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MIXED LIGAND COMPLEXES OF IRON(III) DERIVED FROM ITS DITHIOCARBAMATO COMPLEXES

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Three different types of iron(III) complexes, $Fe(A)_3$, $Fe(A)_2(A')$ and $Fe(A)(A')_2$, where A is either piperidyldithiocarbamate or morpholyl dithiocarbamate and A' is glycine(oxine) acetylacetone have been prepared by reacting Fe(III) salt with sodium salt of piperidinedithiocarbamic acid or morpholine-dithiocarbamic acid and acetylacetone(oxine)-glycine in different ratios. The mixed ligand complexes have been characterised by elemental analysis, magnetic susceptibility measurements, infrared, electronic spectral techniques and by thermal analysis. Electronic spectral studies suggests that all the complexes possess distorted octahedral geometry. The magnetic moment of the high spin iron(III) complexes lies in the range of 5.88-6.00 and for low spin lies in the range of 3.36-4.34 B.M. TG studies show one step decomposition of complexes and formation of Fe_2O_3 at the end of the step.

Metal complexes of dithiocarbamates are well known for their structural and biochemical importance [1, 2]. A large number of metal dithiocarbamates are used as fungicides. The important among these are the iron and zinc salts of dimethyldithiocarbamic acid. Carbamates are the half amides of carbonic acid. The dithiocarbamates are the sulphur analogues of carbamates. The compounds derived from the dithiocarbamate ligands are used in industry as vulcanisation accelerators, as high pressure lubricants. Their use as fungicides and pesticides has resulted in a vast amount of biological and biochemical study [3]. Richard [4] studied the use of dithiocarbamic compounds in cancer therapy as protecting agent. Detcheva *et al.* [5] have described the toxicity of tetramethylthiuramdisulphide to mold and its use as a fungicide for linen containing textiles. The clinical applications [6] and toxicological [7] and inhibitory [8] action of dithiocarbamates are also well known.

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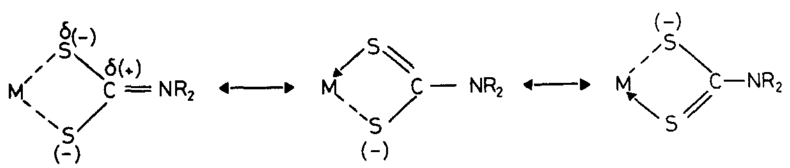
The dithiocarbamate ligands have also proved useful in analytical chemistry, particularly for the estimation of metal ions, for example iron, cobalt and nickel were determined gravimetrically as their diethyldithiocarbamate complexes in the presence of tartarate as masking agent [9]. Saitoh *et al.* [10] have developed a high performance liquid chromatographic determination method for the extraction of Ni(II), Cu(II) and Zn(II) from an aqueous solution into carbon tetrachloride as their diethyldithiocarbamate chelates.

The dithiocarbamate ligands can stabilize higher oxidation states of transition metals in their complexes [2]. These ligands have a special feature in that there is an additional π-electron flow from nitrogen to sulphur via a planar delocalised π-orbital system. Several canonical forms may be written for the structure of the dithiocarbamato moiety in its complexes, $M(S_2CNR_2)_n$, where M is the metal atom and n is its valency.



This effect results in strong electron donation and hence a high electron density on the metal leading to its next higher oxidation state. In this manuscript we report the isolation and spectral characterization, together with magnetic and thermal measurements of mixed ligand iron(III) dithiocarbamates.

Experimental

Preparation

All the chemicals used were of Analar grade. The dithiocarbamate ligands have been obtained as sodium salts. Sodium morpholyldithiocarbamate and sodium piperidinedithiocarbamate has been synthesised by the method of Glev and Schwab [11]. The purity of the ligands was checked by elemental analysis and TLC techniques. Various complexes have been isolated as follows:

$$Fe(pip\text{-}dtc)_3 \qquad \text{(i)}$$

Aqueous solution of sodium salt of piperidine-dtc was added with stirring to an aqueous solution of ferric chloride in 3:1 molar ratio. The compound was separated out on stirring. It was filtered, washed with water and then with ether and dried in vacuo over P_2O_5.

$Fe(pip\text{-}dtc)_2(acac)$ and $Fe(pip\text{-}dtc)_2(oxine)$ (ii)

Ethanolic solution of ferric chloride, sodium salt of piperidinedithiocarbamate and acetylacetone/oxine were reacted in 1:2:1 molar ratio. Ethanolic solution of sodium acetate was added to it till the compounds were separated out. Compounds were filtered, washed with ethanol, ether and dried in vacuo over P_2O_5.

$Fe(pip\text{-}dtc)(acac)_2$ and $Fe(pip\text{-}dtc)(oxine)_2$ (iii)

These compounds were obtained by similar method as described above by reacting $FeCl_3$, sodium salt of corresponding dtc and acac/oxine in 1:1:2 molar ratio in ethanolic medium.

$Fe(pip\text{-}dtc)_2(gly)$ and $Fe(pip\text{-}dtc)(gly)_2$ (iv)

To an ethanolic solution of ferric chloride, was added a mixture of ethanolic solution of sodium salt of piperidinedithiocarbamate and aqueous solution of glycine in stoichiometric ratio. The compounds separated out on stirring were filtered, washed with ethanol, ether and dried in vacuo.

Similarly seven more complexes have been prepared with sodium salt of morpholine-dithiocarbamate by the methods described above.

All the complexes are insoluble in water and dissolve completely in chloroform and acetone, but partially in ethanol.

Physical measurements

Microanalyses for carbon and hydrogen (Table 1) were performed at the USIC, University of Delhi, India. The estimation of sulphur was done by decomposing the complexes with 50% nitric acid, whereupon the sulphur got oxidised to sulphate and then determined as $BaSO_4$ [12]. Iron content was estimated by decomposing a known amount of the complex with concentrated nitric acid and weighed as Fe_2O_3 (Table 1).

Table 1 Physical properties and analytical data of iron(III) complexes

Complexes	Colour	M.p., °C	Analysis, % Found (Calc.)			
			C	H	S	Fe
Fe(pip-dtc)(gly)$_2$	Dark brown	212	33.02(32.96)	5.61(4.94)	15.38(17.58)	14.04(15.38)
Fe(pip-dtc)$_2$(gly)	Blackish brown	237	38.05(37.25)	5.68(5.54)	27.00(28.38)	12.74(12.41)
Fe(pip-dtc)(oxine)$_2$	Grey	243	57.64(56.91)	4.58(4.34)	14.39(12.64)	11.14(11.06)
Fe(pip-dtc)$_2$(oxine)	Grey	246	48.92(48.36)	5.89(5.18)	27.85(24.56)	10.55(10.74)
Fe(pip-dtc)(acac)$_2$	Dark brown	240	46.75(46.15)	6.56(6.25)	14.12(15.38)	13.49(13.46)
Fe(pip-dtc)$_2$(acac)	Brown	204	43.32(42.85)	6.13(5.88)	24.92(26.89)	11.93(11.76)
Fe(pip-dtc)$_3$	Black	208	40.84(40.29)	5.62(5.59)	34.64(35.82)	10.00(10.44)
Fe(morph-dtc)(gly)$_2$	Black	175	29.38(29.50)	4.63(4.37)	18.94(17.48)	14.66(15.30)
Fe(morph-dtc)$_2$(gly)	Brownish black	226	32.48(31.64)	5.02(4.61)	28.83(28.13)	12.27(12.30)
Fe(morph-dtc)(oxine)$_2$	Black	235	54.97(54.33)	4.84(4.33)	13.74(12.59)	11.28(11.02)
Fe(morph-dtc)$_2$(oxine)	Bluish black	No change up to 250	43.69(43.42)	5.20(4.38)	25.18(24.38)	10.69(10.66)
Fe(morph-dtc)(acac)$_2$	Black	185	43.47(43.06)	6.32(5.74)	15.06(15.31)	12.68(13.39)
Fe(morph-dtc)$_2$(acac)	Black	215	37.94(37.50)	6.32(5.00)	25.87(26.66)	12.98(11.66)
Fe(morph-dtc)$_3$	Brown	190	33.49(33.21)	4.68(4.42)	34.68(35.42)	10.12(10.33)

Magnetic susceptibility measurements were carried out according to Gouy method. Mercury tetrathiocyanatocobaltate(II), $Hg[Co(CNS)_4]$ was used as a calibrant ($\chi_g = 16.44\cdot10^{-6}$ c.g.s. units).

The absorption spectra of the complexes were recorded on DMR-21, automatic recording spectrophotometer in chloroform solutions. Infrared spectra in "nujol medium" were recorded on Perkin-Elmer and Shimadzu spectrophotometer IR 435 in the range 400-4000 cm^{-1}. TG was recorded on G-70, thermoanalyser SETARAM Lyon France at the heating rate of 8 $deg\cdot min^{-1}$.

Results and discussion

IR spectra

The infrared spectral bands of the complexes with their tentative assignments are given in Table 2. The ligand dithiocarbamate is known to behave as a bidentate or a monodentate one. The former exhibits ν_{as}(C-S) near 1000 cm^{-1} as a single band whereas the latter shows a doublet in the same region [13]. Also the ν(C=N) in the case of bidentate mode (above 1485 cm^{-1}) is higher than that of the monodentate mode (below 1485 cm^{-1}) [14].

In the present case, the ν_{as} (C–S) band at ~1000 cm^{-1} (Table 2) was obtained as a single band and ν(C=N) band was found above 1485 cm^{-1} in all the mixed ligand compounds indicating thereby that the ligand piperidyldithiocarbamate and morpholyldithiocarbamate are coordinated to iron(III) as uninegative bidentate ligand in each case. The ligand acetylacetone can coordinate either as uninegative bidentate through its enol form or as neutral monodentate through carbonyl atom. In the case of enol form coordination, the ν(C=O) and ν(O=C) bands are found at 1577 and 1529 cm^{-1} respectively [15, 16] whereas the strong band due to ν(C=O) is obtained near 1700 cm^{-1} when it is coordinated through keto form [17]. In the four acetylacetonato complexes of iron(III), the ν(C=O) band was found at 1590 and 1620 cm^{-1} and ν(O=C) at 1530 and 1540 cm^{-1} indicating that the ligand is coordinated to the metal atom as an uninegative bidentate one. Charles *et al.* [18] have reported that in case of oxinate complexes of metals, the ν(C-O) was obtained in 1120 cm^{-1} region, the position of the band slightly varying with nature of the metal. In the present case, the ν(C–O) band due to oxine was found at 1105 and 1110 cm^{-1} indicating the coordination of the ligand through nitrogen and oxygen atoms as uninegative bidentate ons. The

Table 2 IR spectral data for Fe(III) complexes

Complexes	dtc			acac		oxine	glicine		
	ν(C=N)	ν_{as}(C–S)	ν_s(C–S)	ν(C=O)	ν(C=C)	ν(C=O)	ν_s(COO)	ν_{as}(COO)	ν(NH_2)
Fe(pip-dtc)$(gly)_2$	1495vs	1005vs	740vs	-	-	-	1380w	16600w	3365w
Fe$(pip\text{-}dtc)_2$(gly)	1490s	1005vs	720vs	-	-	-	1380w	1665w	3365v
Fe(pip-dtc)$(oxine)_2$	1530s	1020s	720s	-	-	1110s	-	-	-
Fe$(pip\text{-}dtc)_2$(oxine)	1530s	1015s	725s	-	-	1105vs	-	-	-
Fe(pip-dtc)$(acac)_2$	1490s	1000vs	720w	1590s	1530s	-	-	-	-
Fe$(pip\text{-}dtc)_2$(acac)	1500w	1005vs	720w	1600m	1540s	-	-	-	-
Fe$(pip\text{-}dtc)_3$	1515s	995vs	720m	-		-	-	-	-
Fe(morph-dtc)$(gly)_2$	1490s	1000vs	720w	-		-	1375w	1665w	3360w
Fe$(morph\text{-}dtc)_2$(gly)	1505w	1010vs	720s	-		-	1375w	1670w	3350w
Fe(morph-dtc)$(oxine)_2$	1495vs	990vs	710vs	-		1110vs	-	-	
Fe$(morph\text{-}dtc)_2$(oxine)	1500m	1000vs	740vs	-		1105vs	-	-	
Fe(morph-dtc)$(acac)_2$	1505m	1010vs	720s	1600m	1540s	-	-	-	
Fe$(morph\text{-}dtc)_2$(acac)	1510m	1000vs	725s	1620s	1540s	-	-	-	
Fe$(morph\text{-}dtc)_3$	1510s	1010vs	700s	-	-	-	-	-	

vs = very sharp, s = sharp, m = medium, vw = very weak, w = weak

$\nu_s(COO^-)$, ν_{as} (COO^-) and ν (NH_2) bands due to the ligand glycine, were observed at ~1375, 1665 and 3365 cm^{-1} respectively, which indicate that it is coordinated to the metal atom as an uninegative bidentate one.

Magnetic measurements

Magnetic susceptibility measurements were carried out by a Gouy balance using mercurytetrathiocyanato cobalt(II) as the calibrant. The diamagnetic correction was calculated by using Pascal's constant. The high spin iron(III) (S =5/2) with $3d^5$ configuration and $^6A_{1g}$ term is expected to exhibit magnetic moment of 5.92 B.M., while the low spin iron(III) with $^2T_{2g}$ term is expected to exhibit magnetic moment slightly higher than the spin only value of 1.73 B.M. but less than ~2.5 B.M. The reported experimental values of magnetic moment of iron(III) for both $^6A_{1g}$ and $^2T_{2g}$ terms generally respond to the theoretical values. But the dithiocarbamate complexes of iron(III) were found to exhibit magnetic moment values intermediate between spin free and spin paired configurations [19, 20]. Six compounds under present investigations , viz. Fe(pip-dtc)$_2$(gly), Fe(pip-dtc)(oxine)$_2$, Fe(pip-dtc)$_2$(oxine), Fe(morph-dtc)$_2$(gly), Fe(morph-dtc)(oxine)$_2$ and Fe(morph-dtc)$_2$(oxine) were found to exhibit magnetic moment values of 5.98, 5.90, 6.00, 5.88, 5.61 and 5.90 B.M. respectively as expected for $^6A_{1g}$ term (Table 3). The other eight compounds were found to exhibit magnetic moment values (3.36-4.34 B.M.) (Table 3), intermediate between the spin free and spin-paired configuration as suggested by Figgis and Lewis [19]. Mitchell and Parker [20] have suggested that the most plausible explanation of such magnetic properties is the presence of iron(III) in spin state S =3/2, because the low magnetic moment cannot be explained by interactions between the iron atoms and must therefore be due to a change of spin state of iron. The most acceptable spin state in such a case is S =3/2 (spin only moment 3.87 B.M.). Thus it was concluded that the compounds Fe(pip-dtc)$_2$(gly), Fe(pip-dtc)(oxine)$_2$, Fe(pip-dtc)$_2$(oxine), Fe(morph-dtc)$_2$(gly), Fe(morph-dtc)(oxine)$_2$ and Fe(morph-dtc)$_2$(oxine) are high spin type having ground state $^6A_{1g}$ while the other eight compounds show spin equilibrium.

Electronic spectra

Electronic spectra of the complexes are shown in Fig. 1(a) and 1(b). Electronic spectral bands and their tentative assignments are given in Table 3. The electronic spectra of the complexes under study display well

Table 3 Magnetic moment and electronic transition band positions (cm^{-1}) for iron(III) complexes

Complexes	μ_{eff} (B.M.)	$^6A_{1g} \rightarrow {}^4T_{1g}$	$^6A_{1g} \rightarrow {}^4T_{2g}$	$6A_{1g} \rightarrow {}^4E_g$
Fe(pip-dtc)(gly)$_2$	3.36	16286	20576sh	22727
Fe(pip-dtc)$_2$(gly)	5.98	16778	20161sh	23148
Fe(pip-dtc)(oxine)$_2$	5.90	16949	22321sh	23173
Fe(pip-dtc)$_2$(oxine)	6.00	17006	20161sh	23148
Fe(pip-dtc)(acac)$_2$	4.09	17006	20161sh	23255
Fe(pip-dtc)$_2$(acac)	3.86	16556	20325sh	22986
Fe(pip-dtc)$_3$	3.90	16000	20300sh	22350
Fe(morph-dtc)(gly)$_2$	3.74	16891	20242sh	23364
Fe(morph-dtc)$_2$(gly)	5.88	16339	20161sh	23265
Fe(morph-dtc)(oxine)$_2$	5.61	17543	22123sh	-
Fe(morph-dtc)$_2$(oxine)	5.90	17241	22624sh	22972
Fe(morph-dtc)(acac)$_2$	4.04	16447	20161sh	23228
Fe(morph-dtc)$_2$(acac)	4.34	16891	20161sh	-
Fe(morph-dtc)$_3$	4.02	16200	20200sh	22300

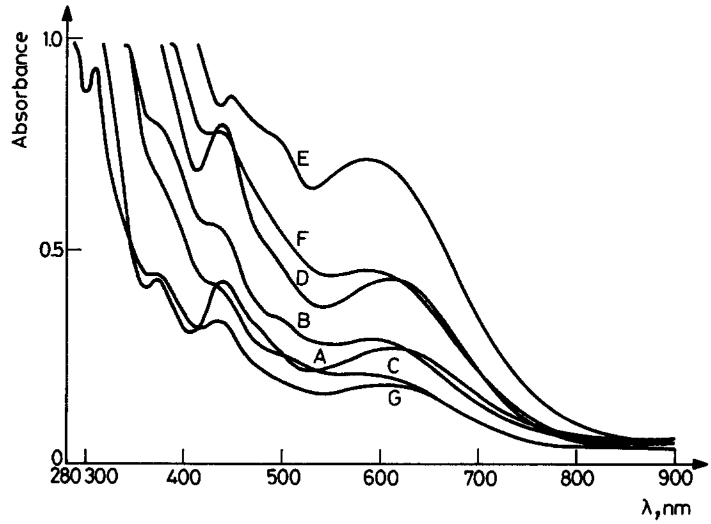


Fig. 1a Electronic spectra of (A) Fe(pip-dtc)(gly)$_2$; (B) Fe(pip-dtc)$_2$(gly); (C) Fe(pip-dtc)(acac)$_2$; (D) Fe(pip-dtc)$_2$(acac); (E) Fe(pip-dtc)(oxine)$_2$; (F) Fe(pip-dtc)$_2$(oxine) and (G) Fe(pip-dtc)$_3$ (in chloroform)

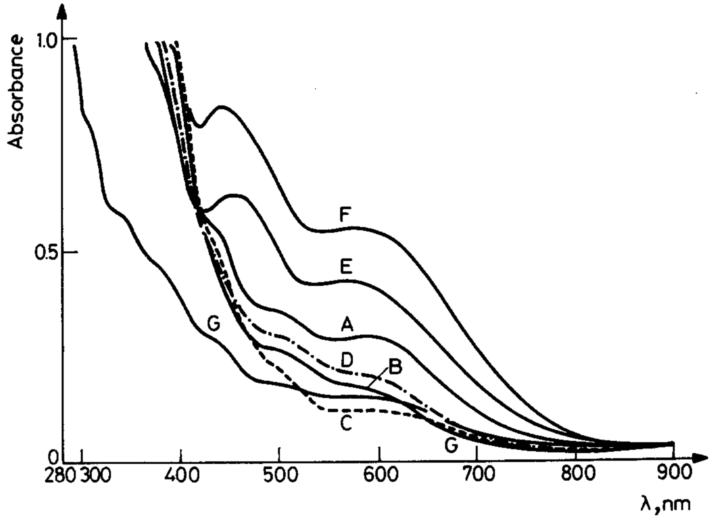


Fig. 1b Electronic spectra of (A) Fe(morph-dtc)(gly)$_2$; (B) Fe(morph-dtc)$_2$(gly); (C) Fe(morph-dtc)(acac)$_2$; (D) Fe(morph-dtc)$_2$(acac); (E) Fe(morph-dtc)(oxine)$_2$; (F) Fe(morph-dtc)$_2$(oxine) and (G) Fe(morph-dtc)$_3$ (in chloroform)

defined absorption bands in the range of 16000-17543, 20161-22624 and 22727-23364 $cm^{-1.}$ The spectra of the complexes are consistent with the octahedral nature of the compounds. The bands at 16000-17543 cm^{-1}, 20161-22624 cm^{-1} and 22727-23364 cm^{-1} may be assigned to the transitions $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4E_g$ respectively as suggested by Ballhausen [21] and Bremen *et al.* [22]

Thermal behaviour of iron(III) complexes

Thermal studies have been carried out to elucidate a number of kinetic parameters. From the TG curves, the order or reaction (n) and activation energy (E) of the reactions have been enumerated. The weight change is plotted on the ordinate with decreasing weight downwards and temperature (T) on the abscissa increasing from left to ringt. The method of Coats and Redfern [23] has been used for deriving kinetic parameters. This method assumes a rate law of the type:

$$\frac{d\alpha}{dt} = K(1-\alpha)^{n} \tag{1}$$

and an Arrhenius equation of the type

$$K = Ze^{-E/RT} \tag{2}$$

to be valid, where 'α' stands for the fraction transformed, 'n' for the reaction order, 'K' for the rate constant, 'E' is the activation energy, 'R' the gas constant and 'Z' stands for pre-exponential or frequency factor and is independent of temperature 'T'.

Integrating a combination of equations (1) and (2) Coats and Redfern derived the equation:

$$\frac{\log F(\alpha)}{T^2} = \frac{\log ZR}{\beta E}\left(1-\frac{2RT}{E}\right) - \frac{E}{2.303RT} \tag{3}$$

where β is the linear heating rate.

The function $F(\alpha) = -\log(1-\alpha)$ for $n = 1$ and thus a plot of $-\log\left[\frac{-\log(1-\alpha)}{T^2}\right]$ *vs.* $1/T$ for $n = 1$ results in a straight line of slope $-E/2.303\,R$ for the correct value of 'n', since for most values of E and for the temperature range over which reactions generally occur.

Table 4a Kinetic parameters from TG for Fe(III) complexes

Temp.,	Fe(pip-dtc)$_2$(gly)$_2$			Fe(pip-dtc)$_2$gly			Fe(pip-dtc)(oxine)$_2$			Fe(pip-dtc)$_2$(oxine)		
K	x	y	z	x	y	z	x	y	z	x	y	z
478	-	-	-	-	-	-	-	-	-	-	-	-
483	-	-	-	-	-	-	-	-	-	-	-	-
493	-	-	-	-	-	-	-	-	-	-	-	-
503	-	-	-	-	-	-	-	-	-	-	-	-
506	-	-	-	0.08	1.976	6.85	-	-	-	-	-	-
508	0.21	1.968	6.37	-	-	-	-	-	-	-	-	-
513	-	-	-	-	-	-	-	-	-	0.10	1.949	6.76
518	0.28	1.930	6.27	-	-	-	-	-	-	-	-	-
523	-	-	-	0.17	1.902	6.54	-	-	-	0.14	1.912	6.62
528	0.35	1.893	6.17	-	-	-	-	-	-	-	-	-
533	-	-	-	0.25	1.876	6.36	-	-	-	0.19	1.876	6.50
538	0.43	1.858	6.07	-	-	-	-	-	-	-	-	-
543	-	-	-	0.29	1.840	6.29	-	-	-	0.24	1.841	6.40
548	0.50	1.820	5.99	-	-	-	-	-	-	-	-	-
553	-	-	-	0.33	1.808	6.24	-	-	-	0.28	1.808	6.33
558	-	-	-	-	-		-	-	-	-	-	-
563	-	-	-	-	-		0.13	1.776	6.72	0.36	1.776	6.21
568	-	-	-	-	-		-	-	-	-	-	-
613	-	-	-	-	-		0.20	1.631	6.59	-	-	-
663	-	-	-	-	-		0.27	1.508	6.52	-	-	-
713	-	-	-	-	-		0.33	1.400	6.46	-	-	-
763	-	-	-	-	-		0.40	1.310	6.41	-	-	-
823	-	-	-	-	-		0.46	1.215	6.39	-	-	-

where $x = \alpha; y = 1/T \cdot 10^3; z = -\log\left[\frac{-\log(1-\alpha)}{T^2}\right]$

Table 4b Kinetic parameters from TG for Fe(III) complexes

Temp.,	$Fe(pip\text{-}dtc)_3$			$Fe(morph\text{-}dtc)(gly)_2$			$Fe(morph\text{-}dtc)_2(gly)$		
K	x	y	z	z	y	z	x	y	z
478	-	-	-	0.12	2.090	6.63	-	-	-
483	0.16	2.070	6.49	-	-	-	-	-	-
493	0.22	2.030	6.35	0.18	2.030	6.46	-	-	-
503	0.33	1.990	6.16	0.23	1.990	6.35	-	-	-
506	-	-	-	-	-	-	-	-	-
508	-	-	-	-	-	-	-	-	-
513	0.44	1.949	6.02	0.29	1.950	6.24	0.18	1.950	6.49
518	0.55	1.930	5.88	0.35	1.930	6.15	-	-	-
523	-	-	-	0.41	1.910	6.07	0.23	1.910	6.38
528	-	-	-	-	-	-	-	-	-
533	-	-	-	-	-	-	0.29	1.876	6.28
538	-	-	-	0.47	1.860	6.02	-	-	-
543	-	-	-	-	-	-	0.35	1.840	6.19
548	-	-	-	-	-	-	0.41	1.820	6.11
553	-	-	-	-	-	-	-	-	-
558	-	-	-	-	-	-	0.47	1.790	6.05
563	-	-	-	-	-	-	-	-	-
568	-	-	-	-	-	-	0.53	1.760	5.99
613	-	-	-	-	-	-	-	-	-
663	-	-	-	-	-	-	-	-	-
713	-	-	-	-	-	-	-	-	-
763	-	-	-	-	-	-	-	-	-
823	-	-	-	-	-	-	-	-	-

The expression $\frac{\log ZR}{\beta E}\left(1-\frac{2RT}{E}\right)$ is sensibly constant.

The complexes Fe(pip-dtc)(gly)$_2$, Fe(pip-dtc)$_2$(gly), Fe(pip-dtc)(oxine)$_2$, Fe(pip-dtc)$_2$(oxine), Fe(pip-dtc)$_3$, Fe(morph-dtc)(gly)$_2$, Fe(morph-dtc)$_2$(gly) remain stable upto 483, 503, 513, 515, 473, 443, 503 K respectively, then start decomposing. The decomposition of these complexes continues upto 813, 873, 1213, 1173, 823, 993, 1023 K respectively. The weight loss of 83.02% (calc. 83.57%) for Fe(pip-dtc)(gly)$_2$, 83% (calc. 82.25%) for Fe(pip-dtc)$_2$(gly), 90.93% (calc. 89.73%) for Fe(pip-dtc)(oxine)$_2$, 84.56% (calc. 84.61%) for Fe(pip-dtc)$_2$(oxine), 84% (calc. 85%) for Fe(pip-dtc)$_3$, 78.51% (calc. 78.11%) for Fe(morph-dtc)(gly)$_2$, 82.21% (calc. 82.41%) for Fe(morph-dtc)$_2$(gly) corresponds to the formation of Fe_2O_3 finally. The relevant data needed for plotting the linearization curves are recorded in Table 4 and the linearization plot is shown in Fig. 2a, b.

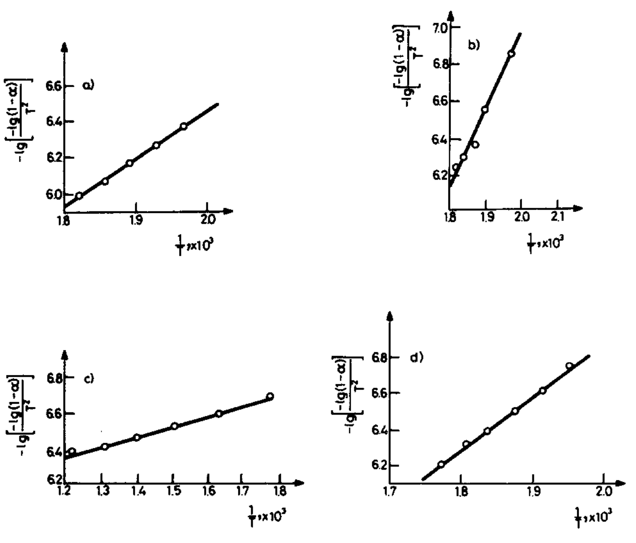


Fig. 2a Kinetic parameters from TG (a) Fe(pip-dtc)(glycine)$_2$; (b) Fe(pip-dtc)$_2$(glycine); (c) Fe(pip-dtc)(oxine)$_2$; (d) Fe(pip-dtc)$_2$(oxine)

The decomposition temperature for the complexes lies in the range of 443-1213 K (Table 4). The decomposition takes place in one step in each case leading to the formation of Fe_2O_3 at the end of the step. The order of

Table 5 Thermal data for mixed ligand iron(III) complex

Complexes	TG		
	Temp. range, K	n, (order of reaction)	E^*, kcal·mol^{-1}
Fe (pip-dtc)(gly)$_2$	483-813	1	10.95
Fe (pip-dtc)$_2$(gly)	503-873	1	16.99
Fe (pip-dtc)(oxine)$_2$	513-1213	1	12.67
Fe (pip-dtc)$_2$(oxine)	515-1173	1	14.64
Fe (pip-dtc)$_3$	473-823	1	16.77
Fe (morph-dtc)(gly)$_2$	443-993	1	12.92
Fe (morph-dtc)$_2$(gly)	503-1023	1	11.26

reaction in each case in one and the activation energy is higher in the case of complexes where the ratio is 1:2:1 (f2 for dtc) for pip-dtc complexes (Table 5). No such observation has been observed for morph-dtc complexes.

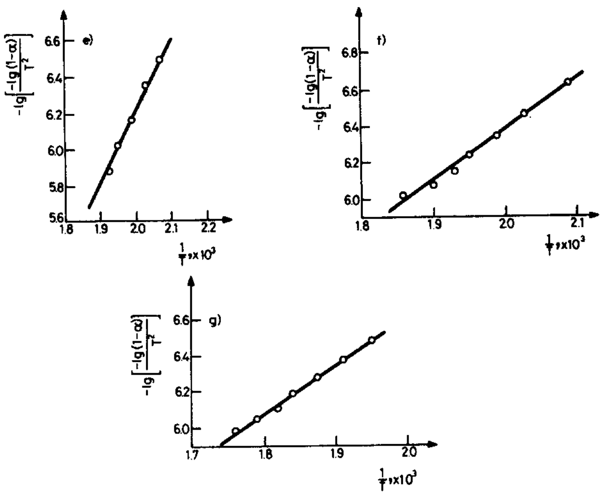
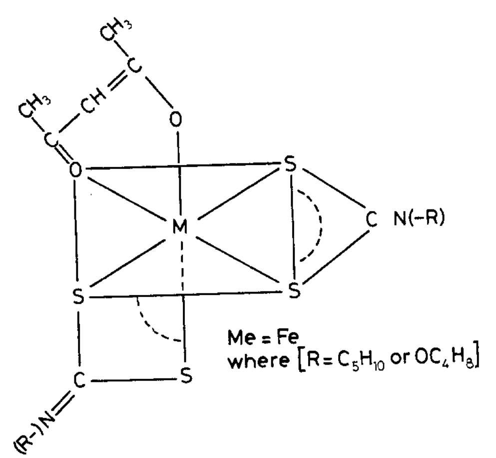


Fig. 2b Kinetic parameters from TG (e) Fe(pip-dtc)$_3$; (f) Fe(morph-dtc)$_2$(gly)$_2$; (g) Fe(morph-dtc)$_2$(glycine)

On the basis of studies reported so far mixed ligand complexes of iron(III) are octahedral in nature. Some of the complexes are high spin com-



plexes and some are low spin complexes. Tentative structures to one of them may be assigned as follows (i.e. for glycine complex).

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Zusammenfassung — Durch Reaktion von Fe(III)-salzen mit dem Natriumsalz der Piperidin-dithiocarbaminsäure oder der Morpholin-dithiocarbaminsäure und Acetylaceton/Oxin/Glycin in verschiedenem Molverhältnis wurden drei Typen von Fe(III)-komplexen hergestellt: $Fe(A)_3$, $Fe(A)_2(A')$ und $Fe(A)(A')_2$ mit A = Piperidyldithiocarbamat oder Morpholyldithiocarbamat und A' = Glycin/Oxin/Acetylaceton. Die einzelnen Komplexe wurden mittels Elementaranalyse, Messungen der magnetischen Suszeptibilität, IR- und Elektronenspektren sowie Thermoanalyse beschrieben. Elektronenspektren zufolge verfügen alle der Komplexe über eine verzerrte oktaedrische Geometrie. Bei diesen Eisen(III)-komplexen liegt das magnetische Moment der Normalkomplexe im Bereich 5.88-6.00 und das der Durchdringungskomplexe im Bereich 3.36-4.34 B.M. TG-Untersuchungen zeigten eine einstufige Zersetzung der Komplexe unter Bildung von Fe_2O_3 als Endprodukt.