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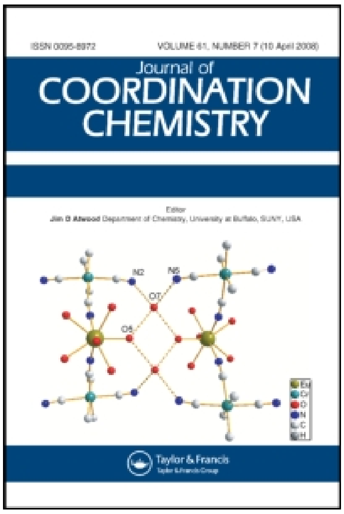

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Synthesis and characterization of N,N-diethylnicotinamide-acetylsalicylato complexes of Co(II), Ni(II), Cu(II), and Zn(II)

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N,N-diethylnicotinamide-acetylsalicylato complexes of Co(II), Ni(II), Cu(II), and Zn(II) were synthesized and investigated by elemental analysis, magnetic susceptibility, solid state UV–Vis, direct injection probe mass spectra, FTIR spectra and thermoanalytic TG-DTG methods. The complexes contain two waters, two acetylsalicylate (asa) and two N,N-diethylnicotinamide (dena) ligands per formula unit. The acetylsalicylate and N,N-diethylnicotinamide are monodentate through acidic oxygen and nitrogen of pyridine ring. Decomposition of each complex starts with dehydration then decomposition of N,N-diethylnicotinamide and acetylsalicylate, respectively. The thermal dehydration of the complexes takes place in one or two steps. 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 metal oxides.

Keywords: N,N-diethylnicotinamide; Acetylsalicylate; Thermal decomposition; Metal complexes; Mixed ligand complexes

1. Introduction

Acetylsalicylic acid or aspirin (asa, $C_9H_8O_4$) was first synthesized by Felix Hoffmann in 1897 and tested pharmacologically by H. Dreser in 1899; Wohlgemuth and Witthauer have undertaken clinical studies and documented the anti-rheumatic, anti-pyretic and analgesic properties of salicylic acid [1]. Not only acetylsalicylic acid, but also its derivatives are well known as anti-pyretic, anti-septic and anti-inflammatory agents and have found widespread applications in medicine. Metal complexes of inactive ligands and anti-inflammatory organic drugs are generally more active than those of free ligands or organic drugs [2–11]. Investigations revealed that $[Cu_2(asa)_4]$ is more effective as an anti-inflammatory agent than aspirin alone. In addition, the copper complex has

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anti-ulcer activity while aspirin has ulcerogenic properties. The $[Cu_2(asa)_2(py)_2]$ adduct has also been reported to be an effective anti-inflammatory, anti-cancer and anti-convulsant agent [12–14]. Zinc salicylate and a number of substituted salicylates have been employed in article coating to produce carbonless copying article and as an antioxidant or stabilizer in polymers [15].

N,N-diethylnicotinamide or 3-pyridinediethylcarboxyamide (dena), a derivative of nicotinamide, has a pyridine ring and can coordinate from N(1) of pyridine to metals. It has been used as a respination stimulant, named nicetamide or cordiamine in the market.

Studies on mixed-ligand complexes have importance with special interest on complexes between transition metal ions, salicylate ion and a nitrogen base. Various studies on the mixed-ligand metal complexes of the salicylate and N,N-diethylnicotinamide have been reported [16–20]. Structures of metal-N,N-diethylnicotinamide-benzoate complexes and their derivatives have been studied by Hökelek and Necefoglu [21–24].

In this work, complexes of Co(II), Ni(II), Cu(II), and Zn(II) with acetylsalicylate-N,N-diethylnicotinamide (Scheme 1) have been synthesized and their thermal decompositions reported. The decomposition pathways of the investigated complexes are discussed in connection with spectroscopic data.

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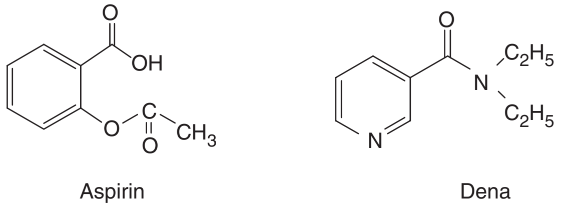
2. Experimental

2.1. *Materials and instrumentation*

All chemicals used were analytical reagent grade. $CoSO_4 \cdot 6H_2O$, $NiSO_4 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$, acetylsalicylic acid and N,N-diethylnicotinamide were obtained 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 temperature 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 analyzer combined with a TAS 100 thermogravimetric analyzer was used to record simultaneous TG, DTG and DTA curves. The experiments were performed in static air with a heating rate of 10 K min^{-1} from room temperature to 1000°C in platinum crucibles. The samples were approximately 10 mg and highly sintered α-Al_2O_3 was used as a reference material. The DTG sensitivity was 0.05 mg s^{-1}. Electronic spectra were recorded by a Shimadzu



Scheme 1. Structure of the acetylsalicylic acid (Aspirin) and N,N-diethylnicotinamide (Dena).

3600/UV-VIS-NIR spectrophotometer. Mass spectral data were recorded with an Agilent Technologies 5973 spectrophotometer using DIP-MS method.

2.2. *Preparation of acetylsalicylate complexes*

In the first step, acetylsalicylic acid sodium salt was prepared and metal acetylsalicylic acid salts were synthesized from Na(asa). The $M(asa)_2 \cdot nH_2O$ solution crystallized 5–7 days at room temperature. In the second step, a solution of dena (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 vacuum.

$C_{38}H_{46}N_4O_{12}Co$ (808.93); C 55.90 (56.50); H 5.94 (5.73); N 7.29 (7.00).
$C_{38}H_{46}N_4O_{12}Ni$ (808.69); C 56.50 (57.01); H 5.92 (5.67); N 7.28 (7.00).
$C_{38}H_{46}N_4O_{12}Cu$ (813.55); C 55.50 (56.00); H 5.74 (5.70); N 7.20 (6.92).
$C_{38}H_{46}N_4O_{12}Zn$ (815.39); C 56.06 (56.00); H 5.95 (5.70); N 7.83 (7.00).

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3. Results and discussion

The elemental analyses indicated that the complexes contain two acetylsalicylate and N,N-diethylnicotinamide ligands per formula unit. Effective magnetic moments and compositions of the complexes are given in table 1 in accord with literature values for similar complexes [25–28].

Octahedral coordination of the metal ions, confirmed by magnetic data, have two carboxylic oxygens from two acetylsalicylates, two nitrogens from two N,N-diethylnicotinamides, and two waters. The metal complexes are paramagnetic, except for Zn(II).

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 d–d transitions at 7016 cm^{-1} ($^4T_{1g} \rightarrow {}^4T_{2g}$) and 20150 cm^{-1} ($^4T_{1g} \rightarrow {}^4T_{1g}$)($^4P$) for Co(II) complex and three d–d transitions at 7860 cm^{-1} ($^3A_{2g} \rightarrow {}^3T_{2g}$), 15,600 cm^{-1} ($^3A_{2g} \rightarrow {}^3T_{1g}$)($^3F$), and 25,350 cm^{-1} ($^3A_{2g} \rightarrow {}^3T_{1g}$)($^3P$) for Ni(II). The Cu(II) complex has multiple overlapped

Table 1. Characteristic data of the metal complexes.

Complex	M ($g\,mol^{-1}$)	Yield (%)	Color	d.p.[a] (°C)	μ_{eff} (BM)
$[Co(asa)_2(dena)_2(H_2O)_2]$ $C_{38}H_{46}N_4O_{12}Co$	808.93	85	Pink	64	4.54
$[Ni(asa)_2(dena)_2(H_2O)_2]$ $C_{38}H_{46}N_4O_{12}Ni$	808.69	73	Green	67	2.93
$[Cu(asa)_2(dena)_2(H_2O)_2]$ $C_{38}H_{46}N_4O_{12}Cu$	813.55	87	Blue	60	1.46
$[Zn(asa)_2(dena)_2(H_2O)_2]$ $C_{38}H_{46}N_4O_{12}Zn$	815.39	89	Colorless	44	Diamagnetic

[a] Decomposition point.

Table 2. Selected characteristic FT-IR peaks of metal complexes.

Mode	asa	$II_{[B1]}$	IV	VI	VIII
ν(–OH)	2860–3100	–	–	–	–
$\nu(\text{–OH})_{\text{H2O}}$, ν(NH)	–	3570–3040	3500–3060	3550–3130	3500–3050
$\nu(\text{C=O})_{\text{carboxy}}$	1760	1626	1616	1630	1685
$\nu(\text{COO}^-)_{\text{as}}$	1691	1563	1584	1567	1565
$\nu(\text{COO}^-)_{\text{s}}$	1462	1459	1469	1462	1464
$\Delta\nu$	159	172	199	184	175
ν(C–O–C)	1190	1193	1143	1145	1144
$\nu(\text{C–H})_{\text{CH}_3}$	1374	1391	1385	1383	1390
$\nu(\text{C–N})_{\text{py}}$	–	1490	1485	1510	1525
$\nu(\text{C–N})_{\text{amid}}$	–	1256	1259	1254	1258
$\nu(\text{C–H})_{\text{CH}_5}$	–	2980	2990	2983	2984
ν(Me–N)	–	563	543	560	570
ν(Me–O)	–	460	466	463	459

absorption bands at 11,340 cm^{-1}–16,550 cm^{-1}. The absorption band at about 13,200 cm^{-1} was assigned to ($^2\text{E}_\text{g} \rightarrow {}^2\text{T}_{2\text{g}}$) for Cu(II) complex. The $\pi \rightarrow \pi^*$ transitions in the ligands were observed at 270 and 320 nm [27, 28], shifted to longer wavelength as a consequence of coordination.

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3.1. *FT-IR spectra*

Characteristic FT-IR peaks of the complexes are given in table 2. Absorptions in the range 3750–3040 cm^{-1} correspond to stretching vibrations of water. The asa-dena mixed ligand complexes have strong bands from C=O stretching. Conjugation between carbonyl and the amide nitrogen causes small frequency shifts. Strong bands at 1720 cm^{-1} are assigned to this mode, which remained in the same range as the amide of free dena, indicating that dena does not coordinate through amide. Pyridine ring vibration of free diethylnicotinamide at 1595 cm^{-1} shifts to 1500 cm^{-1} in the complexes indicating that pyridine is coordinated. The main difference in the spectrum of acetylsalicylic acid is that the C=O stretch of the carboxyl at 1760 cm^{-1} shifts to 1616–1685 cm^{-1} in the metal complexes, showing coordination of the carboxyl [29–31]. The –OH bending for the acetylsalicylic acid remained almost in the same position at 1270 cm^{-1} in all metal complexes. Low intensity bands in the 600–400 cm^{-1} region are attributed to M–N and M–O vibrations [32, 33].

3.2. *Thermal analysis*

The thermoanalytical curves of the studied complexes are shown in supplementary material. The corresponding thermal decomposition data are summarized in table 3.

3.2.1. $[\text{Co}(\text{C}_9\text{H}_7\text{O}_4)_2(\text{C}_{10}\text{H}_{14}\text{N}_2\text{O})_2(\text{H}_2\text{O})_2]$. The decomposition of the Co(II) complex starts at 64°C and two moles of coordination water are eliminated in a single step accompanied by a single endothermic DTA peak at 89°C. In the second stage, two N,N–diethylnicotinamide molecules are lost in two consecutive steps (DTG peaks at 185 and 213°C). There is good agreement between the experimental and calculated

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Table 3. Thermal analysis data of metal complexes.

Complex	Temp. range (°C)	Max. Dec. Temp. (°C) DTG max	Remove group	Weight loss (%) Exp. – Calcd	Total weight loss (%) Exp. – Calcd	Decomposition product	Color
$[Co(C_{10}H_{14}N_2O)_2\ C_9H_7O_4)_2(H_2O)_2]$ M.A=808,93							Light-pink
1	64–112	89(+)	$2H_2O$	4,50 – 4,45		$[Co(C_{10}H_{14}N_2O)_2(C_9H_7O_4)_2]$	
2	137–268	185(+) 213(+)	$2(C_{10}H_{14}N_2O)$	42,16 – 44,01		$[Co(C_9H_7O_4)_2$	
3	280–368	338(+)		24,28			
4	380–572	429(+)		17,95			
5	796–828	818(+)		0,90	89,79 – 90,74	CoO	Black
$[Ni(C_{10}H_{14}N_2O)_2(C_9H_7O_4)_2(H_2O)_2]$ M.A=808,69							Green
1	67–108	94(+)	$2H_2O$	3,30 – 4,45		$[Ni(C_{10}H_{14}N_2O)_2(C_9H_7O_4)_2]$	
2	129–290	229(+)	$2(C_{10}H_{14}N_2O)$	44,65 – 44,02		$[Ni(C_9H_7O_4)_2]$	
3	319–480	392(+) 414(+)		39,00			
4	496–568	–		4,01	90,76 – 90,66	NiO	Black-yellow
$[Cu(C_{10}H_{14}N_2O)_2(C_9H_7O_4)_2(H_2O)_2]$ M.A=813,55							Blue
1	60–89	77(+)	$2H_2O$	4,10 – 4,45		$[Cu(C_{10}H_{14}N_2O)_2(C_9H_7O_4)_2]$	
2	132–212	203(+)		26,53			
3	215–317	222(+) 254(+)		43,25			
4	318–380	347(+)		7,44			
5	381–436	396(+)		6,19			
6	834–908	875(+)		1,41	89,92 – 90,22	CuO	Black
$[Zn(C_{10}H_{14}N_2O)_2(C_9H_7O_4)_2(H_2O)_2]$ M.A=815,39							Colorless
1	44–70	56(+)	H_2O	2,20 – 2,21		$[Zn(C_{10}H_{14}N_2O)_2(C_9H_7O_4)_2(H_2O)]$	
2	77–110	84(+)	H_2O	2,13 – 2,21		$[Zn(C_{10}H_{14}N_2O)_2(C_9H_7O_4)_2$	Colorless
3	150–235	222(+)		37,68			Colorless
4	236–361	242(+) 247(+) 255(+) 270(+) 283(+)		27,51			
5	362–446	400(+)		16,02			
6	447–588			4,57	90,11 – 90,22	ZnO	Colorless

values for the mass loss (exp. 44.01%; Calcd 44.16%). In the following two steps, $[Co(C_9H_7O_4)_2]$ decomposes to give Co_2O_3 in the temperature range 280–572°C. In the last process, there is an endothermic peak at 818°C corresponding to the transformation of the Co_2O_3 to CoO. This behavior was also observed in the decomposition of the other Co(II) complexes [34].

3.2.2. $[Ni(C_9H_7O_4)_2(C_{10}H_{14}N_2O)_2(H_2O)_2]$. Elimination of water occurs between 67 and 108°C and the DTA curve shows an endothermic effect at 98°C indicating formation of the anhydrous complex. The anhydrous complex is stable to 120°C and reveals a 44.65% (Calcd 44.06%) mass loss between 129–290°C corresponding to release of two N,N-diethylnicotinamides. In the temperature range 319–568°C the remaining complex $[Ni(C_9H_7O_4)_2]$ decomposes in three consecutive steps (DTG peaks at 392, 414 and 532°C). The product was found to be NiO.

3.2.3. $[Cu(C_9H_7O_4)_2(C_{10}H_{14}N_2O)_2(H_2O)_2]$. The first step in the decomposition at 77°C corresponds to dehydration [33]. The anhydrous complex exists between 89–132°C and begins to decompose at 147°C with melting (DTA curve). The following steps involve consecutive decomposition of acetylsalicylate and N,N-diethylnicotinamide in the temperature range 132–436°C. A peak at 862°C (DTG curve) belongs to conversion of Cu_2O to CuO [25]. This conversion appeared in our previous studies with Cu complexes [30, 31, 34]. CuO is the final decomposition product.

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3.2.4. $[Zn(C_9H_7O_4)_2(C_{10}H_{14}N_2O)_2(H_2O)_2]$. Thermal dehydration of this complex occurs in two steps. In the first stage, one water is removed at 44–70°C (exp. 2.20%; Calcd 2.21%) and the remaining water between 71 and 110°C (exp. 2.20%, Calcd 2.13%). The anhydrous complex, $[Zn(asa)_2(dena)_2]$, is not stable and begins to decompose. At 282, 400 and 502°C DTA peaks, N,N-diethylnicotinamide and acetylsalicylate decompose producing ZnO (exp. 9.65%; Calcd 9.98%). Similar decomposition behavior is shown in literature [30, 31, 36].

3.3. *Mass spectra*

Mass spectrum of $[Ni(asa)_2(dena)_2(H_2O)_2]$ does not show the molecular ion and is relatively complex, exhibiting a number of peaks above m/z 815 (supplementary material).

4. Conclusion

Thermal decompositions of the complexes take place in three steps, dehydration, elimination of N,N-diethylnicotinamide and decomposition of acetylsalicylate. The Co(II), Ni(II) and Cu(II) complexes lose water in one step, whereas the Zn(II) complex loses water in two steps. $[Cu(C_9H_7O_4)_2(C_{10}H_{14}N_2O)_2(H_2O)_2]$ melts during decomposition, different than Co(II), Ni(II) and Zn(II) complexes. Releasing of N,N-diethylnicotinamide is an endothermic process and resembles thermal

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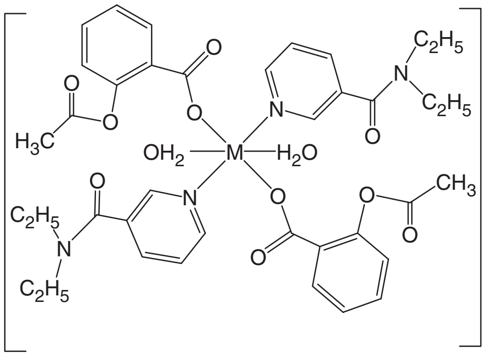

Figure 1. Suggested structures for metal complexes (M = Co(II), Ni(II), Cu(II) and Zn(II)).

decomposition of diethylnicotinamide complexes reported previously [37]. Decomposition of acetylsalicylato includes both endothermic and exothermic processes. Thermal stability of hydrated complexes follow the order:

$$\underset{67^\circ\mathrm{C}}{[\mathrm{Ni(asa)_2(dena)_2(H_2O)_2}]} > \underset{64^\circ\mathrm{C}}{[\mathrm{Co(asa)_2(dena)_2(H_2O)_2}]} > \underset{60^\circ\mathrm{C}}{[\mathrm{Cu(asa)_2(dena)_2(H_2O)_2}]}$$
$$> \underset{44^\circ\mathrm{C}}{[\mathrm{Zn(asa)_2(dena)_2(H_2O)_2}]}$$

compatible with 2+ ions. The final decomposition products were metal oxides formed between 600–900°C. All ligands are monodendate. The IR spectra of all products are similar with $(\mathrm{COO^-})_{\mathrm{asym.}}$ peaks at $1563\,\mathrm{cm^{-1}}$ for Co(II), $1584\,\mathrm{cm^{-1}}$ for Ni(II), $1567\,\mathrm{cm^{-1}}$ for Cu(II) and $1565\,\mathrm{cm^{-1}}$ for Zn(II), $(\mathrm{COO^-})_{\mathrm{asym.}}$ peaks at $1391\,\mathrm{cm^{-1}}$ for Co(II), $1385\,\mathrm{cm^{-1}}$ for Ni(II), $1383\,\mathrm{cm^{-1}}$ for Cu(II) and $1390\,\mathrm{cm^{-1}}$ for Zn(II) complexes. The shift (Δ) between the $\nu_{\mathrm{asym.}}$ and $\nu_{\mathrm{sym.}}$ bands of $\mathrm{COO^-}$ groups are almost identical for all complexes (172–$199\,\mathrm{cm^{-1}}$) and indicate monodentate carboxylate [30, 38, 39].

The structures presented in figure 1 are consistent with their chemical, thermal and spectroscopic properties.

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