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# Spectral and thermal study of the ternary complexes of nickel with sulfasalazine and some amino acids

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#### Abstract

The ternary complexes of Ni(II) with sulfasalazine ( $H_3SS$ ) as a primary ligand and alanine (ala), aspartic acid (asp), histidene (hist), methionine (meth) and serine (ser) amino acids as secondary ligands have been synthesized. Characterization of the complexes was based on elemental analyses, IR, UV–vis, mass spectra, magnetic moment and thermal analysis (TG). The isolated complexes were found to have the general formula  $[M(HSS)(AA)]4H_2O$  (AA = ala, asp, hist, meth, or ser amino acid) where nickel is tetra-coordinated. The thermal stability of the complexes was studied and the weight losses for the decomposition of the complexes were calculated and correlated with the mass fragmentation pattern. In most cases, the amino acid moiety is removed along with the Schiff base moiety leaving NiO as a metallic residue. The metallic residue was confirmed by powder XRD measurements.

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# 1. Introduction

Sulfa drugs have attracted special attention for their therapeutic importance as they were used against a wide spectrum of bacterial ailments [1–8]. Also, some sulfa drugs were used in the treatment of cancer, malaria, leprosy and tuberculosis [4]. Although the complexes of some sulfa drugs have been investigated in the solid state, no much data is reported about their mixed-ligand complexes [8,9]. The formation and characterization of binary and mixed-ligand complexes, involving iminodiacetic acid and sulfa drugs as sulfadiazine and sulfadiamidine, were investigated [8–10].

Binary and ternary complexes of transition metals are commonly found in biological media and might play important roles in process as diverse as the catalytic interaction of viruses with bacterial cell walls, the transport and storage of oxygen, etc. [10].

Continuing my pervious studies on the binary complexes of sulfasalazine with Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ce(IV), Th(IV) and UO<sub>2</sub>(IV) [11,12], the present work throws

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more insight on chelation behavior of sulfasalazine ( $H_3SS$ ) (Scheme 1), through the synthesis and characterization of the nickel(II) ternary system with some amino acids.

## 2. Experimental

All chemicals used were of the highest purity grade. They included: sulfasalazine (Sigma), nickel nitrate hexahydrate (BDH), amino acids (Merk) and ammonium hydroxide (Merck).

Sulfasalazine has four ionization constants [10]: 0.62, 2.9, 8.7 and 11.1 corresponding to the deprotonation of the protonated pyridine nitrogen, carboxylic OH, phenolic OH and sulfonamide hydrogen, respectively. The free carboxylic form of sulfasalazine is insoluble in water or ethanol, so that ammonical ethanolic solutions were used (pH 6.0) at which the carboxylic acid group is ionized. In addition, the sulfonamide NH ( $pK_a$  11.1) does not participate in bonding due to structure complication. Hence, sulfasalazine can be symbolized as HSS<sup>-</sup> (Scheme 2).

#### 2.1. Preparation of complexes

The 1:1:1 [Ni:HSS:AA] complexes were prepared from hot ethanolic solutions ( $60 \circ C$ ) by the addition of 50 ml of the nickel

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Scheme 1. Structure of sulfasalazine (H<sub>3</sub>SS).

nitrate hexahydrate (2 mmol, 0.58 g) dropwisely to 50 ml of an ammonical solution of sulfasalazine (HSS<sup>-</sup>) (2 mmol, 0.80 g) and 2 mmole amino acid (AA) (0.18 g ala, 0.27 g asp, 0.42 g hist, 0.30 g meth and 0.21 g ser). The mixtures were adjusted to be slightly alkaline (pH 7.5–8.5) to ensure the complete solubility of sulfasalazine and to assist the formation of the ternary complexes, which are usually formed at higher pH than the binary ones [13]. The mixtures were then stirred for 1 h and left in refrigerator overnight whereby the complexes were precipitated. The isolated complexes were filtered, washed thoroughly by warm ammonical ethanol and then by diethyl ether. The solid complexes were then dried in vacuum desiccator and subjected to elemental microanalyses.

#### 2.2. Measurements

Elemental analyses (C, H, N and S) were performed in the Centeral Laboratory Unit (CLU) of UAE University; the analyses have been repeated twice. The IR spectra have been recorded using NEXUS 470 FT-IR spectrometer, Thermo Nicolet Corporation, running under OMNIC software package in wave number region 4000–400 cm<sup>-1</sup>. The spectrum recorded as a KBr pellets. UV–vis measurements for the binary and ternary complexes were performed using Cary 50 Conc UV–vis spectrophotometers, VARIAN; in the wavelength range 200–900 nm. The con-



Scheme 2.  $HSS^-$  (R =  $-N_2PhSO_2NHPy$ ; py = pyridine).

ductometric measurements of the complexes were carried out as DMF solutions at 25 °C using Metrohm 660 conductivity meter. The molar magnetic susceptibilities were measured on powdered samples (Gouv method) using a Sherwood Scientific magnetic susceptibility balance. Mass spectra of the solid complexes were recorded by FAB technique at (410 keV) using JMS-AX500 Double focusing mass spectrometer. Thermogravimetric analysis (TG) of the complexes was carried out in a dynamic nitrogen atmosphere  $(20 \text{ ml min}^{-1})$  at different heating rates of 5, 10 and 15 °C min<sup>-1</sup> using Shimadzu TGA-50H analyzer. X-ray powder diffraction (XRD) was carried out at ambient temperature using Philips Analytical X-Ray B.V. with PC-APD, Diffraction Software. The instrument is equipped with a copper anode generating Ni-filtered Cu K<sub> $\alpha$ </sub> radiation ( $\lambda = 1.54056$  Å, 40 kV, 55 mA). Diffractograms were recorded in the  $2\theta$  range between 2.0 and 90.0 with a step size  $(2\theta)$  of 0.080.

## 3. Results and discussion

The results of the elemental analyses and mass spectrometry data are presented in Table 1. The results obtained are in good agreement with those calculated for the suggested formulae of the complexes (Ni:HSS:AA:4H<sub>2</sub>O). The molar conductance values in DMF (Table 1) for the complexes were found to be in the range 16.90–32.00 S cm<sup>2</sup> mol<sup>-1</sup>. The relatively low values indicate the non-electrolytic nature of these complexes [11,14]. This can be accounted for by the satisfaction of the bivalency of nickel by the carboxylate group of sulfasalazine (used as ammonium salt) and the amino acid carboxylic group which deprotonated upon complex formation. This implies the coordination of the phenolic OH of sulfasalazine and the NH<sub>2</sub> of the amino acids without proton displacement.

#### 3.1. Infrared spectra

The IR spectra of the free ligand and its metal complexes were carried out in the range of  $4000-400 \text{ cm}^{-1}$  and the important bands were listed in Table 2. The IR spectrum of sulfasalazine showed a medium broad band at  $3439 \,\mathrm{cm}^{-1}$ , which was attributed to OH of the phenolic and carboxylic OH groups. The carboxylic OH group was not considered in the spectra of complexes since ammonical solution of sulfasalazine was used in which the carboxylic group was used as an ammonium salt. The existence of water of hydration in the spectra of the complexes rendered it difficult to get conclusion from the phenolic OH group of the sulfasalazine, which would be overlapped by those of the water molecules. The participation of the phenolic group was deduced by clarifying the effect of chelation on the  $\nu$ (C–O) stretching vibration. The shift in  $\nu$ (C–O) of phenolic group, from  $1281 \text{ cm}^{-1}$  in the free sulfasalazine ligand to  $1268-1260 \text{ cm}^{-1}$  in the complexes indicated the participation of the phenolic group in complex formation [14–17]. Also the participation of the OH group was apparent from the shift in position of the  $\delta(OH)$  in-plane bending from 1393 cm<sup>-1</sup> in the free sulfasalazine ligand to  $1388-1346 \text{ cm}^{-1}$  in the complexes.

The presence of water molecules in the above mentioned complexes was ascertained by the appearance of bending vibra-

tion modes of the water molecules;  $\delta(OH_2)$ , found in the range 996–962 cm<sup>-1</sup>. The other bending vibration of the water molecules;  $\delta(OH_2)$ , is usually around 1600 cm<sup>-1</sup> which always interferes with the skeleton vibration of the benzene ring (C=C vibration).

The participation of the carboxylic group in chelation could be indicated from the changes of the bands of the asymmetric and symmetric stretching vibrations of the carboxylate group upon complex formation. The spectrum of sulfasalazine showed medium strong bands at 1625 and 1475 cm<sup>-1</sup> assigned for asymmetric and symmetric stretching vibrations of the carboxylate moiety, respectively. These two bands are either slightly shifted to lower frequencies ( $\approx 1600 \text{ cm}^{-1}$ ) or remained but decreased markedly in intensity. This indicates that the carboxylate group was participated in complex formation with the metal ions [18]. Participation of the phenolic and carboxylic OH groups is also confirmed by the appearance of new bands in the spectra of the complexes in the 472–439 cm<sup>-1</sup> regions which may be assigned to the  $\nu$ (M–O) stretching vibration [19].

The amino acid was found to be a bidentate ligand and bound to the central nickel ion through the carboxylic OH and the amino group. The  $\delta NH_3^+$  band, which is a characteristic for the zwitter ion, disappeared in the spectra of the complexes. This fact indicates that the NH<sub>2</sub> group must be involved in coordination. This is supported by the appearance of broad and split bands in the spectra of the complexes, in the regions 3429-3405 and  $3266-3200 \text{ cm}^{-1}$  (vNH<sub>2</sub>) as well as sharp bands in the region 1520–1516 cm<sup>-1</sup> (in-plane deformation;  $\delta NH_2$ ), assigned for the coordinated amino group [20-22]. The bands in the regions 1594–1586 and 1412–1408 cm<sup>-1</sup>, due to  $v_{asym}$  (COO<sup>-</sup>) and  $v_{sym}$  (COO<sup>-</sup>) of the amino acids appeared in the complexes at 1550-1540 and 1391-1389 cm<sup>-1</sup>. The shift of these two bands suggests the involvement of the carboxylic groups of the amino acids in complex formation [23,24]. Hence, the amino acid moiety is chelated to the metal ion through five-member ring. However, the lower values of the two carboxylic vibrations compared to those of the free ligand suggests that the carboxylic group interacts weakly with the metal ions.

#### 3.2. Magnetic susceptibility measurements

The magnetic moment values of the complexes are calculated and reported in Table 1. The tetra-coordinated nickel species in the [Ni(HSS)(AA)]·4H<sub>2</sub>O tris complexes has  $\mu_{eff}$  of 2.62–3.0 BM, which is close to the value of two unpaired electrons. This suggests that the complexes have a tetrahedral geometries with a slight orbital contribution to the magnetic moment [11].

#### 3.3. The electronic absorption spectra

The electronic absorption spectra of sulfasalazine displayed a broad band at 360 nm assigned to the  $n-\pi^*$  transition from the solvent to sulfasalazine moiety. This band was found to be shifted to higher wavelengths in the spectra of the binary (385 nm) and ternary complexes (395–405 nm). This may be related to the chromophoric groups (N=N, SO<sub>2</sub>) affected by

Compound	Color	F. Wt ( <i>m</i> / <i>e</i> )	$\mu_{\rm B}~({\rm BM})$	Molar conductivity	UV-vis <sup>a</sup>	%Found (calc.)			
				$(S \text{ cm}^2 \text{ mol}^{-1})$	λ <sub>max</sub> (nm)	C	Н	N	s
[Ni(HL)(ala)]-4H <sub>2</sub> O C <sub>21</sub> H <sub>27</sub> N <sub>5</sub> NiO <sub>11</sub> S	Red	615.48 (615)	2.62	32.0	395,405	40.89 (40.69)	4.38 (4.43)	13.35 (13.98)	5.19 (5.39)
[Ni(HL)(asp)].4H <sub>2</sub> O C <sub>22</sub> H <sub>27</sub> N <sub>5</sub> NiO <sub>13</sub> S	Orange red	659.49 (660)	2.79	28.1	400	39.38 (39.98)	4.55 (4.10)	11.90 (10.66)	4.7 (4.6)
[Ni(HL)(hist)].4H <sub>2</sub> O C <sub>24</sub> H <sub>29</sub> N <sub>7</sub> NiO <sub>11</sub> S	Orange red	681.54 (682)	3.00	16.9	401	39.40 (42.21)	4.59 (4.25)	14.05 (14.36)	5.62 (4.69)
[Ni(HL)(meth)].4H <sub>2</sub> O C <sub>23</sub> H <sub>31</sub> N <sub>5</sub> NiO <sub>11</sub> S <sub>2</sub>	Orange	675.60 (678)	2.92	23.2	405	39.18 (40.80)	4.58 (4.75)	10.62 (10.35)	9.05 (9.46)
$[Ni(HL)(ser)].4H_2O\ C_{21}H_{27}N_5NiO_{12}S$	Orange	631.48 (630)	3.0	31.1	402	38.52 (39.86)	4.60 (4.27)	10.76(11.07)	5.34 (5.07)
<sup>a</sup> $\lambda_{\text{max}}$ (SS) = 359.9 nm.									

Analytical data of the ternary complexes

Table 1

 Table 2

 Selected IR data for sulfasalazine and its binary and ternary complexes

Compound	$\nu(\mathrm{NH}_2)$	$\nu_{asym}$ (COO)	$\delta(\text{NH}_2)$	v <sub>sym</sub> (COO)	δ(CH)	$\nu$ (C—O) (phenolic)	$\gamma H_2 O$	ν( <b>M</b> -O)	ν(M-N)
SS	_	1625s	_	1427m	1393s	1281	_	_	_
Ni-SS	_	1600s	_	1420m	1386s	1266m	962w	611s	_
[Ni(HL)(ala)]·4H <sub>2</sub> O	3429s	1550m	1517m	13908m	1346m	1260m	964m	615m	578m
[Ni(HL)(asp)]·4H <sub>2</sub> O	3422s	1544m	1517m	1389m	1346m	1267m	978m	616m	577m
[Ni(HL)(hist)]·4H2O	3405s	1543m	1516m	1390m	1347m	1268m	996m	616m	578m
[Ni(HL)(meth)]·4H <sub>2</sub> O	3428s	1545m	1517m	1390m	1346m	1265m	990w	615m	578m
[Ni(HL)(ser)]·4H2O	3406s	1540s	1520m	1391m	1348m	1268m	993m	617m	580m



Fig. 1. TG and DTG data of [Ni(HSS)(meth)]·4H<sub>2</sub>O complex.

overall electronic environment change of sulfasalazine upon complex formation.

## 3.4. Thermogravimetric analysis

The thermogravimetric (TG) and the derivative thermogravimetric (DTG) plots of the complexes were represented in Fig. 1. The assignment of the different decomposition steps were given in Table 3. The decomposition schemes of the complexes can be approached as follows. [Ni(HSS)(ala)]·4H<sub>2</sub>O was thermally decomposed in five successive decomposition steps within the temperature range 304–783 K. The first decomposition step with an estimated mass loss of 11.70% (calc. mass = 72) within the temperature range 304–388 K, may be attributed to the liberation of the four hydrated water molecules. The second and third decomposition steps found within the temperature range 403–617 K with an estimated mass losses of 7.15 and 14.31% (calc. mass losses 44, 88), which are reasonably accounted for by the removal of one CO<sub>2</sub> and the alanine moieties, respectively. The rest

 Table 3

 Thermal analytical data for the ternary complexes

Molecular formula	Molecular weight	DTG <sub>max</sub> (°K)	Decomposition temperature (°C)	Mass loss (%)	Mol. mass found (Calc.)	Eliminated species	Solid residue (%)
[Ni(HL)(ala)]·4H2O	615.48	343	304-388	11.27	72.00	4H <sub>2</sub> O	
C <sub>21</sub> H <sub>27</sub> N <sub>5</sub> NiO <sub>11</sub> S		470	403-524	7.18	44.02	$CO_2$	
		580	530-617	14.56	88.12	C <sub>3</sub> H <sub>6</sub> NO <sub>2</sub>	
		668	622-735	23.08	142.18	C <sub>5</sub> H <sub>4</sub> NSO <sub>2</sub>	
		750	733–783		209.08	C12H9N3	NiO (12.03)
[Ni(HL)(asp)]·4H <sub>2</sub> O	659.49	340	310-381	12.47	76.84	$4H_2O$	
C22H27N5NiO13S		573	400-570	13.25	81.65	$CO_2$	
		631	570–647	56.53	348.38	$(C_{17}H_{13}N_4O_3S + C_4H_7NO_4)$	NiO (11.22)
[Ni(HL)(hist)]·4H2O	681.54	347	306-386	13.25	81.65	$4H_2O$	
C24H29N7NiO11S		568	400-570	11.75	72.40	$CO_2$	
		628	570–647	57.98	357.27	$(C_{17}H_{13}N_4O_3S+C_6H_8N_3O_2)\\$	NiO (10.86)
[Ni(HL)(meth)]·4H <sub>2</sub> O	675.60	337	313-402	12.75	78.57	$4H_2O$	
C23H31N5NiO11S2		582	404-559	11.75	72.40	$CO_2$	
		623	557-675	56.09	345.63	$(C_{17}H_{13}N_4O_3S + C_5H_{11}NO_2S)$	NiO (10.93)
[Ni(HL)(ser)]·4H2O	631.48	340	310-378	12.50	77.025	4H <sub>2</sub> O	
C21H27N5NiO12S		559	386-561	10.75	66.24	$CO_2$	
		632	563-686	55.01	338.97	$(C_{17}H_{13}N_4O_3S + C_3H_7NO_3)$	NiO (11.72)





Scheme 4. Decomposition of [Ni(HSS)(meth)]·4H2O.

of sulfasalazine molecule was removed on the fourth and fifth steps within the temperature range 622-783 K (calc. mass losses = 142, 195). The decomposition of the ligand molecule ended with a final oxide residue of NiO (12.11%, mass = 74)(Scheme 3).

[Ni(HSS)(meth)]·4H<sub>2</sub>O decomposed in three steps within the temperature range 313-675 K. The first decomposition step, observed within the temperature range 304-388 K, with an estimated mass loss of 10.64% (calc. mass = 72) may be attributed to the liberation of the four hydrated water molecules. The second decomposition step associated with the removal of CO<sub>2</sub> moiety was observed in the temperature range 404-559 K with an estimated mass loss of 6.50% (calc. mass = 44). The third step observed in the temperature range 563-686 K with an estimated mass loss of 69.91% (calc. masses = 337 + 104) which was assigned to the removal of the sulfasalazine and amino acid moieties. The mass of the metallic residue remained at the end of the decomposition was 11.72% (calc. mass = 74) which was assigned for NiO (Scheme 4). The other ternary complexes have the same decomposition scheme of  $[Ni(HSS)(meth)] \cdot 4H_2O.$ 

#### 3.5. XRD analysis

The metallic residue for all complexes obtained at 800 °C were grounded and subjected to XRD analysis. All metallic residues had the same diffraction pattern (Fig. 2), which indicates that they reach the same metallic moiety at high temperature. The XRD data are listed in Table 4. It is clear from the data that the final decomposition product of all complexes was

Table 4	
Comparison of the X-ray powder diffraction data of Ni metallic residue	

Angle 2θ	Observed		Reference <sup>a</sup>		
	d-Value (Å)	I/Io	d-Value (Å)	I/Io	$\overline{\Delta d}(\text{\AA})^{b}$
36.75	2.44	49.3	2.41	91	0.03
42.81	2.11	100	2.09	100	0.03
62.45	1.48	76.7	1.48	57	0.00
74.98	1.26	33.0	1.26	16	0.00
78.97	1.211	24.4	1.21	13	0.00

<sup>a</sup> JCPDS-ICDD 4-835.

<sup>b</sup>  $\Delta d = d_{\text{obsd.}} - d_{\text{ref.}}$ 



Fig. 2. XRD powder diffractogram of the metallic residue of the complexes.



Scheme 5. The proposed structure of [Ni(HSS)(AA)]·4H<sub>2</sub>O ternary complexes.

NiO whose XRD data matches the reference for nickel oxide (JCPDS-ICDD 4-835). This conclusion is consistent with the results of the TG analysis.

#### 3.6. Conclusion

As a general conclusion, the sulfasalazine participated in bonding to nickel as monobasic bidentate (OO) ligand and the amino acids as monobasic bidentate (NO) ligand with a total of four coordination sites around the metal ion whose charges are neutralized by the deprotonation of the sulfasalazine and the amino acid carboxylates. The non-electrolytic nature of the complexes was evidenced from the low values of the molar conductance of the complexes. The elemental analysis suggested the presence of four water molecules, which is evidenced, from the thermal analysis to be hydrated water. All the tetra-coordinated nickel ( $d^8$  configuration) complexes have net magnetic values, which suggest a tetrahedral geometry (Scheme 5).

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