmin^{-1}$ from room temperature to 1000°C in platinum crucibles. The samples were weighed approximately 10 mg and highly sintered α-Al_2O_3 was used as a reference material. The DTG sensitivity was 0.05 mgs^{-1}. Electronic spectra were recorded by a Schimadzu 3600/UV-VIS-NIR Spectrophotometer. Mass spectral data were recorded Agilent Technologies 5973 spectrophotometer using DIP-MS method.



Scheme 1.

Preparation of acetylsalicylate complexes

In the first step, acetylsalicylic acid sodium salt was prepared according to the following equation:

$2\ asa^* + 2NaHCO_3 \rightarrow 2\ Na(asa) + 2CO_2 + 2H_2O$
(*: asa:acetylsalicylic acid)

In the second step, metal acetylsalicylic acid salts were synthesized from Na(asa) salt by the following substitution reaction:

$2Na(asa) + MSO_4.nH_2O \rightarrow M(asa)_2.nH_2O + Na_2SO_4$
[M=Co(II),Ni(II),Cu(II),Zn(II)]

The $M(asa)_2$.nH2O solution was allowed 5-7 days for crystallization at room temperature. The crystals formed were filtered and washed with cold distilled water and acetone and dried in vacuo.

Synthesis of mixed-ligand complexes

A solution of na (2 mmol) in distilled water (30 mL) was added dropwise to a stirred solution of $M(asa)_2(H_2O)_n$ (1 mmol) in hot distilled water (50 mL). The resulting solution was heated to 50°C in a temperature-controlled bath and stirred for 4 h and then cooled to room temperature and allowed 15-17 days for crystallization. The crystals formed were filtered and washed with cold water and acetone and dried in vacuo. The mixed-ligand complexes were prepared according to the following equations:

$M(asa)_2(H_2O)^n + 2\ na \rightarrow M(asa)_2(na)_2(H_2O)_n$
(na:nicotinamide)

Found: C, 51.25; H, 4.50; N, 8.04. Calc. For $C_{30}H_{28}N_4O_{12}Co$: C, 51.65; H, 4.35; N, 9.00.

Found: C, 52.00; H, 4.44; N, 9.00. Calc. For $C_{30}H_{28}N_4O_{12}Ni$: C, 51.67; H, 4.34; N, 8.05.

Found: C, 52.05; H, 4.17; N, 7.80. Calc. For $C_{30}H_{28}N_4O_{12}Cu$: C, 51.99; H, 4.20; N, 8.08.

Found: C, 48.05; H, 4.35; N, 7.50. Calc. For $C_{30}H_{31}N_4O_{13.5}Zn$: C, 49.00; H, 4.50; N, 6.85.

Results and Discussion

Effective magnetic moments and compositions of the complexes are given in Table 1 in accord with literature values for similar complexes [20,21]. The results of the elemental analysis indicated that the complexes contain two moles of acetylsalicylate and nicotinamide ligands per mole formula unit.

All of the complexes contain two moles of aqua ligand that are directly coordinated to metal ion. The octahedral coordination of the metal ions are completed by two carboxylic oxygen atoms from two acetylsalicylate and two nitrogen atoms from two nicotinamides. Octahedral structure are confirmed by magnetic data. According to the magnetic susceptibility results, the metal complexes are paramag¬netic, except for Zn(II) complexes. As expected, the Zn(II) complexes are diamagnetic. All of the complexes may be thought octahedral coordination around the metal ions.

Due to the low solubility of the complexes, the electronic spectrum of the complexes were taken in the solid state. The electronic spectra showed two absorption bands and d–d transition at 7016 cm^{-1} (${}^4T_{1g} \rightarrow {}^4T_{2g}$) and 20100 cm^{-1} (${}^4T_{1g} \rightarrow {}^4T_{1g}$)(${}^4P$) for Co(II) complex; three absorption bands and d–d transition at 7830 cm^{-1} (${}^3A_{2g} \rightarrow {}^3T_{2g}$), 15640 cm^{-1} (${}^3A_{2g} \rightarrow {}^3T_{1g}$)(${}^3F$), and 25550 cm^{-1} (${}^3A_{2g} \rightarrow {}^3T_{1g}$)(${}^3P$) for Ni(II) complex respectively. In the Cu(II) complex is observed multiple absorbsition band at about 11200 cm^{-1} – 16500 cm^{-1} but they are overlapped. Because, octahedral complexes of Cu(II) are observable distorted by Jahn-Teller effect and the structure of complex is to name pseudo-octahedral. It was to taken notice of top of the peak as absorption band and d–d transition at about 13000 cm^{-1} (${}^2E_g \rightarrow {}^2T_{2g}$) for Cu(II) complex. The UV-visible peaks corresponding to the the $\pi \rightarrow \pi^*$ transitions in the ligands were observed at 270 and 320 nm [22]. The peaks belonging to the $\pi \rightarrow \pi^*$ transitions are shifted to a longer wavelength as a consequence of co-

Table 1. Characteristic data of the metal complexes.

Complex	M / g mol^{-1}	Yield (%)	Color	d.p.^{a}(˚C)	$\mu_{eff.}$/B.M
$[Co(asa)_2(na)_2(H_2O)_2]$ $C_{30}H_{28}N_4O_{12}Co$	695.50	80	pink	84	4.68
$[Ni(asa)_2(na)_2(H_2O)_2]$ $C_{30}H_{28}N_4O_{12}Ni$	695.26	82	green	98	2.96
$[Cu(asa)_2(na)_2(H_2O)_2]$ $C_{30}H_{29}N_4O_{11.5}Cu$	700.11	92	blue	107	1.49
$[Zn(asa)_2(na)_2(H_2O)_2].3/2H_2O$ $C_{30}H_{31}N_4O_{13.5}Zn$	726.96	87	colorless	45	diamagnetic

ordination when binding with metal, confirming the formation of asa–na metal complexes.

FT-IR spectra

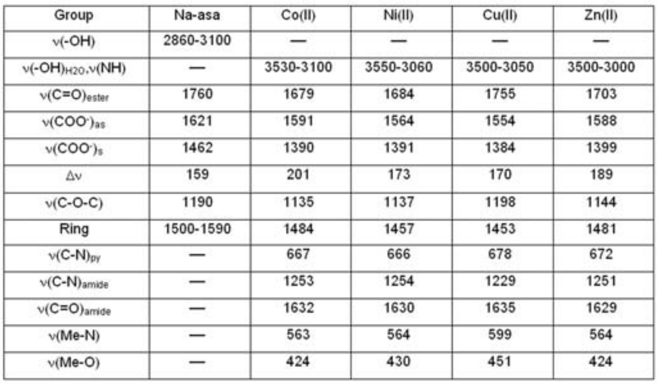
Characteristic FT-IR peaks of the complexes are given in Table 2. The absorption bands in the range of 3550–3050 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of water molecules. The peaks for the N–H stretches of primary amides are strong in the range of 3495-3350 cm^{-1}. Also N-H bending vibrations appear approximately in the range of 1590 cm^{-1}. The asa-na mixed ligand complexes give rise to strong bands responsible from the C=O stretching. Conjugation between the carbonyl group and the amide nitrogen causes small frequency shifts. The strong bands observed at around 1630 cm^{-1} are assigned to this mode. This band remained almost in the same range as the amide group of the free na ligand, indicating that the na ligand does not coordinate through amide group. Pyridine ring vibration of free nicotinamide at 1565 cm^{-1} shifts to 1480 cm^{-1} in the complexes indicating that the pyridine ring is coordinated. The main difference in the spectrum of acetylsalicylic acid is that the C=O stretching vibration of the carboxyl group at 1718 cm^{-1} shifts to lower frequency in all the metal complexes. The carboxylate peaks in the metal complexes appear in the range of 1565 cm^{-1}. This shows that the coordination takes place through the carboxyl group [23]. The –OH bending peak for the acetylsalicylic acid remained almost in the same position at around 1270 cm^{-1} in all metal complexes. The low intensity bands in the region of 600–400 cm^{-1} are attributed to M–N and M–O vibration [24,25].

Thermal Analysis

$[Co(C_9H_7O_4)_2(C_6H_6N_2O)_2(H_2O)_2]$

The one-step dehydration of the Co(II) complex occurs in the temperature range of 84-135°C (DTG peak. Figure 1). The endotherm (DTA peak at 111°C) corresponds to release of two water molecules that are coordinated to metal ion. In the second stage, the nicotinamide and acetylsalcylato ligands decompose. Furthermore, in the second stage melting occurs at 190°C (DTA curve). A descending continuous TG curve is obtained in the temperature range of 271-504°C (DTG peaks at 316, 365, 405, 433°C) and these are relevant to the decomposition of acetylsalicylato ligands. In the seventh stage, an instantaneous weight lost is observed (DTG peak at 557°C). This incidence may be attributed to violently oxidation of the residual carbon [26], The endothermic peak at 834°C is due to the conversion of Co_3O_4 to CoO.

Table 2. Characteristic FT-IR peaks of metal complexes.



Group	Na-asa	Co(II)	Ni(II)	Cu(II)	Zn(II)
ν(-OH)	2860-3100	—	—	—	—
$\nu(-OH)_{H2O}$,ν(NH)	—	3530-3100	3550-3060	3500-3050	3500-3000
$\nu(C=O)_{ester}$	1760	1679	1684	1755	1703
$\nu(COO^-)_{as}$	1621	1591	1564	1554	1588
$\nu(COO^-)_{s}$	1462	1390	1391	1384	1399
$\Delta\nu$	159	201	173	170	189
ν(C-O-C)	1190	1135	1137	1198	1144
Ring	1500-1590	1484	1457	1453	1481
$\nu(C-N)_{py}$	—	667	666	678	672
$\nu(C-N)_{amide}$	—	1253	1254	1229	1251
$\nu(C=O)_{amide}$	—	1632	1630	1635	1629
ν(Me-N)	—	563	564	599	564
ν(Me-O)	—	424	430	451	424

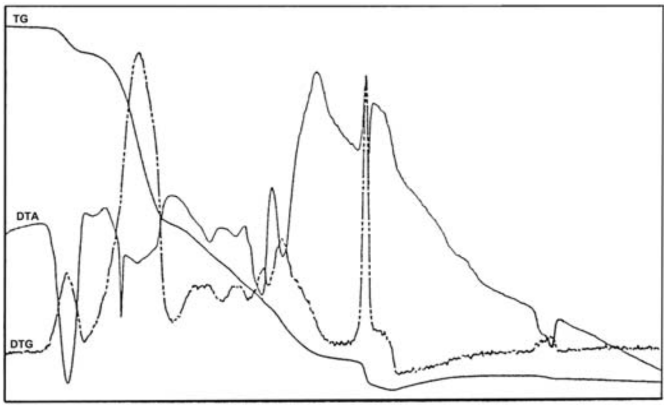


Figure1. TG/DTA/DTG curves of $[Co(C_9H_7O_4)_2(C_6H_6N_2O)_2(H_2O)_2]$.

$[Ni(C_9H_7O_4)_2(C_6H_6N_2O)_2(H_2O)_2]$

This complex decomposes in five steps [DTG peaks at 123, 215, 332, (428, 437, 450; triplet), 584°C, Figure 2]. The endotherm in the temperature range 98-141°C corresponds to the loss of two moles of aqua ligands. In the second stage, nicotinamides and one acetysalcylato ligand in the complex probably decompose by releasing CO_2 (exp. 43.55%; calcd. 41.32%). In the following steps, both the intermediate formed by CO_2 release and the other remaining acetysalcylato ligand decomposes to give NiO (exp. 89.08%; calcd. 89.28%).

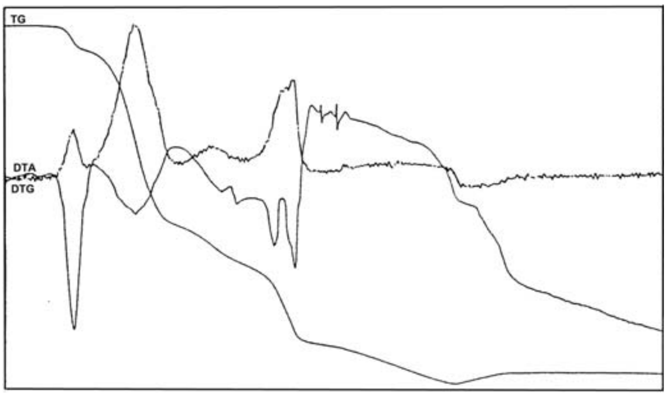


Figure 2. TG/DTA/DTG curves of [Ni($C_9H_7O_4$)$_2$($C_6H_6N_2O$)$_2$(H_2O)$_2$].

[Cu($C_9H_7O_4$)$_2$($C_6H_6N_2O$)$_2$(H_2O)$_2$]

The TG/DTG and DTA curves for the Cu(II) complex are given in Figure 3. This complex is stable in air up to 107°C. Further heating causes two moles of water are released by an accompanying endothermic effect with the DTA curve at 133°C. The anhydrous complex begins to decompose with melting at 192°C (DTA curve). The next five steps are consecutive and endothermic (TG curve 173-540°C). A number of undefined processes take place in this range eventually produce CuO. A peak is observed at 862°C (DTG curve) that is belong to conversion of CuO to Cu_2O [27]. This conversion was appeared in our previous studies with Cu complexes [28-30].

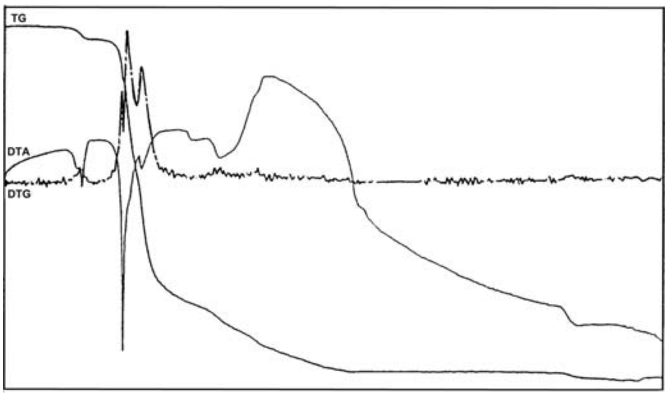


Figure 3. TG/DTA/DTG curves of Cu($C_9H_7O_4$)$_2$($C_6H_6N_2O$)$_2$(H_2O)$_2$]

[Zn($C_9H_7O_4$)$_2$($C_6H_6N_2O$)$_2$(H_2O)$_2$].1.5H_2O

Thermal decomposition characteristics of this complex are given in Figure 4. The complex contains both of the crystallization and coordination water. The thermal dehydration of the complex occurred in two steps by giving endothermic effect at 61 and 87°C. One and half moles of crystallization water are released in the first stage of dehydration (exp. 3.07%; calcd. 3.70%). In the second stage, two moles of coordination water are removed (exp. 5.53%; calcd. 4.93%). This behaviour was also observed in our early studies with Zn(II) complexes [31]. The anhydrous complex is stable up to 180°C and decomposes in the 181-635°C temperature intervals. The final product obtained at 635°C is ZnO.

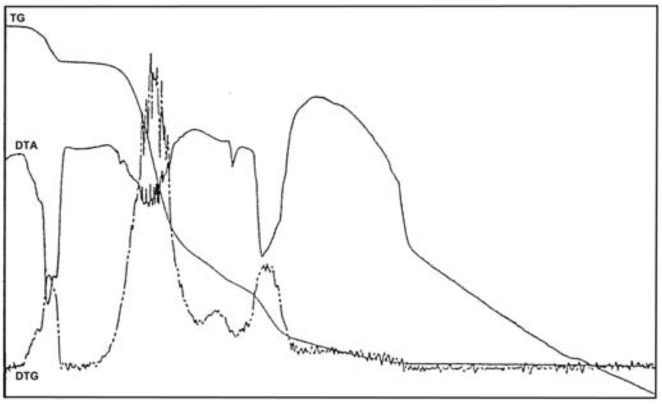


Figure 4. TG/DTA/DTG curves of [Zn($C_9H_7O_4$)$_2$($C_6H_6N_2O$)$_2$(H_2O)$_2$].3/2H_2O

Mass Spectra

To conclude the thermal decomposition pathway of the [Ni(asa)$_2$(na)$_2$(H_2O)$_2$] complex, mass spectrum was recorded (Figure 5) using direct insertion probe pyrolysis mass spectrometry method. The molecular ion peak was not detected the mass specrum recorded. The obtained pattern is relatively complex and exhibits a large number of peaks that extend to m/z value above 694 belonging to the decomposition products of the complex and ligands. Suggested structure of the complexes are given Figure 6.

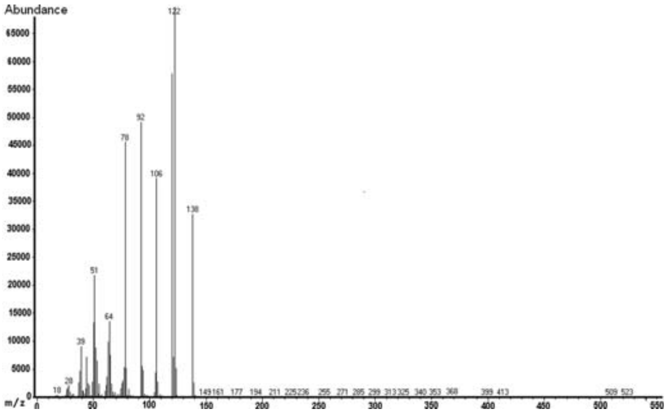


Figure 5. Mass Spectrum of [Ni(asa)$_2$(na)$_2$(H_2O)$_2$] complex.

Conclusion

The thermal decomposition of the investigated complexes takes place in three steps: dehydration, the elimination of the nicotinamide (na) ligand and the decomposition of acetylsalicylato ligand. Regardless of the coordination, the decomposition of the complexes starts with dehydration process. The complexes of Co(II), Ni(II) and Cu(II) lose water molecules in one step, whereas the complexes of Zn (II) lose water in two steps. This behaviour was also observed in our early studies and this may be attributed to the electron density of Zn(II) ion [32]. After the dehydration process, decomposition stages of the anhydrous complexes are related to the release of nicotinamide and partial decomposition of acetylsalicylate with the release of CO_2. Previous studies showed that the benzoate-metal complexes decompose by releasing of CO_2 [33,34]. According to the results, releasing of the nicotinamide ligand is an endothermal process and resembles to the thermal decomposition of nicotinamide complexes reported by the previous investigators [35]. On the other hand, the decomposition of acetylsalicylato ligand includes both an endothermal and exothermal process. Early releasing of the nicotinamide than that of acetylsalicylato ligand by volatilisation may be due to the non-ionic bonding to metal ion. The thermal stability of hydrated complexes follows the order:

	DTGm;lx
$[Cu(asa)_2(na)_2(H_2O)_2]$	133°C
$[Ni(asa)_2(na)_2(H_2O)_2]$	123°C
$[Co(asa)_2(na)_2(H_2O)_2]$	111°C
$[Zn(asa)_2(na)_2(H_2O)_2].1.5H_2O$	61°C

This order is competible with Pearson arrangement of 2+ ions of metals.

The final decomposition products were found to be the respective metal oxides formed in the 600–900°C temperature intervals.

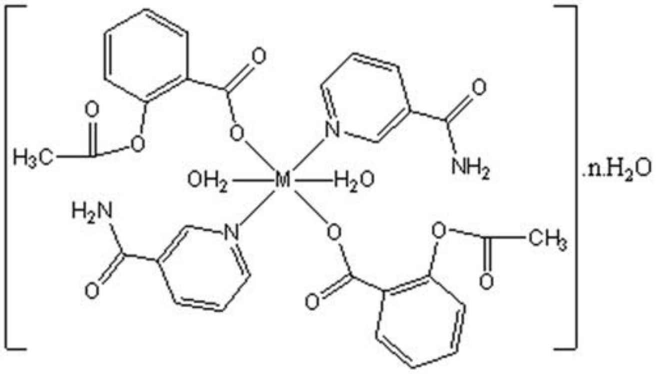


Figure 6. Suggested structure of the complexes.

In complexes, all ligands are coordinated to the metal ion as monodendate ligands. The IR spectra of the intermediate products showed similar results. The $(COO^-)_{sym.}$ peaks are located at 1591 cm^{-1} for Co(II), 1564 cm^{-1} for Ni(II), 1554 cm^{-1} for Cu(II) and 1588 cm^{-1} for Zn(II) complexes. $(COO^-)_{asym.}$ peaks are observed at 1390 cm^{-1} for Co(II), 1391 cm^{-1} for Ni(II), 1384 cm^{-1} for Cu(II) and 1399 cm^{-1} for Zn(II) complexes. The shift (Δ) between of the $\nu_{asym.}$ and $\nu_{sym.}$ bands of COO^- groups are for all of the complexes almost identical (170-201 cm^{-1}) and more than for the sodium salt acetylsalicylic acid (159 cm^{-1}) that monodentate carboxylate group exist [32,36].

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