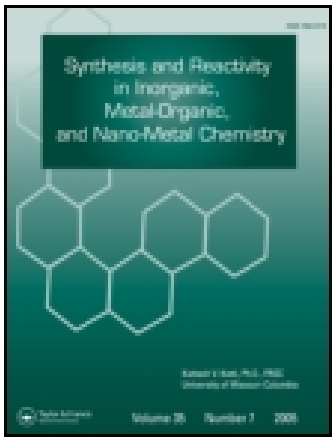

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Spectroscopic and Thermal Studies of bis(N,N′-Dimethylethylenediamine) and bis(N,N-Dimethylethylenediamine)saccharinato Complexes of Co(II), Ni(II), and Cu(II)

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Spectroscopic and Thermal Studies of *bis*(N,N′-Dimethylethylenediamine) and *bis*(N,N-Dimethylethylenediamine)saccharinato Complexes of Co(II), Ni(II), and Cu(II)

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ABSTRACT

The mixed-ligand saccharin (Hsac) complexes of Co(II), Ni(II) and Cu(II) with N,N′-dimethylethylenediamine (dmen), and N,N-dimethylethylenediamine (ndmen) (Figure 1) were synthesized and characterized by elemental analysis, magnetic susceptibility, spectral (UV-Vis and FT-IR) methods, and simultaneous TG, DTG and DTA techniques. The complexes have pseudooctahedral geometries with two dimethylethylenediamine molecules coordinated to the metal ions as chelating ligands

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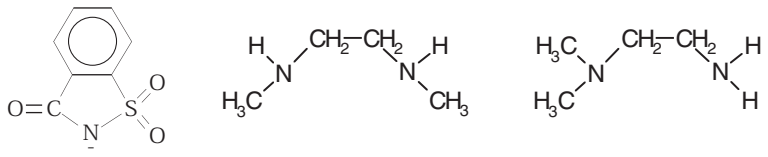
through their two nitrogen atoms and two monodentate saccharinato ligands in the trans positions for the complexes of the type $[M(sac-O)_2(dmen)_2]$ (M = Co(II), Ni(II)), and $[M(sac\text{-}N)_2(ndmen)_2]$ (M = Co(II), Ni(II), Cu(II)) and two aqua ligands in the trans positions in $[Cu(H_2O)_2(dmen)_2](sac)_2$. (sac–O; sac–N = the saccharinato ligand may be coordinated to the metal ions through their carbonyl oxygen or their nitrogen atom, respectively). The decomposition mechanism and thermal stability of the solid complexes are interpreted in terms of their structures. The thermal stability order of the investigated complexes is Cu(II) > Co(II) > Ni(II) while the bis(N,N′,-dimethylethylenediamine) complexes are thermally less stable than those of bis(N,N-dimethylethylenediamine). The final decomposition products—the respective metal oxides—were identified by FT-IR spectroscopy.

Key Words: Saccharinato complexes; N, N′-Dimethylethylenediamine; ve N, N-Dimethylethylenediamine; Thermal analysis.

INTRODUCTION

Saccharin (Hsac, also known as o-benzosulfimide, 2,3-dihydro-3-oxobenzisosulfonazole, 1,2-benzisothiazol-3(2H)-one 1,1-dioxide) is widely used as food additive, artificial sweetener and electroplating brightener. However, the suspected carcinogenic nature of saccharin has resulted in much scientific attention and in studies of the saccharinates of various metals. Because of the biological significance of saccharin, there has been increased interest in metal complexes, especially first-row transition metals. A suggestion has been made that the importance of saccharin complexes lies in the potential use of saccharin as an antitode for metal poisoning; the 1,10-phenantroline chelator may act as potential antitumor agent. The biological activities of many metal complexes are found to vary with small changes in their composition and configuration.[1,2] Ethylenediamine chelator is an N-



sac dmen ndmen

Figure 1. Structures of the ligands: sac = deprotonated saccharin; dmen = N,N′-dimethylethylenediamine; ndmen = N,N-dimethylethylenediamine.

donor ligand like 1,10-phenantroline. In the last two decades, the synthesis and spectroscopic properties,[3–7] particularly, systematic vibrational properties[8–12] of the metal saccharinates and metal complexes including saccharin and various N-donor ligands (mono- or bidentate) have been intensively studied by many investigators. A number of crystal structures of metal saccharinate complexes have been determined.[13–17] The thermal properties of the metal saccharinates and mixed-ligand complexes have also been investigated.[18–21]

In the present paper, we report the synthesis, spectroscopic, and thermal properties of some new mixed-ligand complexes of Co(II), fNi(II) and Cu(II) containing saccharin, N,N′-dimethylethylenediamine, and N,N-dimethylethylenediamine. The structures of the ligands are shown in Figure 1.

EXPERIMENTAL

Materials and Instrumentation

All chemicals used were analytical regent products. Sodium saccharinate was used in the preparations of the complexes. Elemental analyses for C, H, and N were carried out at the TÜBİTAK Marmara Research Centre. Magnetic susceptibility measurements at room temperatures were performed using a Sherwood Scientific MXI model Gouy magnetic balance. UV-Vis spectra were obtained for the aqueous solutions of the complexes with a Unicam UV2 spectrometer in the range 900–190 nm. IR spectra were recorded in the 4000–200 cm^{-1} region with a Mattson 1000 FT-IR spectrometer using KBr pellets. Thermal analysis curves (TG-DTG and DTA) were recorded simultaneously in a static air atmosphere with a Rigaku TG8110 thermal analyser. The heating rate was 10 °C min^{-1} and the DTG sensitivity was 0.05 mg s^{-1}.

Synthesis of $[M(sac)_2(H_2O)_4]\cdot 2H_2O$ Complexes

A solution of sodium saccharinate (1.025 g, 5 mmol) in distilled water (50 mL) was added drop wise with stirring at 80 °C to a solution of $MSO_4\cdot xH_2O$ (2.5 mmol; M = Co(II), 0.703 g; Ni(II), 0.657 g; and Cu(II), 0.624 g; $x = 7$, 6, and 5, respectively) in distilled water (50 mL). The mixture was stirred for 4 h at 80 °C and then cooled to room temperature. The crystals formed were filtered and washed with 10 mL of cold distilled water and dried in vacuo.[2]

Synthesis of Mixed-Ligand Complexes

A solution of dmen or ndmen (0.176 g, 2 mmol) in distilled water (30 mL) was added drop-wise with stirring to a solution of $[M(sac)_2(H_2O)_4]\cdot 2H_2O$ (1.0 mmol; M = Co(II), 0.531 g; Ni(II), 0.530 g; and Cu(II), 0.535 g) in hot distilled water (50 mL). The solutions were heated to 80 °C in a temperature-controlled bath and stirred for 4 h. The reaction mixture was then cooled to room temperature. The crystals formed were filtered and washed with 10 mL of cold distilled water and acetone and dried in vacuo. In the case of the Co(II) complexes butanol was used as a solvent.

RESULTS AND DISCUSSION

Synthesis and Structures of the Complexes

The mixed-ligand complexes were prepared according to the following equations:

$$MSO_4 + 2sacNa + 6H_2O \rightarrow [M(sac)_2(H_2O)_4]\cdot 2H_2O + Na_2SO_4$$

$$[M(sac)_2(H_2O)_4]\cdot 2H_2O + 2dmen \rightarrow [M(sac)_2(dmen)_2] + 6H_2O$$

$$(M = Co(II), Ni(II))$$

$$[Cu(sac)_2(H_2O)_4]\cdot 2H_2O + 2dmen \rightarrow [Cu(H_2O)_2(dmen)_2](sac)_2 + 4H_2O$$

$$[M(sac)_2(H_2O)_4]\cdot 2H_2O + 2ndmen \rightarrow [M(sac)_2(ndmen)_2] + 6H_2O$$

$$(M = Co(II), Ni(II), Cu(II))$$

Analytical results and the compositions of the complexes are listed in Table 1. The complexes were synthesized in good yields and with high purity. The results of elemental analyses show that two ligand molecules have been incorporated into the M(II) saccharinates. The $[Cu(H_2O)_2(dmen)_2](sac)_2$ complex contains 2.0 water molecules per formula unit. The presence of aqua ligand was confirmed by the IR spectra and the weight loss and endotherms in the temperature range 68–148 °C in the TG and DTA curves. The complexes have pseudooctahedral geometries with two

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Table 1. Analytical data of the metal complexes.

Complex	F.W. (g mol^{-1})	Found (calc.) %			Colour	D.p.[a] (°C)	Yield (%)
		C	H	N			
$[Co(sac)_2(dmen)_2]$ $C_{22}H_{32}N_6O_6S_2Co$	599.61	43.61 (44.03)	5.37 (5.34)	13.40 (14.02)	Pink	233	58.02
$[Ni(sac)_2(dmen)_2]$ $C_{22}H_{32}N_6O_6S_2Ni$	599.37	43.55 (44.05)	5.43 (5.34)	14.03 (14.02)	Violet	266	65.82
$[Cu(H_2O)_2(dmen)_2](sac)_2$ $C_{22}H_{36}N_6O_8S_2Cu$	640.22	41.03 (41.24)	5.75 (5.62)	12.67 (13.13)	Dark-blue	97	88.54
$[Co(sac)_2(ndmen)_2]$ $C_{22}H_{32}N_6O_6S_2Co$	599.61	43.89 (44.03)	5.44 (5.34)	13.56 (14.02)	Light-brown	245	54.03
$[Ni(sac)_2(ndmen)_2]$ $C_{22}H_{32}N_6O_6S_2Ni$	599.37	44.07 (44.05)	5.58 (5.34)	13.79 (14.02)	Light-blue	288	67.34
$[Cu(sac)_2(ndmen)_2]$ $C_{22}H_{32}N_6O_6S_2Cu$	604.22	43.53 (43.69)	5.43 (5.30)	13.57 (13.91)	Violet	177[b]	90.12

[a]Decomposition point.
[b]Melting point.

dimethylethylenediamine molecules (dmen or ndmen) coordinated to the metal ions as chelating ligands through their two N atoms and two monodentate saccharinato ligands in the trans positions for the complexes of the type $[M(sac\text{-}O)_2(dmen)_2]$ (M = Co(II), Ni(II)), and $[M(sac\text{-}N)_2(ndmen)_2]$ (M = Co(II), Ni(I), Cu(II)), and two aqua ligands in the *trans* positions for $[Cu(H_2O)_2(dmen)_2](sac)_2$. sac-O and sac-N means that the saccharinato ligand is coordinated to the metal ions through the carbonyl oxygen or the nitrogen atom, respectively. The elemental analysis data in Table 1 confirm the proposed formulae of the complexes.

UV-Vis Spectra

The λ_{max} values of the various absorption bands, Δ_o values of d–d transitions displayed by the complexes, assignment of d–d transitions, and the effective magnetic moment values of the complexes are given in Table 2. The assignments of the d–d transitions corresponded to an octahedral coordination geometry of the metal ions and the values of the Δ_o parameter were found using Tanabe and Sugano diagrams.[22] The λ_{max} values of the absorption bands in the spectra of $[Co(sac)_2(dmen)_2]$ and $[Co(sac)_2(ndmen)_2]$

Table 2. Electronic spectra and magnetic moments of the metal complexes.

Complex	λ_{max} (nm)	ε ($cm^{-1}M^{-1}$)	Δ_o (cm^{-1})	Assignment of d–d transitions	μ_{eff} (B.M.)
$[Co(sac)_2(dmen)_2]$	368	863		$^4T_{1g} \rightarrow {}^4T_{1g}$ (P)	
	513	131	–	$^4T_{1g} \rightarrow {}^4A_{2g}$	4.41
	–	–		$^4T_{1g} \rightarrow {}^4T_{2g}$	
$[Ni(sac)_2(dmen)_2]$	366	41		$^3A_{2g} \rightarrow {}^3T_{1g}$ (P)	
	600	24		$^3A_{2g} \rightarrow {}^3T_{1g}$ (F)	2.82
	900	23	11,110	$^3A_{2g} \rightarrow {}^3T_{2g}$	
$[Cu(H_2O)_2(dmen)_2]$-$(sac)_2$	563	96	17,760	$^2E_g \rightarrow {}^2T_{2g}$	1.49
$[Co(sac)_2(ndmen)_2]$	375	242		$^4T_{1g} \rightarrow {}^4T_{1g}$ (P)	
	518	157	–	$^4T_{1g} \rightarrow {}^4A_{2g}$	4.65
	–	–		$^4T_{1g} \rightarrow {}^4T_{2g}$	
$[Ni(sac)_2(ndmen)_2]$	371	33		$^3A_{2g} \rightarrow {}^3T_{1g}$ (P)	
	611	25		$^3A_{2g} \rightarrow {}^3T_{1g}$ (F)	3.02
	900	22	11,110	$^3A_{2g} \rightarrow {}^3T_{2g}$	
$[Cu(sac)_2(ndmen)_2]$	565	164	17,700	$^2E_g \rightarrow {}^2T_{2g}$	1.45

are 368, 513 and 375, 518 nm, respectively. These values were assigned to the following d–d transitions: ν_3: $^4T_{1g} \rightarrow {}^4T_{1g}$ (P); ν_2: $4T_1g \rightarrow {}^4A_{2g}$. The ν_1: $^4T_{1g} \rightarrow {}^4T_{2g}$ transition was not observed since ν_1 is of very low energy and shifts to the IR region. The Δ_o values for cobalt compounds could not be calculated since $\Delta_o = \nu_2 - \nu_1$ for d^7 complexes. The λ_{max} values of $[Ni(sac)_2(dmen)_2]$ and $[Ni(sac)_2(ndmen)_2]$ are 366, 600, 900 and 371, 611, 910 nm, respectively. These values were assigned to ν_3: $^3A_{2g} \rightarrow {}^3T_{1g}$ (P); ν_2: $^3A_{2g} \rightarrow {}^3T_{1g}$ (F), and ν_1: $^3A_{2g} \rightarrow {}^3T_{2g}$ d–d transitions. The Δ_o values for $[Ni(sac)_2(dmen)_2]$ and $[Ni(sac)_2(ndmen)_2]$ were calculated as 11,110 cm^{-1} since $\Delta_o = \nu_1$ for d^8 complexes. The λ_{max} values of $[Cu(H_2O)_2(dmen)_2](sac)_2$ and $[Cu(sac)_2(ndmen)_2]$ are 563 and 565 nm, respectively. These values were assigned to the $^2E_g \rightarrow {}^2T_{2g}$ transition. The Δ_o values for $[Cu(H_2O)_2(dmen)_2](sac)_2$ and $[Cu(sac)_2(ndmen)_2]$ were calculated as 17,760 and 17,700 cm^{-1}, respectively, since there is only one transition for d^9 complexes.

It is seen that the Δ_o values increase from the Ni to the Cu–dmen and ndmen complexes separately. The metal complexes are of the high-spin type and paramagnetic. These values suggest octahedral coordination around the metal ions.

FT-IR Spectra

The main IR group frequencies of the metal complexes are presented in Table 3. The IR spectra of all the complexes resemble each other and show the characteristic C=O and O=S=O absorption bands of the sac moiety. The stretching modes of the carbonyl and sulfonyl groups are used most frequently for structural studies of various saccharinates.[5,6,21] The coordination mode of the saccharin entities in the complexes is reflected in the stretching frequencies of the carbonyl groups, the respective band(s) being blue-shifted for N-coordination and red-shifted for O-coordination relatively to the saccharin ion.[4] Strong absorption bands in the range of 1615–1638 cm^{-1} characterize the C=O group of the sac moiety in the complexes. These vibrational frequencies are lower than in saccharin itself (1725 cm^{-1}) owing to the partially ionic character of the M–sac bond, the lowering being dependent on the bond ionicity.[8,21] The existence of only one carbonyl stretching band in the spectra of the complexes would indicate the existence of a single type of saccharinato ligand, although this correlation is not always straightforward. The strong band at 1623 cm^{-1} assigned to the CO stretching vibration in $[Cu(H_2O)_2(dmen)_2](sac)_2$ is shifted to 1615 and 1618 cm^{-1} for $[Co(sac)_2(dmen)_2]$ and $[Ni(sac)_2(dmen)_2]$, respectively. This fact can be attributed to the O-coordination of the sac ligand in the Co(II) and Ni(II) complexes. For $[Co(sac)_2(ndmen)_2]$, $[Ni(sac)_2$-

Table 3. FT-IR spectra[a] of the metal complexes.

	Vibrational frequency (cm^{-1})					
Complex	ν(NH)	$\nu(NH_2)$	ν(C=O)	$\nu_{as}(SO_2)$	$\nu_s(SO_2)$	$\nu_r(CH_2)$
$[Co(sac)_2(dmen)_2]$	3343 w	–	1615 vs	1285 vs	1155 vs	856 m
$[Ni(sac)_2(dmen)_2]$	3311 m	–	1618 vs	1287 vs	1157 vs	863 m
$[Cu(H_2O)_2(dmen)_2]$-$(sac)_2$	3348 m	–	1623 vs	1266 vs	1146 vs	864 m
$[Co(sac)_2(ndmen)_2]$	–	3336–3250 m	1638 vs	1265 vs	1148 vs	854 m
$[Ni(sac)_2(ndmen)_2]$	–	3329–3249 s	1632 vs	1289 vs	1155 vs	892 m
$[Cu(sac)_2(ndmen)_2]$	–	3323–3245 m	1630 vs	1276 vs	1146 vs	899 m

[a]Abbreviations: m-medium; w-weak; s-strong; vs-very strong.

$(ndmen)_2]$ and $[Cu(sac)_2(ndmen)_2]$ this vibration is larger than 1623 cm^{-1} (1638, 1632 and 1630 cm^{-1}, respectively) as a result of coordination of the sac ligand via the nitrogen atom. The saccharin behaves as the O- and N-bonded ligand, and the counter-ion in the outer-sphere of the mixed-ligand saccharin complexes.[13,14,16]

The frequencies of the SO_2 stretching vibrations in metal saccharinates are also lower than that of the saccharin molecule.[8] The frequencies of the $\nu_{as}(SO_2)$ and the $\nu_s(SO_2)$ modes in the studied complexes range from 1289 to 1265 cm^{-1} and from 1157 to 1146 cm^{-1}, respectively. These $\nu_{as}(SO_2)$ frequencies are by 66–90 cm^{-1} lower than the corresponding mode in saccharin itself (1355 cm^{-1}), while the lowering of the $\nu_s(SO_2)$ frequencies is 23–34 cm^{-1} as compared to the value of 1180 cm^{-1} in saccharin. The frequency of the antisymmetric SO_2 stretching vibration is more sensitive to external influences than the symmetric SO_2 mode.[21]

The vibrational frequencies of the CH_2 groups in the dmen and ndmen ligands of the complexes range from 899 to 854 cm^{-1} and are in agreement with coordinated ethylenediamine in the complexes.[5] The M–N stretching frequencies of the studied complexes were observed in the range of 484–460 cm^{-1}.

The symmetric and asymmetric stretching vibration of the NH_2 groups of ndmen occurred at 3336–3245 cm^{-1} in the ndmen complexes, whereas the stretching vibrations of the secondary amine ligands appeared at 3348–3311 cm^{-1} in the dmen complexes, as expected.

The IR spectrum of $[Cu(H_2O)_2(dmen)_2](sac)_2$ has an additional strong and sharp band at 3553 cm^{-1} which is assigned to ν(OH) of the aqua ligand.

Thermal Properties

$[M(sac)_2(dmen)_2]$ (M = Co(II), Ni(II)) and $[Cu(H_2O)_2(dmen)_2](sac)_2$ Complexes

The Co(II) and Ni(II) complexes are thermally stable up to about 200 and 252 °C, respectively, and decompose in five steps as shown by DTG. Thermal analysis curves of Co(II) complex are given in Figure 2 as an example. The first weight loss (WL) decomposition stages of these complexes, in the range of 200–246 °C for the Co(II) complex and 252–277 °C for the Ni(II) complex, are exothermic and related to the decomposition of the neutral dmen ligands. This type of behavior of neutral ligands has been reported earlier.[20] These WL processes were also verified by the IR spectra. The IR spectra of the intermediate products formed in the 250 and 280 °C interval for the Co(II) and Ni(II) complex, respectively, showed that the intensity of the vibration bands of CH_2 and NH groups of the dmen ligand decreased. The second WL process of the two complexes is endothermic and related to the partial decompositions of the ionic sac ligand. The IR spectrum of the intermediate product obtained in this step showed that the saccharinato ligand decomposes to release SO_2. Furthermore, the IR spectra of the intermediate products formed in the 416–462 °C interval are similar. The third WL process of the Co(II) complex and the fourth WL process of the Ni(II) complex are exothermic and the values of DTG_{max} are 534 and 465 °C, respectively. The strong exothermic peaks are associated with the burning of the organic residue, characteristic for the decomposition of sac complexes[19] and leading finally to the corresponding metal

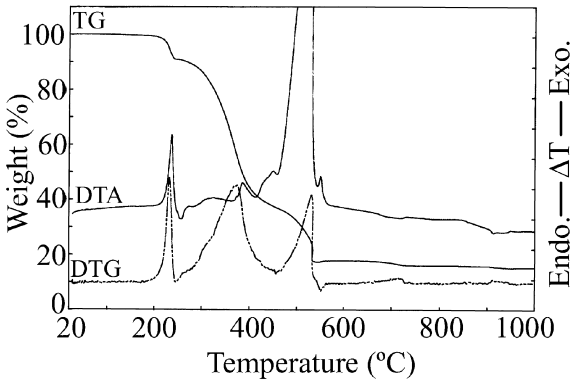


Figure 2. DTA, TG, and DTG curves of $[Co(sac)_2(dmen)_2]$.

oxides. The endothermic peak at 913 °C is related to the conversion of Co_3O_4 to CoO.

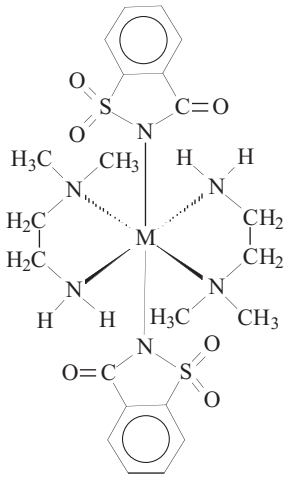
The Cu(II) complex included 2 molecules of water which makes it different from the Co(II) and Ni(II) complexes, exhibiting five steps of decompositions. The first WL process, in the temperature range 74–125 °C, corresponds to the loss of 2.0 moles of aqua ligands in a single step and the frequency of the CO vibration of the Cu(II) complex (1623 cm^{-1}) is shifted to 1628 and 1654 cm^{-1}. The vibration at 1628 cm^{-1} is indicative of the saccharin ion outside of the coordination sphere, while the vibration at 1654 cm^{-1} is indicative of the N-coordinated saccharinato ligand. The anhydrous Cu(II) complex is thermally stable up to 197 °C and begins to decompose with melting at 216 °C (DTA curve). This complex behaviour was not observed for the other two complexes. Probably, one mol of dmen ligand is removed (exp. weight loss is 13.75% which is close to the calculated weight loss of 13.96%) and the geometry of the Cu(II) complex changes from octahedral to square-planar at this stage. This second stage consists of three overlapping thermal steps and the DTG_{max} values of these steps are 208, 228 and 249 °C. In the endothermic third and exothermic fourth stages (DTG_{max} = 380 and 481 °C, respectively), one mole of dmen and two moles of sac ligands are removed and the final decomposition product is CuO.

Based on the initial DTG_{max} temperatures, the thermal stabilities of the dmen complexes follow the sequence: Cu(II); 97 °C > Co(II); 233 °C > Ni(II); 266 °C.

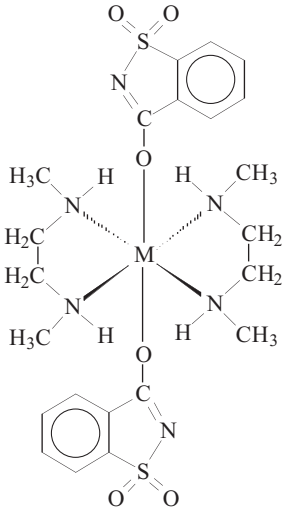
$[M(sac)_2(ndmen)_2]$ Complexes (M = Co(II), Ni(II), Cu(II))

The Co(II) and Ni(II) complexes are thermally stable up to about 220 and 270 °C, respectively. The decomposition of the ndmen ligand at the first step is exothermic for the two complexes [DTG_{max} = 245 °C for Co(II) and 288 °C for Ni(II)]. The characteristic exothermic decomposition process of the sac ligand takes place at 533 and 486 °C (DTG_{max}) for the Co(II) and Ni(II) complexes, respectively.

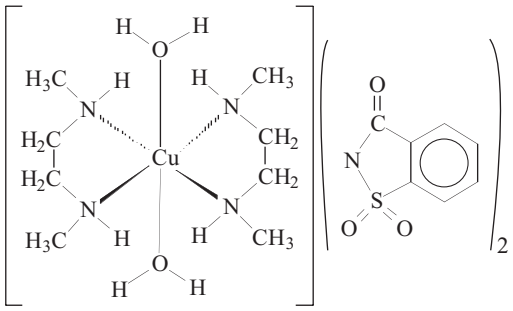
The Cu(II) complex is thermally stable up to 171 °C and begins to decompose with melting at 177 °C (DTA curve). The DTG_{max} values of the successive processes in the second WL stage are 302, 333 and 377 °C. The WL process at 486 °C (DTG_{max}) is highly exothermic and CuO is found to be the final decomposition product. The final decomposition products, namely CoO, NiO and CuO, were identified by IR spectroscopy with the corresponding spectra obtained under the same conditions as the pure oxides.



$[M(sac)_2(dmen)_2]$
(M=Co(II), Ni(II))



$[M(sac)_2(ndmen)_2]$
(M=Co(II), Ni(II), Cu(II))



$[Cu(H_2O)_2(dmen)_2](sac)_2$

Figure 3. Suggested structures of the complexes.

Based on to the initial DTG_{max} temperatures, the thermal stabilities of the ndmen complexes follow the sequence: Cu(II); 191 °C > Co(II); 245 °C > Ni(II); 288 °C.

It is evident that the thermal stability sequences of the dmen and ndmen complexes are the same; however, the thermal stabilities of the ndmen complexes are higher than those of the dmen complexes. This stability behaviour can be attributed to the ligand basicity.[23] This stability difference between the dmen and ndmen complexes was not observed clearly in the spectroscopic studies.

The structures of the synthesized complexes which are presented Figure 3, are consistent with the chemical, thermal and spectroscopic properties which were determined.

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