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Synthesis and Characterization of High-Spin Iron(III)-Sulpha Drug Complexes and Their Biological Activity

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Summary. The iron(III) complexes with sulphathiazole, sulphamethoxazole, sulphadiazine, sulphapyridine and sulphadimidine having the stoichiometric ratio 1 : 2 (metal : ligand) were prepared and characterized on the basis of elemental analysis, conductivity measurements and electronic absorption spectra. The infrared spectra of the complexes revealed that the terminal amino group of the sulpha molecules is not involved in coordination. Similarities in the position of iron-nitrogen and iron-oxygen stretching modes indicate identical configuration of the complexes prepared. Conductivity measurements showed that they are nonelectrolytes. X-ray powder diffraction patterns showed that two of them are crystalline and others are amorphous. Electron spin resonance and iron-57 Mössbauer measurements indicated that the complexes contain high-spin Fe^{3+} species. Thermogravimetric analyses showed that all complexes contain coordinated water which is lost at 141 – 160°C. All the complexes proved to possess higher bacteriostatic activity than the corresponding ligand.

Keywords. Sulpha drugs; Iron(III) complexes; X-ray; Thermogravimetry; Antibacterial.

Synthese und Charakterisierung von High-Spin Eisen(III)-Sulfapräparate-Komplexen und ihre biologische Aktivität

Zusammenfassung. Es wurden die (Metall : Ligand) 1 : 2 Eisen(III)-Komplexe von Sulfathiazol, Sulfamethoxazol, Sulfapyridin und Sulfadimidin hergestellt und mittels Elementaranalyse, Leitfähigkeitsmessungen und Elektronenabsorptionsspektroskopie charakterisiert. Die IR-Spektren der Komplexe zeigten, daß die Amino-Gruppen der Sulfa-Moleküle nicht an der Koordination beteiligt sind. Ähnlichkeiten im Bereich der Eisen-Stickstoff- und Eisen-Sauerstoff-Streckschwingungen zeigten idente Konfiguration der Komplexe an. Leitfähigkeitsmessungen beweisen den Nichtelektrolytcharakter. Röntgen-Pulverdiagramme zeigten, daß zwei der Komplexe kristallin, die anderen hingegen amorph waren. High-Spin Eisen(III)-Spezies wurden mittels Elektrononspinresonanz und Eisen-57-Mössbauer-Messungen nachgewiesen. Die thermogravimetrische Analyse zeigte, daß alle Komplexe koordiniertes Wasser enthielten, das zwischen 141 und 160 °C verloren wurde. Alle Komplexe zeigten eine höhere bakteriostatische Aktivität als die entsprechenden Liganden allein.

Introduction

Sulpha drugs are well known as antibacterial agents [1 – 6]. Recent studies proved that when bioorganic molecules are introduced as transition metal chelates they have increased activites and more therapeutic importance [7 – 11].

Iron among transition metals is being considered the most important one with a functional role in living systems, e.g. proteins containing iron participate in oxygen transport and electron transfer processes [12, 13]. Iron itself is stored or released by various tissues such as hemosiderin and ferritin [14]. On the other hand, iron deficiency in the blood causes anemia. Antibacterial properties of oxine-iron complex are also reported and it was found that the complex is more antibacterially potent than oxine [7, 15]. The current status of iron chelation therapy seems to be crucial and needs more investigation [16]. Stability constants of Cu(II), Zn(II), Ni(II), Co(II), and Mn(II) complexes of sulphapyridine, sulphadimethoxine, sulphamethoxypyridazine and sulphaphenazole have been determined by Lal [17], however, no data are available on the Fe(III)-sulpha complexes and their antibacterial properties. Accordingly, the present work involves preparation, characterization and antibacterial activity of Fe(III) 1 : 2 chelates with sulphathiazole, sulphamethaxazole, sulphadiazine, sulphapyridine, and sulphadimidine.

Experimental

Samples of sulpha drugs were obtained from SID Pham. Co. Assiut. All the other chemicals used were of BDH grade. Due to hydrolysis of ferric chloride and consequently difficult accurate weighing, a stock solution of ferric chloride was prepared by dissolving about ten grams in 100 ml absolute ethanol and the accurate concentration of iron(III) was determined [18]. To an ethanolic solution of 0.004 mol sulpha compound was added 0.002 mol of ferric chloride. The reaction mixture was refluxed about 4 – 8 h, the volume was reduced to 35 ml and left to cool at room temperature. The product was filtered off, washed with ether and then dried in vacuo.

Elemental analyses for C, H, N were carried out using a Perkin-Elmer 240 C instrument. The chlorine content was determined in the microanalytical laboratory of the department. The iron content was determined according to [18].

Electronic absorption spectra were optained by a Schimadzu double beam UV-200 S spectrophotometer with 1 cm matched silica cells in the range of 200 – 850 nm. Infrared absorption spectra were recorded with a Perkin-Elmer 599 B spectrophotometer as KBr pellets in the region between 4000 and 200 cm^{-1}. Conductivity measurements of 10^{-3} M dimethylformamide solutions of the complexes were carried out using a Consort 925 K digital conductance bridge with a cell constant 0.96 cm. X-ray powder diffraction patterns were obtained by a Philips 1 710 diffractometer, the patterns run with copper as target and nickel filtered ($\lambda = 1.54178$ Å) at 40 KV and 30 mA. The scanning speed was 3.6 deg min^{-1} in the range of $2\theta = 5 - 60°$. Electron spin resonance measurements were made on a Joel, Jes FE2XG X-band spectrometer with 100 KH_z field modulation and a TM_{110} cavity at room temperature (Tanta University, Egypt). Iron-57 Mössbauer spectra were collected on an Austin Science Associates acceleration drive spectrometer with a fly back mode. Isomer shifts are referenced to iron foil at room temperature. Thermogravimetric analyses (TGA and DTA) of the complexes were carried out by a Du Pont 1 090 thermal analyzer in static air over a temperature range 20 – 700°C and a heating rate of 10 deg min^{-1}.

The bacteriostatic activity of sulpha drugs and their iron(III) chelates was evaluated against *Esch. coli*, *Staph. aureus* and *Prot. mirabilis* using the agar-cup diffusion technique [19]. Stock solutions (1 mg/ml) of compounds were prepared in dimethylformamide. The solvent was used for further dilutions and tested as blank experiments.

Fe(sulphathiazolyl)$_2$ClH$_2$O. This complex (**1**) was prepared as brown fine crystals, decomposition temperature 240°C. Anal. calcd for $C_{18}H_{18}N_6FeO5Cl$: C 34.98, H 2.93, N 13.59, Cl 5.74, Fe 9.04; found: C 34.90, H 2.85, N 13.35, Cl 5.70, Fe 8.98.

Fe(sulphamethoxazolyl)$_2$ClH$_2$O (**2**). Pale brown powder, decomposition temperature 235°C. Anal. calcd for $C_{20}H_{22}N_6S_2FeO_7Cl$: C 39.13, H 3.61, N 13.69, Cl 5.77, Fe 9.09; found: C 39.60, H 3.43, N 13.77, Cl 5.96, Fe 9.17.

Fe(sulphadiazinyl)$_2$ClH$_2$O (**3**). Dark brown needle crystals, decomposition temperature 242°C. Anal. calcd for $C_{22}H_{22}N_6S_2FeO_5Cl$: C 43.61, H 3.65, N 13.87, Cl 5.85, Fe 9.21; found: C 43.41, H 3.71, N 13.99, Cl 6.01, Fe 9.05.

Fe(sulphapyridinyl)$_2$ClH$_2$O (**4**). Dark brown powder, decomposition temperature 252°C. Anal. calcd for $C_{20}H_{20}N_8S_2FeO_5Cl$: C 39.52, H 3.31, N 18.43, Cl 5.83, Fe 9.18; found: C 39.77, H 3.45, N 18.19, Cl 5.96, Fe 9.32.

Fe(sulphadimidinyl)$_2$ClH$_2$O (**5**). Red-brown powder, decomposition temperature 250°C. Anal. calcd for $C_{24}H_{28}N_8S_2FeO_5Cl$: C 43.41, H 4.24, N 16.87, Cl 5.34, Fe 8.41; found: C 43.60, H 4.29, N 17.03, Cl 5.18, Fe 8.66.

Results and Discussion

Five complexes of iron(III) with sulpha compounds were prepared having the molar ratio 1 : 2. Coordination takes place through the enolic oxygen of the SO_2 group and either oxygen or nitrogen of the heterocyclic ring as shown in Fig. 1.

Molar Conductance

The values of 10^{-3} *M* solutions of the complexes **1**–**5** in dimethylformamide, as shown in Table 1, are in the range $11.0-23.4\,\Omega^{-1}\,mol^{-1}\,cm^2$. These values indicate that the complexes are nonelectrolytes and the chlorine atom is inside the coordination sphere. Higher molar conductance values are due to the solvent molecules which act as a ligand [20].

Electronic Absorption Spectra

The electronic spectra were obtained for iron(III) complexes with different concentrations ($10^{-3}-10^{-5}$ *M*) and recorded in the range 200–850 nm. They are similar as a result of identical chemical structure. The electronic absorption spectra of the Fe(III)-sulphadiazine complex shown in Fig. 2 exhibit three shoulders at 625, 560, and 500 nm with molar absorbitivities 48, 133, and 3351 $mol^{-1}\,cm^{-1}$, respectively. The absorption shoulder appearing at 630 nm gives an evidence for the presence of a chlorine ligand coordinated to one iron(III) atom [18]. The two shoulders appearing at 560 and 500 nm are assigned to $^4T_{2g}\leftarrow{}^6A_{1g}$ and ^4E_g,

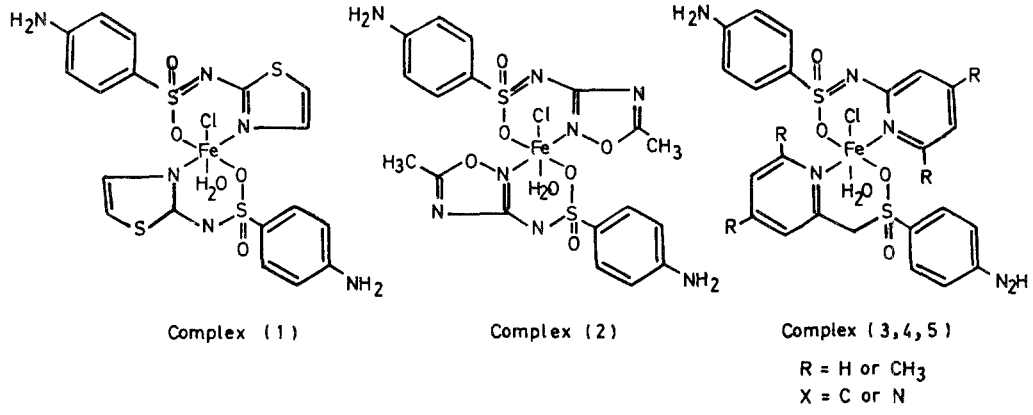

Fig. 1. Possible structure for the Fe(III) sulpha drug complexes **1**–**5**

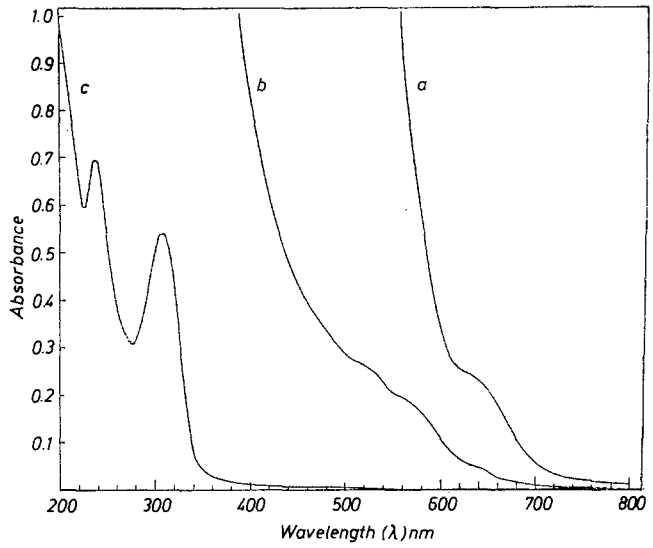

Fig. 2. Electronic absorption spectra of the Fe(III)-sulphadiazine complex run in *DMF*. (*a*) $4.60 \cdot 10^{-3} M$; (*b*) $1.12 \cdot 10^{-3} M$; (*c*) $1.03 \cdot 10^{-5} M$

$^4A_{1g} \leftarrow {}^2A_{1g}$ respectively. The two shoulders occur on a broad CT band and hence have comparatively higher intensities [21, 22]. The spectra show also two bands appearing at 320 nm ($\varepsilon = 2\,000$) and 278 ($\varepsilon = 3\,100$), which are due to charge transfer and $\pi - \pi^*$ transitions, respectively [23]. The data obtained are given in Table 1.

X-Ray Diffraction Data

The X-ray diffraction patterns of complexes **1**–**5** have been investigated and revealed that the complexes of sulphathiazole and sulphadiazine (**1**, **3**) are crystalline,

Table 1. Electronic absorption data and molar conductance

Complex	λ_{max} (nm)	ε ($1\,cm^{-1}\,mol^{-1}$)	Molar cond. ($\Omega^{-1}\,cm^2\,mol^{-1}$)
1	625 sh	45	11.0
	560 sh, 500 sh	125, 330	
	320, 270	2 000, 3 100	
2	620 sh	50	11.0
	560 sh, 500 sh	130, 340	
	320, 275	2 000, 3 200	
3	625 sh	48	12.5
	565 sh, 500 sh	133, 335	
	320, 275	2 000, 3 100	
4	630 sh	50	23.4
	560 sh, 500 sh	140, 340	
	320, 278	2 100, 3 150	
5	625 sh	52	20.5
	560 sh, 500 sh	142, 345	
	320, 274	2 150, 3 200	

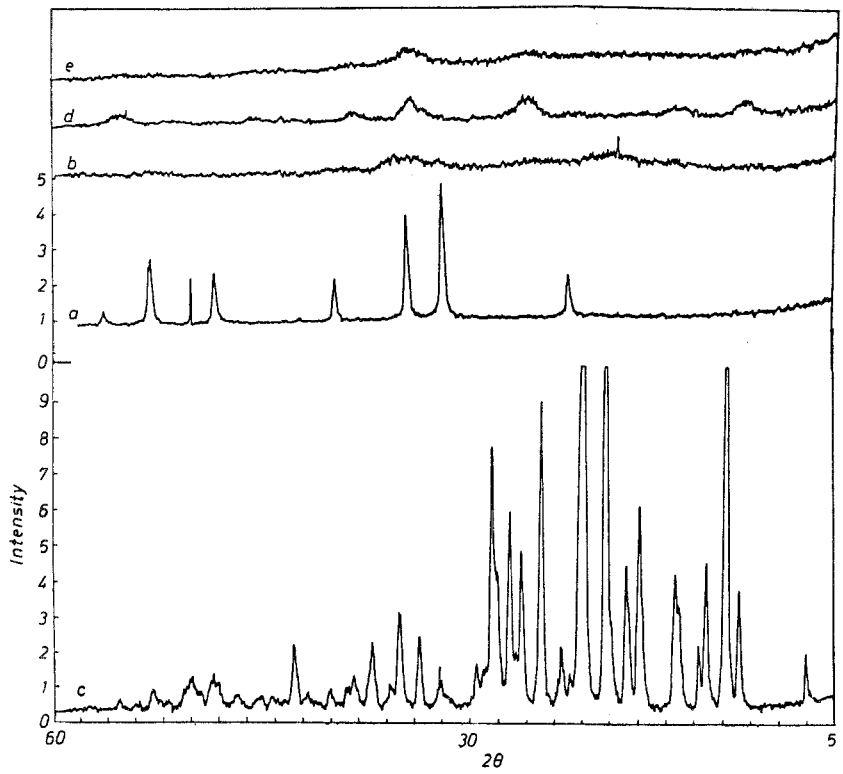

Fig. 3. X-ray powder diffraction patterns of Fe(III) complexes with: (*a*) sulphathiazole; (*b*) sulphamethoxazole; (*c*) sulphadiazine; (*d*) sulphapyridine; (*e*) sulphadimidine

Table 2. X-ray powder diffraction data for the Fe(III)-sulphadiazine complex

2θ	*d*(A°)	I/I_0	2θ	*d*(A°)	I/I_0
7.0	12.46	0.111	30.5	2.92	0.098
11.8	7.46	0.208	33.2	2.69	0.060
12.8	6.86	0.742	34.6	2.58	0.136
14.2	6.23	0.260	36.1	2.48	0.185
14.7	6.01	0.133	36.7	2.44	0.063
16.2	5.46	0.178	38.0	2.36	0.125
18.9	4.67	0.359	39.4	2.28	0.065
19.8	4.47	0.261	39.8	2.26	0.050
21.4	4.15	1.000	41.1	2.19	0.051
22.9	3.87	0.992	43.6	2.07	0.129
23.9	3.71	0.082	45.2	2.60	0.043
24.5	3.63	0.115	46.0	1.97	0.040
26.0	3.42	0.516	47.7	1.90	0.043
27.4	3.25	0.250	49.1	1.85	0.065
28.2	3.16	0.338	49.4	1.84	0.064
29.2	3.04	0.179	53.8	1.70	0.042
			56.1	1.63	0.039

whereas the complexes of sulphamethoxazole, sulphapyridine, and sulphadimidine (**2**, **4**, **5**) are amorphous as shown in Fig. 3. The powder diffraction data such as (d) spacing and relative intensities (I/I_0) for the Fe(III)-sulphadiazine complex is given in Table 2.

Infrared Spectra

The infrared spectra of the complexes are shown in Fig. 4 and the assignments are made in Table 3. Sharp bands attributable to NH_2 motions may be described as the symmetric (3 360 − 3 320 cm^{-1}) and asymmetric (3 450 − 3 400 cm^{-1}) N − H stretches, the NH_2 deformation (1 570 − 1 550 cm^{-1}), twisting (1 390 − 1 375 cm^{-1}) and rocking (890 − 880 cm^{-1}) [24]. The presence of coordinated water in the infrared spectra of all complexes is indicated by a broad band (3 460 − 3 200 cm^{-1}) and in the deformation band region (1 690 − 1 680 cm^{-1}) [25], a fact which is confirmed by the results of elemental and thermal analyses. The spectra of all complexes show two strong bands at 1 145 cm^{-1} and 1 330 cm^{-1} due to symmetric and asymmetric SO_2 stretches. These two bands are shifted to lower frequencies, indicating that the sulfonyl group participates in complex formation. The infrared bands appearing at 570, 375, and 240 cm^{-1} are attributable to stretching vibrations of Fe − O, Fe − Cl, and Fe − N, respectively [18, 26].

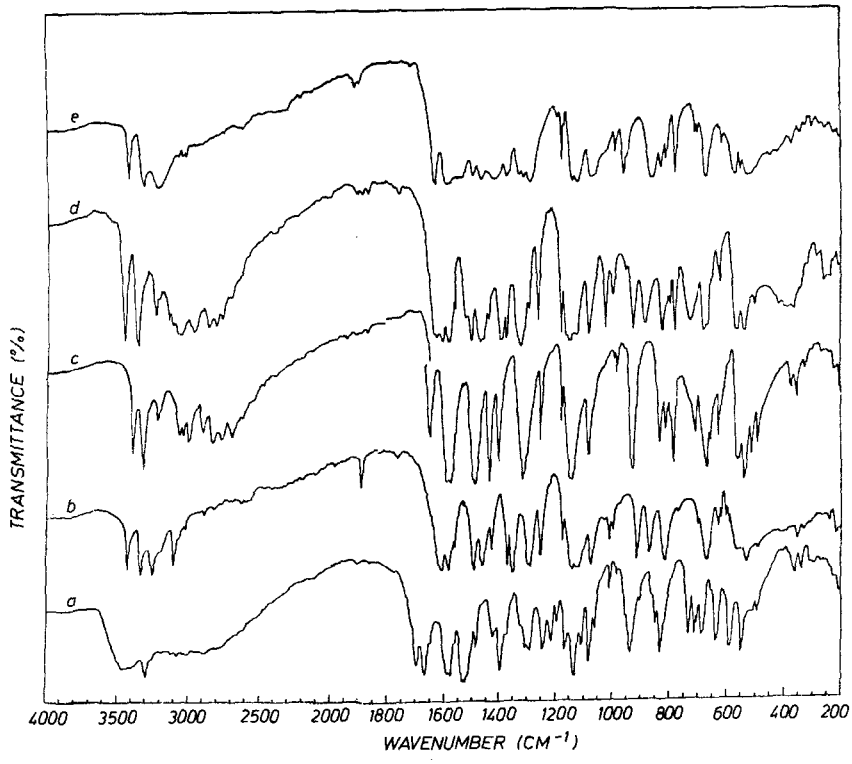

Fig. 4. The infrared spectra of 1 : 2 iron(III) complexes with: (*a*) sulphathiazole; (*b*) sulphamethoxazole; (*c*) sulphadiazine; (*d*) sulphapyridine; (*e*) sulphadimidine

Table 3. Infrared spectra (cm^{-1})

Complex					Assignment
1	**2**	**3**	**4**	**5**	
3450 vs	3450 vs	3400 vs	3400 vs	3420 vs	NH str
3300 vs	3360 vs	3340 vs	3330 vs	3320 vs	
1565 s	1560 s	1555 s	1570 s	1560 s	NH_2 def
1380 m	1385 m	1375 m	1390 m	1380 m	NH_2 twist
885 s	890 s	885 s	880 s	880 s	NH_2 rock
3310–	3460–	3250–	3380–	3300–	H_2O str
3000 br	3290 br	2850 br	2800 br	3000 br	
1685 s	1690 s	1690 s	1680 s	1680 s	H_2O def
1330 s	1330 s	1330 s	1330 s	1330 s	S=O sym str
1145 s	1145 s	1145 s	1145 s	1145 s	S=O asym str
555 m	550 m	550 m	555 m	550 m	Fe–O str
373 w	368 w	370 w	370 w	370 w	Fe–Cl str
242 w	240 w	242 w	240 w	240 w	Fe–N str

Mössbauer and ESR Data

The Mössbauer spectra were recorded at 300 K. In each case the spectrum consists of a single quadrupole-split doublet. All complexes have very similar ^{57}Fe Mössbauer data with isomer shifts in the range between (δ) = 0.035 and 0.038 mm s^{-1} relative to iron and quadropole splitting in the range between (G_s) = 0.7 and 0.77 mm s^{-1} attributable to high-spin Fe^{3+} species; a Mössbauer spectrum of Fe(III)-sulphadiazine complex is shown in Fig. 5.

For further confirmation of our results ESR spectra of the complexes **2** and **3** have been recorded as shown in Fig. 6. The electron spin resonance spectrum of the powder of the Fe(III) sulphadiazine complex (**3**) consists of a single sharp (H = 13.6 G) isotropic line with a g-value of 2.0039 superimposed on the much broader resonance (H = 408 G) due to Fe^{3+} ions in the complex. The sharper g-value at 2.0039 is attributed to the high-spin Fe^{3+} in a weakly coordinating distorted

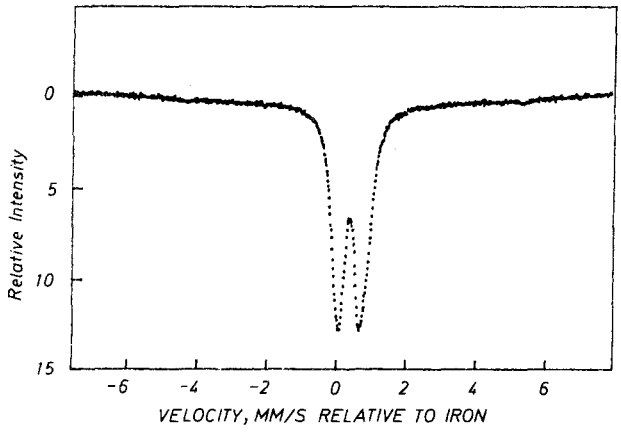

Fig. 5. Mössbauer spectrum of the Fe(III)-sulphadiazine complex in the solid state at 300 K

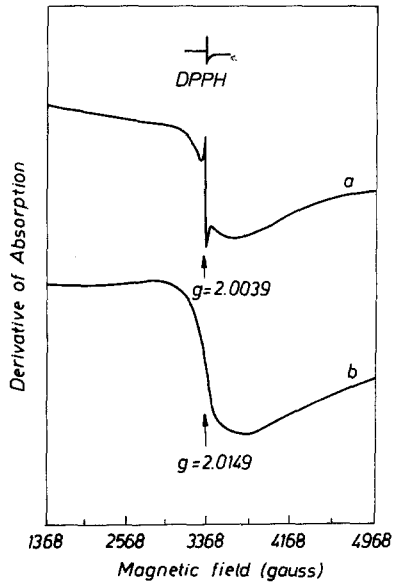

Fig. 6. ESR spectra of (*a*) Fe(III)-sulphadiazine complex and (*b*) Fe(III)-sulphamethoxazole complex at 300 K

Table 4. Temperature ranges, decomposition chromophores and their calculated/(found)% of weight loss

Stage	Decomposition chromophore	Complex				
		1	**2**	**3**	**4**	**5**
I	CH_3	–	120 – 140[a] 2.0[b] (2.45)[c]	–	–	120 – 142 4.0 (4.57)
II	H_2O	141 – 160 3.0 (2.92)	141 – 162 3.0 (2.93)	144 – 165 3.0 (2.97)	130 – 155 3.0 (2.96)	142 – 160 3.0 (2.71)
III	Cl	161 – 185 6.0 (5.74)	162 – 190 6.0 (5.771)	166 – 195 6.0 (5.85)	155 – 190 6.0 (5.83)	161 – 193 5.0 (5.34)
IV	SO_2	205 – 420 20 (20.70)	200 – 430 20 (20.85)	210 – 430 21 (21.13)	205 – 420 21 (21.06)	215 – 425 20 (19.27)
V	*L*[e]	420 – 450 45	430 – 451 43	430 – 450 44	420 – 445 43	425 – 450 43
	Residue	420 – 700 26 (25.84)	430 – 700 26[d] (26.01)	430 – 700 26 (26.36)	430 – 700 27 (26.27)	425 – 700 25 (24.05)

[a] Temperature range
[b] % Wt. loss observed
[c] % Wt. loss calculated
[d] % Wt. calculated for Fe_2O_3
[e] *L*...Ligand pyrolysis products

octahedral structure [27]. The absence of additional Fe^{3+} ($s = 5/2$) fine structure (Fig. 6, *a*) is consistent with a distorted environment. On the other hand, the electron spin resonance spectrum of the Fe(III) sulphamethoxazole complex (**2**) (Fig. 6, *b*) has a broad ($H = 408$ G) asymmetric line with a *g*-value of 2.0149. The dominant ferric ions in the two complexes are responsible for the broad ESR signal observed in the spectra [27]. These results are in agreement with the X-ray powder diffraction patterns which reflect a high degree of crystallinity of the sulphadiazine complex and the amorphous nature of the sulphamethoxazole complex (see Fig. 3).

Thermogravimetric Analyses

Thermal analyses of the prepared complexes **1**–**5** were made in air in the temperature range of 20–700°C to establish their compositional differences as well as to ascertain the nature of associated water. The TGA curves consist of four or five stages ending with the same residue in each case, which is identified from its weight as ferric oxide (see Table 4). Thermograms of Fe(III) complexes with sulphamethoxazole and sulphadimidine (**2**, **5**) showed that the methyl groups are departed earlier in the range 120–142°C [29]. TGA curves of all complexes showed an endothermic loss of about 3% at the temperature range 141–165°C attributed to the loss of one water molecule [29, 30] indicating its coordination nature. This is in agreement with elemental analyses and infrared data. The extent of the temperature range of this stage is not variable from one complex compared with others, a fact arising from the similarity of the strength of the chelate structure generated by the O_2N_2 donor set in all complexes. It was stated by Burger that the decrease in the strength of the metal-donor atom causes a decreasing trend in the decomposition temperature of other donor ligands [31]. The third stage at the temperature range 161–195°C corresponds to a weight loss of about 6% attributed to decomposition of one coordinated chlorine atom [32]. The temperature range 200–430°C represented by a slow decomposition stage in the TGA thermograms and in the same time with a sharp narrow endotherm centered at the decomposition temperature (240–250°C) followed directly by an exthotherm in the DTA curves. The weight loss in this stage of about 20% corresponds to the evolution of two molecules of SO_2 [33]. The last pyrolytic stage (420–450°C) is fast and corresponds to a weight loss of about 43% and its TGA and DTA representation is exothermic attributed to ligand pyrolysis. The resulting residue has a constant weight of about 26% and is stable up to 700°C, which is in agreement with the calculated mass of ferric oxide.

Antibacterial Activity

The antibacterial activity of the prepared complexes **1**–**5** and their reference sulpha drugs was evaluated against *Esch. Coli*, *Staph. aureus* and *Prot. mirabilis*.

The minimum inhibitory concentrations (MIC) of the tested compounds along with the reference drugs were determined and the results are given in Table 5. Analyses of these results showed that Fe(III) complexes are more potent antibacterial compounds than the reference drugs. It was found that the Fe(III)-sulphadiazine complex was 2.9, 1.8, and 2.5 times as effective as sulphadiazine against *E. coli*, *Staph. aureus*, and *Prot. mirabilis*, respectively; the Fe(III) sulphadimidine complex was 2.3, 2.8, and 2.5 times as effetive as the reference drug.

Table 5. Antibacterial activity of sulpha drugs and their Fe(III) complexes

Compound	MIC (μg/ml) against		
	Esch. coli	*Staph. aureus*	*Prot. mirabilis*
Sulphathiazole	48.2	38.7	26.3
Fe-complex	21.9	29.8	17.5
Sulphamethoxazole	52.6	41.4	28.5
Fe-complex	20.2		10.5
Sulphadiazine	54.5	39.0	27.6
Fe-complex	18.8	21.1	11.1
Sulphapyridine	40.3	36.6	25.2
Fe-complex	23.7	33.3	21.0
Sulphadimidine	51.2	38.1	20.4
Fe-complex	22.3	13.6	8.2

On the other hand, the Fe(III)-sulphapyridine complex has the least pronounced improvement of the antibacterial activity and was 1.7, 1.1, and 1.2 times as effective as the reference drug.

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