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Wafaa M. Hosny [a]

[a] Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt

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COMPLEXES OF SULPHADIAMIDINE. PART II. EQUILIBRIUM AND THERMODYNAMIC STUDIES OF IRON(II) AND IRON(III) WITH SULPHADIAMIDINE

Wafaa M. Hosny

Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt

ABSTRACT

Binary complexes of 4-amino-N-(2,6-dimethyl-4-pyrimidinyl)benzensulfonamide (sulphadiamidine) (HL) with Fe(II) and Fe(III) were studied at an ionic strength of 0.1 M KNO_3 and at 25° C. The formation constants of these binary complexes were determined using the MINIQUAD program. The solid complexes were prepared and characterized by elemental analyses, electrolytic conductance, electronic, IR, mass spectra and thermogravimetric (TG, DTG and DTA) measurements. The ligand forms 1:2 complexes (metal:ligand). An octahedral geometry is suggested for the complexes where two coordination sites are occupied by two water molecules or one chloride ion and a water molecule, $[ML_2(H_2O)_nCl_m]$, where M = Fe(II) (n = 2, m = 0) or Fe(III) (n = 1, m = 1) and HL = sulphadiamidine.

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INTRODUCTION

It has been widely accepted that iron plays an important role in metabolisms. More specifically, its deficiency and oversupply cause serious diseases[1,2]. Natural iron-carrier compounds termed siderophores have been known to transport iron by making use of a mutual transformation between the more stable iron(III) and the less stable iron(II) complexes. In the present work the stability constants of Fe(II) and Fe(III) with HL have been determined in EtOH-water mixture using the MINIQUAD program. Conductometric titrations were carried out to obtain further information concerning the stoichiometry of the complexes in solution. IR, electronic, molar conductance, magentic susceptibility and thermal studies of Fe(II) and Fe(III) with HL were performed to elucidate their structures.

EXPERIMENTAL

Solutions of Fe(II) and Fe(III) were prepared from the following analytical grade salts: iron(II) sulphate and iron(III) chloride. All solutions were standardized by standard procedures[3]. Sulphadiamidine (HL) was obtained from E. Merck and is represented by the structure in Fig. 1.

A 0.01 M stock solution of HL was prepared by dissolving an equivalent amount in 25 mL 0.10 M HNO_3; two mixtures were prepared as previously described[4] and titrated potentiometrically against standard 0.0964 M sodium hydroxide solution at 25° C using a Metrohm 686 titroprocessor (Switzerland) equipped with a 665 Dosimat. The electrode and the titroprocessor were calibrated with standard buffer solutions prepared according to NBS specifications[5]. This potientiometric study has been carried out in an ethanol-water mixture (50% v/v). The pH values recorded in $EtOH\text{-}H_2O$ solution were calculated using the equation given by Uitert and Hass[6]. The equilibrium constants of Fe(II) and Fe(III) complexes were evaluated from titration data. These are defined by eqs (1) and (2),

$$p(M) + q(L) + r(H) \rightleftharpoons (M)_p(L)_q(H)_r \qquad (1)$$

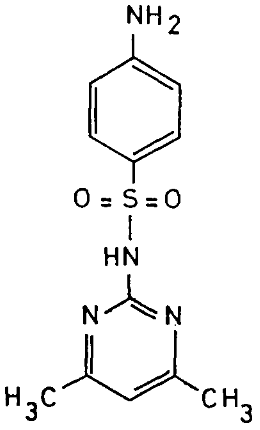


Fig. 1. Structure of HL

$$\beta_{pqr} = \frac{[(M)_p(L)_q(H)_r]}{[M]^p[L]^q[H]^r} \qquad (2)$$

where p, q and r are the stoichiometric coefficients corresponding to Fe(II) or Fe(III), H_2L^+ and H^+, respectively, and M, L and H stand for metal, ligand and protons, respectively. To calculate equilibrium constants of binary complexes, H_2L^+ with Fe(II) or Fe(III) from eq (2) the values of these constants are found in Table II. For Fe(II) they equal 5.25, 1.32 (with p, q and r being 1, 1, 0 or 1, 1, -1). Thus, Fe(II) forms with H_2L^+ binary complexes in the mole ratio 1 : 1, $[FeL]^+$ and a hydroxy complex FeL(OH)], respectively. It is clear from Table II, that the binary complexes between Fe(III) and H_2L^+ for which the equilibrium constants equal 8.46, 0.81 (with p, q and r being 1, 1, 0 or 1, 1, -1), are more stable than that between Fe(II) and H_2L^+. The calculation of the equilibrium constants were carried out using the computer program[7] MINIQUAD-75 and were conducted on an IBM computer. Conductimetric titrations of 40 mL alcohol-water solutions containing the same concentration of H_2L^+, Fe(II) and Fe(III) (5×10^{-4} M) against 0.0964 M NaOH were carried out using a WTW conductivity bridge, model LBR. The separated solids were subjected to elemental analyses, IR, mass spectroscopy, molar conductance, magnetic susceptibility, electronic spectra,TGA and DTA measurements.

The IR spectra of HL and its complexes were recorded as KBr pellets on a Perkin-Elmer 1430 spectrophotometer. Electronic spectra were taken by a Shimadzu UV-160 A spectrophotometer. Mass spectra were recorded on a Hewlett-Packard model MS-5988. The mass spectra were carried out at 220°C and 70 eV. The magnetic susceptibility of the solid complexes were measured at room temperature by the Gouy method using a Johnson Matthey Alfa products, UK, model MKI, magnetic susceptibility balance. Differential thermal analysis (DTA) and thermogravimetric analysis (TG and DTG) were recorded using computerized Shimadzu DTA-50 and Shimadzu TGA-50H instruments in platinum crucibles with a scanning rate of 20^0 C min^{-1} in nitrogen atmosphere.

Synthesis of the Complexes

Both iron complexes were prepared in the ratio of 1:2 (metal ion : ligand) as follows: The corresponding iron salt (1 mmol) dissolved in 10 mL of ethanol was added to HL (0.01 g, 2 mmol) dissolved in aqueous sodium hydroxide solution (20 mL, 2 mmol). The reaction mixture was refluxed on a water bath for 3 h and then concentrated to 1/3 of its volume. On cooling, the crystals of the complexes formed which were filtered, washed with ethanol and dried in a vacuum desiccator over P_4O_{10}, the yields are 70% -75%. The analytical data are listed in Table I.

RESULTS AND DISCUSSION

The protonation constants pK_a of HL were obtained previously[4]. The equilibrium constants of the Fe(II) and Fe(III) complexes were determined, and Table II lists the equilibrium constants together with their standard deviation and the sum of the square of the residuals as obtained from the program[7] MINIQUAD-75. From the potentiometric titration and conductometric curves, Fe(II) and Fe(III) complexes are formed

Table I. Analytical Data and Physical Properties of the HL[a] Complexes

Complex	Mass (molecular ion) m /z (calc.)	Colour	Yield %	Dec. Point °C	Analyses %: Found (Calculated) C	H	N	M	Cl	Λ $ohm^{-1}.cm^2.mol^{-1}$	$\mu_{eff.}$ B.M.
1. $FeL_2.2H_2O$ $[C_{24}H_{30}N_8O_6S_2Fe]$	645 (646)	Pale gray	70	170.5	44.4 (44.6)	4.8 (4.6)	17.0 (17.3)	8.8 (8.7)	----	8.0	5.8
2. $FeL_2Cl.H_2O$ $[C_{24}H_{28}N_8O_5S_2ClFe]$	663 (663.5)	Pale brown	75	190	43.4 (43.4)	4.4 (4.2)	16.8 (16.9)	8.7 (8.4)	5.2 (5.4)	11.0	1.8

[a] HL = Sulphadiamidine

Table II. Formation Constants of the Metal Complexes of H_2L^+

Complex	p	q	r[a]	Logβ[b]	N[c]	S[d]
H_2L^+	0	1	1	8.67(0.01)[e]	52	3.8E-9
	0	1	2	11.45(0.02)		
$[Fe(II)L]^+$	1	1	0	5.25(0.02)	48	3.2E-8
	1	1	-1	-1.32(0.05)		
[Fe(III)L]	1	1	0	8.46(0.01)	55	5.1E-8
	1	1	-1	-0.81(0.05)		

[a] p, q and r are the stoichiometric coefficients corresponding to metal ion, ligand and H^+, respectively; [b] Standard deviations are given in parentheses; [c] Number of data points; [d] Sum of square of residuals; [e] reference 4.

through the neutralization of the NH group and the formation of 1:1 species, $[Fe(L)]^+$ and [Fe(L)], for Fe(II) and Fe(III), respectively, where $[H_2L]^+$ = sulphadiamidine which in acid medium behaves as a diprotic acid.

Infrared Spectra

The main IR bands for HL and its metal complexes were given in Table III. The HL spectrum displays a sharp, medium intensity stretching band at 3400 cm^{-1} (Fig. 2) attributed to $\nu(NH_2)$ in which is shifted to higher energy in the metal complexes. This together with a weak band at 1600 cm^{-1} is due to δ(NH). Also, the HL spectrum exhibits a strong band at 1080 cm^{-1} as a result of the C-N deformation[8,9]. The latter band disappears upon complex formation. This result is in support of the formation of the six-membered chelate ring involving the O=S-N=C-N group. The strong band of $\nu(SO_2)$ at 1350 cm^{-1} undergoes a bathochromic shift in the spectra of the complexes, indicating a change in the

Table III. Fundamental IR Bands (cm^{-1}) for the Ligand (HL) and its Metal Complexes

Complex	$\nu(NH_2)$	$\delta(NH_2)$	$\nu(NH)$	$\nu(SO_2)$	$\nu(M-O)$	$\nu(M-N)$	$\nu(M-Cl)$
HL	3400 (br)	1600	3100 (w)	1350 (s)	----	----	----
$FeL_2.2H_2O$	3440	1640 (br)	----	1330	440 (s)	540 (w)	----
$FeL_2Cl.H_2O$	3420	1680 (m)	----	1310 (w)	455	505	290 (w)

s: strong; m: medium; w: weak; br: broad

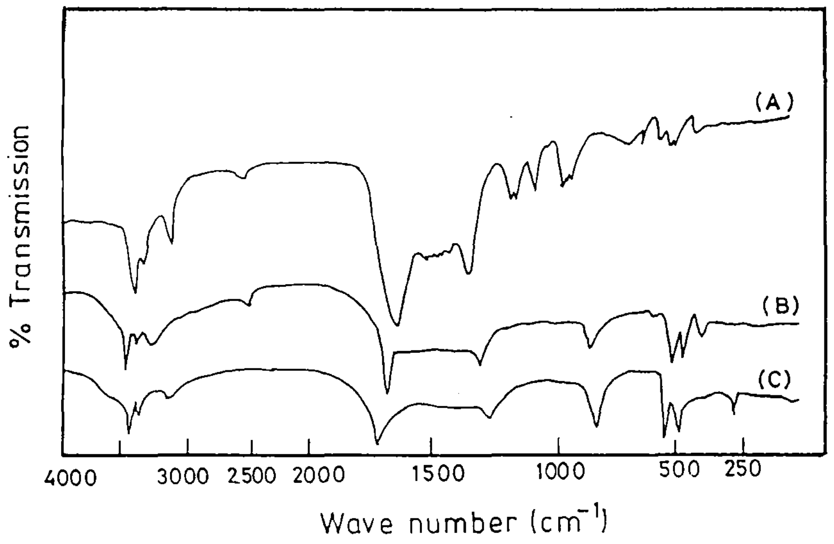


Fig. 2. Infrared Spectra of HL complexes: (A) HL; (B) Fe(II)L_2 x $2H_2O$; (C) Fe(III)L_2Cl x H_2O

bond order and strong electron delocalization on the oxygen atom, suggesting coordination of SO_2. The ν(OH) stretching vibration of coordinated water of the complexes appears in the region[10] 3140-3240 cm^{-1}. New bands around 440-480, 540-580 and 290 cm^{-1} are seen in the spectra of the complexes which are assigned[11-13] to ν(M-O), ν(M-N) and ν(M-Cl), respectively.

Molar Conductivity

The molar conductivity values in 1x10 $^{-3}$ M DMF solutions of the solid complexes measured for 1:2 (M:L) solutions are quite low and are in the range 6.0-9.2 ohm^{-1} cm^{2} mol^{-1}, which indicates the non-electrolytic nature of these complexes.

Magnetic Studies

For octahedral Fe(II) coordination complexes, where the orbital contribution should be appreciable, the magnetic moment of such complexes [14] is 5.6 BM. Based on this reasoning, the Fe(II)-HL complex is assumed to be octahedral with a magnetic moment of 5.8 BM.

The room temperature magnetic moment of the iron(III)-HL complex (1.8 BM) is of the low-spin type but is higher than the value expected for temperature independent paramagnetism. The magnetic moment variation with temperature (Table IV) shows that, at low temperature, the ground state is ^2T but with increasing temperature up to 390K, the ^6A state becomes populated[15,16].

Electronic Spectra

The electronic spectrum of the iron(II) complex exhibit a weak intensity band in the 11,600-11,700 cm^{-1} region, which may reasonably be assigned to the $^5T_{2g}$-^5E_g transition, consistent[17] with an octahedral geometry around the iron(II) ion. The magnetic moment value further confirms the above proposed geometry. Strikingly, all the complexes exhibit strong absorption around 30,000 cm^{-1}, which may be due to a charge transfer band.

The absorption bands of the iron(III) complex appear at 20,000 cm^{-1}, corresponding to a ligand-to-metal $T_{2g} \leftarrow \pi$ charge transfer (CT) band from the lower energy side[18]. The addition of Cl^- (LiCl) to the solution resulted in a shift of about 500 cm^{-1} toward lower wave numbers. In addition to shifting of the bands as above, the presence of Cl^- yields a new band at about 20,580 cm^{-1} which indicates the change in electronic structure[19] caused by the introduction of another Cl^- into coordination with the iron(III).

Thermal Analysis

The purposed of this study is to reveal the stability of the complexes on thermal decomposition, as well as to obtain different final products that may lose novel catalytic properties. Table V lists the steps, the initial and final temperatures (^{0}C), partial and total weight losses (%), enthalpy (endothermic or exothermic) and peak

Table IV. Variation of the Magnetic Moment of $FeL_2Cl.H_2O$ with Temperature

T(K)	240.0	255.5	273.0	295.0	310.5
μ_B(BM)	1.42	1.45	1.60	1.70	1.90
T(K)	325.0	340.0	360.5	380.0	390
μ_B(BM)	2.10	3.21	4.02	5.12	5.22

Table V. Thermal Analysis Data for Fe(II) and Fe(III) Complexes

Complex	Step	T_i (^{0}C)	T_f (^{0}C)	T_m[a] (^{0}C)	Δm[b] (%)
$FeL_2.2H_2O$	1[c]	110	156		5.6
	2	156	179.5	170.5 (-)	1.9
	3[c]	179.5	229.5		0.9
	4[c]	229.5	335.5		7.8
	5	335.5	429.5	400 (+)	28.9
	6[c]	429.5	555.5		23.3
	7[c]	555.5	600		31.0 (99.4)
$FeL_2Cl.H_2O$	1[c]	105	150		2.7
	2[c]	150	291.5		2.3
	3[c]	291.5	310		20
	4	310	350	312 (+)	21
	5[c]	350	430		14
	6	430	510	470 (+)	17.3
	7[c]	400	600		19.3 (96.6)

T_i = Initial temperature. T_f = Final temperature.

T_m = Temperature of peak maximum. [a]Endothermic (-) or exothermic (+) process.

[b]Total mass losses are shown in parentheses.

[c]Progressive mass loss without clear peaks in DTG and/or DTA curves.

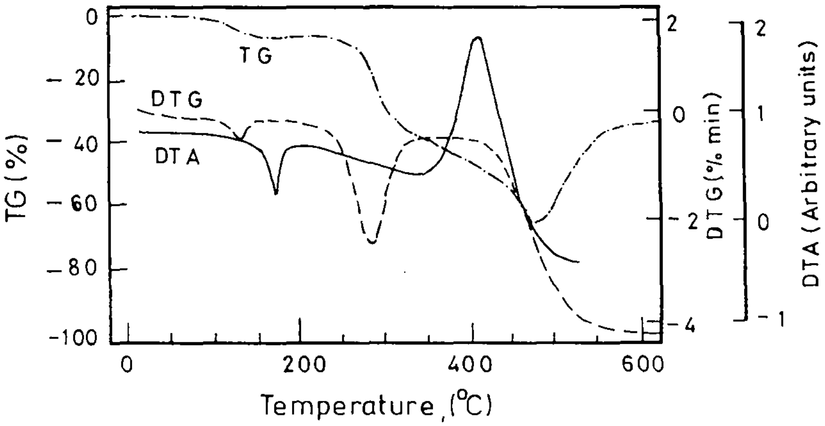


Fig. 3. Thermograms of Fe(II)L_2 x $2H_2O$

maxima for each step in the thermal decompositions of the two compounds in nitrogen atmosphere. The TG-DTG-DTA curves for the compounds under nitrogen atmosphere are shown in Figs. 3 and 4. The thermal processes and the final residues are strongly influenced by the atmosphere and the starting compound[20,21]. The thermogravimetric curves indicate that the decomposition processes are not simple, since most of the stages overlap. The final products were identified by elemental analyses and mass spectroscopy.

The thermogravimetric curve indicates that the Fe(II) complex is stable up to 110-156^0 C beyond which weight loss of 5.6% takes place, corresponding to loss of two water molecules. Between 156 and 179.5^0 C an endothermic peak, centered at 170.5^0 C in the DTA curve, is seen corresponding to melting point of the Fe(II) complex. Between 179.5 and 229.5^0 C, two progressive overlapping mass losses occur, followed by a strong exothermic peak centered at 400^0 C in the DTA curve. The great diversity of possible products prevents exhaustive interpretation of these last degradation processes, however, they could be due to the reordering of the inorganic residues obtained after the breakdown of the pyrimidinyl during the exothermic step. The solid residue at 600^0 C was identified[22] as Fe_2O_3.

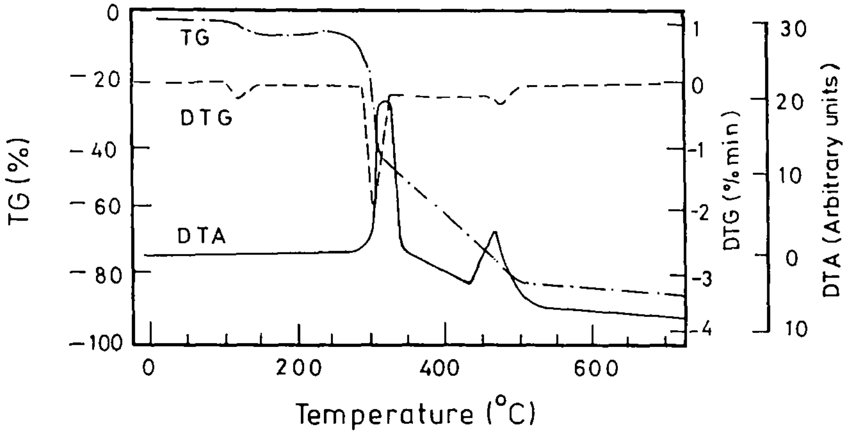
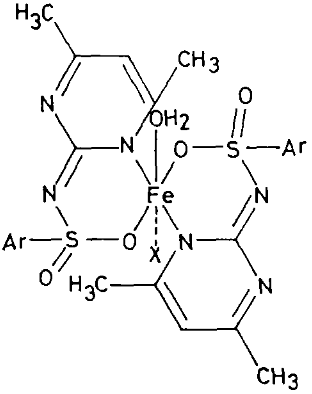


Fig. 4. Thermograms of Fe(III)L$_2$Cl x H$_2$O



X = H_2O for the Fe(II) Complex; X = Cl for the Fe(III) Complex and Ar = 4-$NH_2C_6H_4$ ·

Fig. 5. Suggested Structures of the HL Complexes

The thermal decomposition of the Fe(III) complex starts at 105 to 150^0 C with a weight loss of 2.7% corresponding to loss of one water molecule, followed by two progressive mass losses in the ranges 150-291.5^0 C and 291.5-310^0 C, followed by two exothermic peaks centered at 312^0 C and 470^0 C in the DTA curve. The solid residue[23] at 600^0 C was Fe_2O_3, which was identified by elemental analysis, IR and mass spectroscopy.

Due to the magnetic moment of these complexes, NMR studies could not be done. Based on previous studies[4], the most probable structures for these complexes may be represented in Fig. 5.

REFERENCES

1. C. Chimiak, R. C. Hider, A. Lui, J. B. Neilands, K. Nomato and Y. Sugiura, "Siderophores from Microorganisms and Plants", Springer, Berlin (1984).
2. T. Ozawa, K. Iwai, K. Jistukawa, H. Masuda and H. Einaga, Polyhedron, 13, 1523 (1994).
3. F. J. Welcher, "The Analytical Uses of Ethylenediaminetetraacetic Acid", 4th Edn., Van Nostrand, Princeton (1965).
4. W. M. Hosny, Syn. React. Inorg. Met.-Org.Chem., 27, 197 (1997).
5. R. C. Bates, "Determination of pH-Theory and Practice", 2nd. Edn., Wiley Interscience, New York (1975).
6. L. G. Van Uitert and C. G. Hass, J. Amer. Chem. Soc., 75, 451 (1983).
7. P. Gans, A. Sabatini and A. Vacca, Inorg. Chim. Acta, 18, 237 (1976).
8. C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon, London (1965).
9. A. El-Dissouky, A. Kasem. and A. El-Sonbati, Transition Met. Chem., 12, 500 (1987).
10. N. Ohkahu and K. Nakamoto, Inorg. Chem., 10, 798 (1971).
11. W. Brzyska, Z. Rzaczyska and A. Kula, Montsh. Chem., 120, 211 (1989).
12. W. M. Hosny, A. H. Basta and H. El-Saied, Polym. Int., 42, 157, (1997).

13. Z. Jawarska, C. Jose and J. Urbanski, Spectrochim. Acta, 30A, 1161 (1974).

14. F. A. Cotten, G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, p. 857 (1966).

15. A. El-Dissouky and A. Z. El-Sonbati, Synth. React. Inorg. Met.-Org. Chem., 16, 1035 (1986).

16. B. N. Figgis and J. Lewis, Prog. Inorg. Chem., 6, 37 (1964).

17. A. B. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam (1984).

18. H.Kuna, K. Okamoto, J. Hidak and H. Einaga, Bull. Chem. Soc. Japan, 62, 2824 (1989).

19. V. M. Leovac, L. S. Jovanovic, V. B. Arion and N. V. Gerbeleu, Polyhedron, 13, 3005 (1994).

20. P. Roman, J. I. Beitia, A. Luque and C. Guzman-Miralles, Polyhedron, 14, 1091 (1995).

21. P. Roman, J. I. Beitia and A. Luque, Polyhedron, 12, 2831 (1993).

22. D. Broadbent, D. Dailimore and J. Dollimore, J. Chem. Soc.(A), 451 (1980).

23. T. K. Sanyal and N. N. Dass. J. Nucl. Chem., 42,811 (1993).

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Referee II: D. J. Casadonte, Jr.