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MASS SPECTRAL AND THERMOGRAVIMETRIC STUDIES OF SOME IRON(III) BINUCLEAR COMPLEXES WITH BRIDGING THIURAM DISULFIDE LIGANDS

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Mass spectral and thermal studies by TG and DTG of some iron(III) binuclear complexes of the general type $Fe_2(R_2dtc)_2(tds^\circ)X_2X'_2$ have been carried out to determine their modes of decomposition. Fragmentation patterns are given and possible mechanisms are discussed.

In addition to the variety of products formed [1–4] during the reaction of iron(III) halobisdithiocarbamates, $[Fe(R_2dtc)_2X]$, with halogens, X'_2, some novel homobinuclear iron(III) complexes with two different coordination spheres around the magnetic centers have also been synthesized and studied [5]. The formation of these products, formulated as $Fe_2(R_2dtc)_2(tds^\circ)X_2X'_2$ [R = Me; R_2 = Pyrr; X = Cl, Br; and X' = Br, I], depends on the natures of both the molecular halogen and the reagent complex, as well as on the reaction conditions. In particular, the proposed mechanism [5] which accounts for the synthesis of these compounds involves as a first step the formation of the corresponding dihalide-bridged dimers, $[Fe(R_2dtc)_2X]_2(\mu\text{-}X'_2)$. Analogous iron(III) complexes have already been isolated and their structures were established on the basis of spectroscopic [1, 3, 4] and X-ray crystal structure [6] determination methods, as well as the results of thermoanalytical studies [7]. Depending on the redox capacities of both the halogens and the dithiocarbamato ligands, an intramolecular electron transfer could take place resulting in the oxidation of half of the dithiocarbamate groups into thiuram disulfide. In this case, the dimeric compounds studied in the present paper are formed.

Continuing our interest in the thermal investigation of metal dithiocarbamate complexes [7–10], we report in this paper results concerning mass spectral and thermogravimetric studies of complexes $Fe_2(R_2dtc)_2(tds^\circ)X_2X'_2$. The E^* values for the main decomposition stage, derived from the Piloyan method [11], TTN calculations [12], and a proposed mechanism of the decomposition are also reported and discussed.

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Experimental

The halobis(*N*, *N*-dialkyldithiocarbamato)iron(III) complexes were obtained from the reaction between an iron(III) trisdithiocarbamate and aqueous hydrohalic acid [13, 14]. The dihalide iron(III) dimers were prepared as previously reported [5]; they were recrystallized several times from methylene chloride–cyclohexane mixtures and dried under vacuum. The thermal decomposition was carried out on a TGS-2 Perkin–Elmer thermobalance at a heating rate of 5 deg/min, in the temperature range 20–1000°, with a sample mass of 5 mg and α-Al_2O_3 as reference. The measurements were performed in a dynamic atmosphere of nitrogen. Mass spectra were measured on an RMU-6L Hitachi Perkin–Elmer mass spectrometer with an ionization source of T-2p type operating at 70 eV. X-ray powder diffraction analyses of the final residues were made with a Phillips PW 1130/00 X-ray diffractometer, using CuK_α radiation. For the determination of TTN, the areas of the TG curves were measured with a Coradi Cora-Senior planimeter.

Results and discussion

Table 1 contains the most relevant mass spectral peaks of the compounds under study. The molecular ions of the dimeric species are not detected in the mass spectra. The absence of molecular ions can be attributed either to pyrolytic

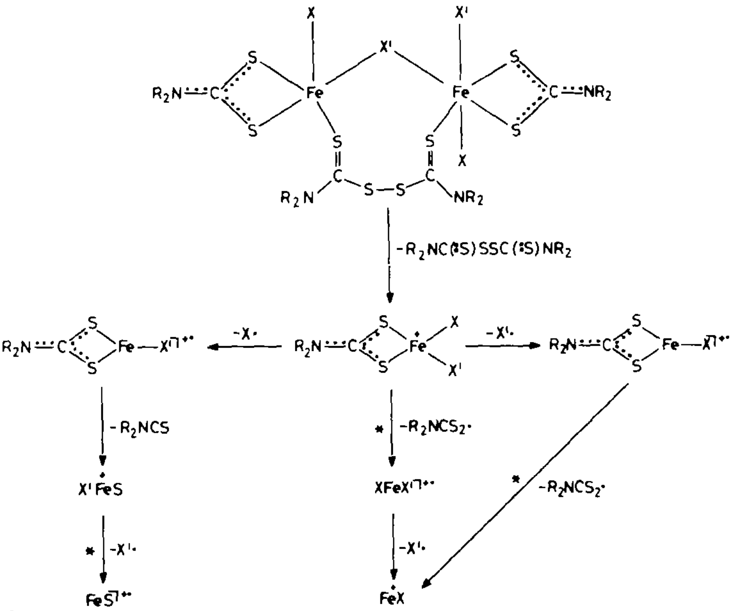
Table 1 Most relevant mass spectral peaks of the iron(III) binuclear complexes under study

Complex	*m*/*e* (R.I.)*
$Fe_2(Me_2dtc)_2(tds^{\ominus})Cl_2Br_2$	35 (10), 37 (6), 44 (28), 64 (80), 76 (100), 79 (20), 81 (17), 88 (35), 91 (12), 120 (75), 123 (31), 135 (17), 167 (21), 170 (24), 176 (11), 211 (15), 240 (3), 255 (11), 280 (8).
$Fe_2(Pyrrdtc)_2(tds^{\ominus})Cl_2Br_2$	27 (20), 33 (28), 35 (8), 39 (10), 43 (19), 44 (57), 55 (39), 59 (16), 64 (41), 70 (16), 71 (23), 76 (100), 79 (24), 81 (22), 88 (12), 91 (35), 114 (68), 123 (4), 135 (23), 146 (21), 147 (37), 167 (15), 170 (15), 237 (5), 281 (3), 292 (8), 316 (5).
$Fe_2(Pyrrdtc)_2(tds^{\ominus})Cl_2I_2$	27 (15), 33 (18), 35 (14), 37 (8), 43 (20), 44 (63), 55 (40), 59 (23), 64 (35), 70 (25), 71 (34), 76 (100), 88 (41), 91 (28), 114 (60), 127 (21), 146 (23), 147 (48), 215 (18), 218 (12), 237 (10), 292 (7), 329 (5), 364 (3).
$Fe_2(Pyrrdtc)_2(tds^{\ominus})Br_2I_2$	27 (30), 33 (12), 43 (15), 44 (63), 55 (31), 59 (15), 64 (33), 70 (25), 71 (18), 76 (100), 79 (15), 81 (12), 88 (39), 114 (39), 127 (18), 135 (21), 146 (27), 147 (43), 215 (11), 262 (7), 281 (4), 292 (5), 329 (3), 408 (1)

* R.I. = Relative Intensity

decomposition in the direct inlet under the high temperature used (200–280°), or to electron impact. However, in all spectra the ion $[Fe(R_2dtc)XX']^+$ is present and can be regarded as a direct fragment of the molecular ion upon elimination of the bridging thiuram disulfide ligand. This is supported by the detection of a peak with variable relative intensity (35–80%) due to the $S_2\urcorner^{+\cdot}$ ion.

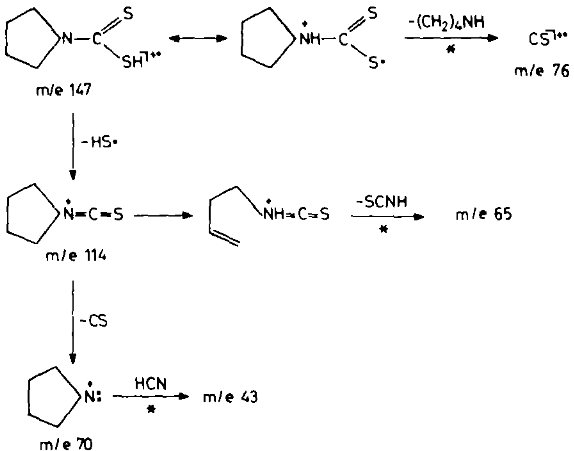
The highest mass number ions observed for all compounds, which might be direct fragments of the parent ion after the elimination of one halide ligand, are those of the general formulae $[Fe(R_2dtc)X]^{+\cdot}$ and $[Fe(R_2dtc)X']^{+\cdot}$. We might expect low relative abundances of these ions considering the known thermal instability of similar compounds [15–17] and organometallic compounds in general. A number of daughter ions besides the ones mentioned above were also detected. The genesis of these ions is demonstrated by the general fragmentation pattern shown in Scheme 1. Support for the fragmentation pathways comes from the presence of metastable peaks.



Scheme 1 Possible fragmentation pattern of the $Fe_2(R_2dtc)_2(tds^{\circ})X_2X'_2$ complexes

Among the most interesting and prominent peaks detected in the high mass region of the spectra of all the examined compounds are those corresponding to the ions $[R_2NC(:S)SSC(:S)NR_2]^{+\cdot}$ and $[R_2NC(:S)SNR_2]^{+\cdot}$. These ions may be partly considered to be pyrolytic products, because their relative intensities are affected by the temperature and the time spent in the direct inlet. The peaks of these ions are more pronounced in the spectra of the pyrrolidyldithiocarbamates than that of the dimethyl derivative, for in the latter compound it is possible to have one or two alkyl groups detached. Another prominent peak, and in most cases the base peak of the spectra, is the peak at *m/e* 76 due to the ion $[CS_2]^{+\cdot}$. The relative abundance of this peak is affected by the temperature of the direct inlet and is considered at least in part to be a direct thermolytic product.

In the low mass number region of the spectra of the pyrrolidyl compounds, a number of the detected peaks can be satisfactorily accounted for by the fragment ion $[Fe(Pyrrdtc)X]^{+\cdot}$. The formation of these ions may be explained with a mechanism according to Scheme 2. The observed metastable peaks support the suggested mechanism.



Scheme 2

The thermoanalytical curves (TG and DTG) of the investigated dimers in dynamic nitrogen atmosphere are given in Figs 1–4. The temperature ranges and percentage mass losses of the decompositions, as well as the temperatures of the greatest rate of decomposition (DTG_{max}) and the theoretical percentage mass

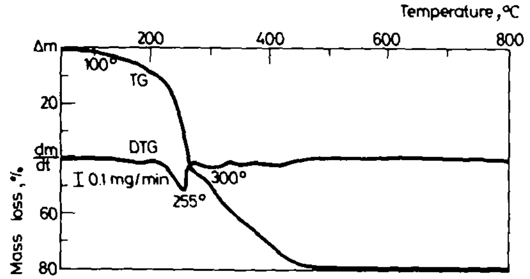


Fig. 1 TG and DTG curves for $Fe_2(Me_2dtc)_2(tds^{\circ})Cl_2Br_2$ in nitrogen

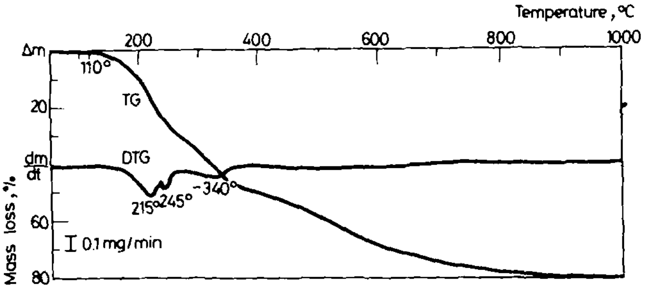


Fig. 2 TG and DTG curves for $Fe_2(Pyrrdtc)_2(tds^c)Cl_2Br_2$ in nitrogen

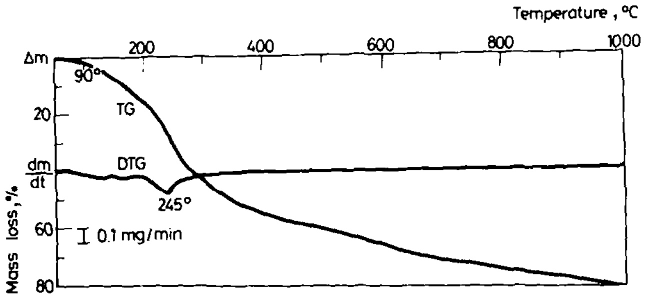


Fig. 3 TG and DTG curves for $Fe_2(Pyrrdtc)_2(tds^c)Cl_2I_2$ in nitrogen

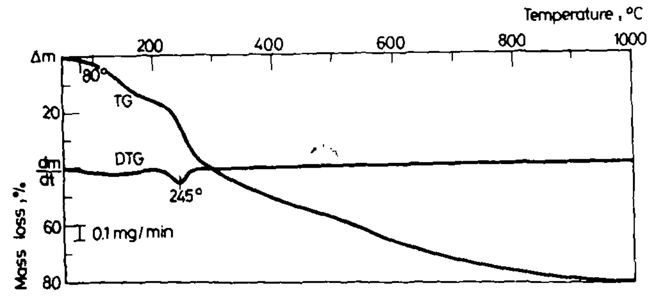


Fig. 4 TG and DTG curves for $Fe_2(Pyrrdtc)_2(tds^c)Br_2I_2$ in nitrogen

losses, are presented in Table 2. The obtained data on the complexes $Fe_2(R_2dtc)_2(tds^c)X_2X'_2$ show that the main decomposition stage involves the elimination of the bridging thiuram disulfide moiety plus the molecular halogen group, X_2. However, in several cases the DTG curves show that the main decomposition process consists of two consecutive steps. It is logical to assume that one dithiocarbamato group is primarily evolved after breaking of an Fe—S bond and the homolytic dissociation of the S—S bond, followed by elimination of the other dithiocarbamato group and the molecular halogen moiety. The possible intermediate after this stage is considered to be $[X'Fe(R_2dtc)]_2$. This is thermally

Table 2 Thermoanalytical results (TG/DTG) of the investigated iron(III) dimers in nitrogen atmosphere

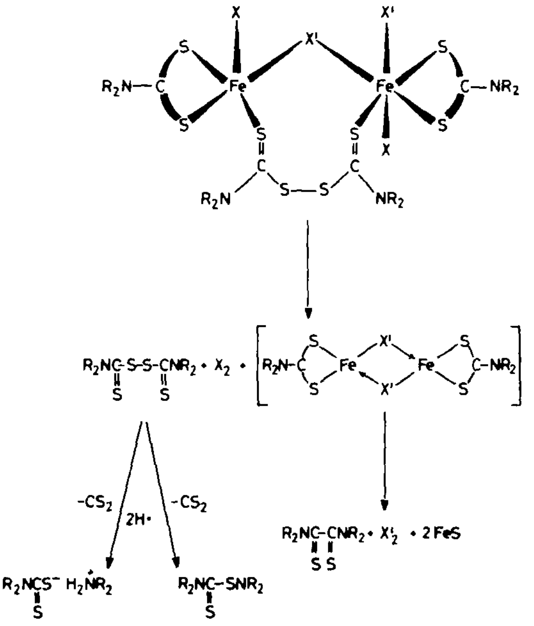
Complex	Stage	Temperature range, °C	DTG_{max}, °C	TTN, °C	Mass loss, %	Evolved moiety formula	Mass calcd., %
$Fe_2(Me_2dtc)_2(tds^{\circ})Cl_2Br_2$	1	100–210		95	10.0	$SCN(CH_3)_2$	10.69
	2	210–290	255		38.0	$(CH_3)_2NC(:S)SSC(:S)N(CH_3)_2 + Cl_2$	37.78
	3	290–330	300		11.0	$SCN(CH_3)_2$	10.69
	4	330–460			20.0	Br_2	19.44
	residue	>460			21.0	2 FeS	21.38
$Fe_2(Pyrrdtc)_2(tds^{\circ})Cl_2Br_2$	1α	110–240	215	105	23.0	$S_2CN(CH_2)_4 + Cl_2$	23.39
	β	240–270	245		7.0	$N(CH_2)_4$	7.55
	2	270–360	~340		17.0	Br_2	17.25
	3	360–520			13.0	$SCN(CH_2)_4$	12.29
		+					
	4	520–900			21.0	$CS_2 + SCN(CH_2)_4$	20.48
	residue	>900			19.0	2 FeS	18.98
$Fe_2(Pyrrdtc)_2(tds^{\circ})Cl_2I_2$	1	90–260	245	85	36.0	$(CH_2)_4NC(:S)SSC(:S)N(CH_2)_4 + Cl_2$	35.54
	2	260–490			26.0	I_2	24.87
	3	490–660			11.0	$SCN(CH_2)_4$	11.16
	4	660–990			11.5	$SCN(CH_2)_4$	11.16
	residue	>990			17.5	2 FeS	17.24
$Fe_2(Pyrrdtc)_2(tds^{\circ})Br_2I_2$	1	80–180		83	13.0	$S_2CN(CH_2)_4$	13.15
	2	180–300	245		27.5	$S_2CN(CH_2)_4 + Br_2$	27.56
	3	300–540			22.5	I_2	22.88
	4	540–930			20.5	2 $SCN(CH_2)_4$	20.54
	residue	>930			16.5	2 FeS	15.85

unstable and decomposes further by elimination of the halide ligands plus one or two thiocarbamoylo moieties of the remaining dithio ligands. According to the results of X-ray powder diffraction analysis, the final residue is FeS.

The whole procedure in the thermal decompositions of the studied complexes seems to depend on the natures of both the halogens and the substituents in the amine group. This was established by determining the TTN values [12] of the dimers from their TG curves in nitrogen atmosphere. Thus, the TTN values (Table 2) for the compounds with the same halide ligands indicated that the pyrrolidyl derivatives are more stable, in accordance with the increasing basicity of the corresponding amines.

Finally, the calculated apparent activation energy, E^*, of 205.8 kJ/mol, derived from Piloyan's TG method [11] for the complex $Fe_2(Me_2dtc)_2(tds^\circ)Cl_2Br_2$, is fairly close to those reported for the dihalide-bridged iron(III) complexes [7], since the metal is the same in every case. Unfortunately, this method cannot be applied to the pyrrolidyl derivatives, because the obtained plot does not fit a straight line.

By combining the mass spectral and the thermogravimetric analysis data on the investigated iron(III) dimers, we can propose a possible mechanism for their thermal decomposition, as shown in Scheme 3. This mechanism involves the elimination of the bridging thiuram disulfide ligand, which decomposes further to



Scheme 3 Thermal decomposition of the investigated iron(III) binuclear complexes

yield carbon disulfide and either dithiocarbamate salt or sulfenamide [7–10]. The halide ligand X^- is also evolved, whereas the possible intermediate $[X'Fe(R_2dtc)]_2$ can decompose to give halogen, X'_2 and FeS as final residue. Also, dithio-oxamide may be a possible product [7]. Conclusively, this mechanism is analogous to that proposed for the dihalide-bridged iron(III) complexes, $[Fe(R_2dtc)_2(\mu\text{-}X'_2)$, of the same stoichiometry [7], where the molecular halogen bridging unit, X'_2, was primarily evolved. However, this is not the case for the studied compounds, as the halide ligand X'^- is more strongly bonded to the magnetic centers through the formation of three-center four-electron bonds.

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Zusammenfassung — Massenspektrometrische und thermische Untersuchungen (TG und DTG) einiger zweikerniger Eisen(III)-Komplexe des allgemeinen Typs $(R_2dtc)_2(tds^{\circ})X_2X'_2$ wurden ausgeführt, um deren Zersetzungsmechanismus zu ermitteln. Fragmentspektren werden angegeben und mögliche Mechanismen diskutiert.

Резюме — Проведено масс-спектрометрическое и термическое (ТГ и ДТГ) исследование некоторых двуядерных комплексов трехвалентного железа общей формулы $Fe_2(R_2dtc)_2(tds)X_2X'_2$ с целью установления характера их разложения. Приведена схема их распада и обсужден механизм реакций.