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Note

Spectral and thermal characterization of mixed-ligand coordination complexes of Fe(II) and Fe(III) with 2-furan thiocarboxyhydrazide as primary and picolinic/dipicolinic acid as co-ligand

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INTRODUCTION

In addition to the donor capability [1] of sulphur it has been observed that sometimes the presence of sulphur in a compound increases its therapeutic value. Chelates of metal ions with acylthiohydrazides have been reported in the literature [2–5] but the thermal behaviour of the mixed-ligand complexes of Fe(II) and Fe(III) with 2-furan thiocarboxyhydrazide as primary ligand and picolinic or dipicolinic acid as co-ligand has not been studied previously. In the present study, we report the spectral and thermal characterization of these compounds.

EXPERIMENTAL

Materials and methods

2-Furan thiocarboxyhydrazide (fthH) was prepared according to a literature procedure [6]. The metal was analysed gravimetrically as oxide after decomposing the complexes with concentrated HNO_3. IR spectra were scanned on Beckmann and Perkin–Elmer-221 spectrophotometers. Thermogravimetric analyses were carried out on a Stanton automatic electrobalance with a heating rate of $5\,^\circ C\ min^{-1}$.

Preparation of the complexes

Fe(III) complexes

To a hot ethanolic solution (10 mmol) of the metal(III) salt, a hot ethanolic solution of the thiohydrazide (10 mmol) was gradually added. The reaction mixture was refluxed for 3 h on a water bath. Brick red and light brown solids separated out on cooling the solution in an ice bath. They were filtered off, washed with acetone and dry ether, and then dried in vacuo.

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A mixture of an aqueous suspension of the complex and an ethanolic solution of the pyridine carboxylic acid (picolinic/dipicolinic acid) (picH/dipic) was refluxed for 2 h, and then sodium acetate trihydrate (1 g) was added. The solution was kept in a refrigerator for 12 h and the precipitated compounds were filtered off, washed with acetone and dry ether and then dried in vacuo.

Fe(II) complexes

A hot ethanolic thiohydrazide solution (10 mmol) and an aqueous solution of the metal(II) salt were mixed with stirring, then ethanolic KOH was added drop by drop to the reaction mixture. The reddish solid complexes which separated out in a nitrogen atmosphere were filtered off, washed, and dried in vacuo over anhydrous $CaCl_2$. In the case of the iodo complex, an aqueous solution of KI was added in slight excess over the stoichiometric amount.

An aqueous suspension of the complex was refluxed with the ethanolic solution of picolinic/dipicolinic acid for 4 h. The mixed complexes which separated out on cooling were filtered off and washed with a little ethanol and dry ether, and then dried in vacuo.

RESULTS AND DISCUSSION

The mixed complexes are fairly stable, except the iodo complex which slowly decomposes after some time. They are insoluble in water, chloroform, acetone and ethanol, but dissolve appreciably in dimethylformamide (DMF) and dimethyl sulphoxide (DMSO). Analytical data tabulated in Table 1 suggest a 1 : 1 : 1 (M–L–L′) stoichiometric composition for all the complexes. Conductance data in DMSO (10^{-3} M solution) recorded in Table 1 show their electrolytic nature except that of [Fe(fthH)(dipic)]. The magnetic moment values (5.84–5.98 BM) suggest a spin-free octahedral structure [7].

Thermal behaviour

The perchlorate complex decomposes violently with the evolution of heat. A DTG curve of this complex reveals one sharp exothermic peak at about 160 °C. At this temperature, the complex explodes with generation of much smoke due to the oxygen content of the perchlorate. TG studies of the present mixed coordination complexes revealed that first of all water is lost at 150–160 °C from the Fe(II) sulphate, Fe(II) chloride and Fe(II) chlorate complexes of the thiohydrazide and picolinic acid. The weight loss corresponds to one molecule of water; moreover, the water molecule is present in the coordination sphere of these complexes as it is lost above 150 °C. The presence of a water molecule in the coordination sphere is further verified by the IR spectra of the complexes. Further, sharp decomposition accompanied

TABLE 1

Analytical and conductance data of Fe(II) and Fe(III) coordination complexes

Complex	Analysis found (Calc.)						ΔM
	%C	%H	%N	%M	%S	%Halogen	(ohm^{-1} cm^2 mol^{-1})
[Fe(fthH)(picH)H_2O]SO_4	32.50	3.18	10.36	13.77	15.88	–	42.10
	(32.76)	(3.20)	(10.42)	(13.86)	(15.88)		
Fe(fthH)(dipic)	39.92	2.49	11.50	15.30	8.76	–	3.20
	(39.68)	(2.48)	(11.57)	(15.39)	(8.81)		
[Fe(fthH)(picH)H_2O]Cl_2	34.68	3.42	11.01	14.86	8.53	18.64	78.20
	(34.94)	(3.44)	(11.11)	(14.78)	(8.47)	(18.76)	
[Fe(fthH)(picH)I]I	22.87	1.90	7.34	9.67	5.52	44.48	40.91
	(22.98)	(1.91)	(7.30)	(9.71)	(5.56)	(44.16)	
[Fe(fthH)(picH)Cl]Cl_2	30.71	2.56	9.89	13.15	7.45	24.74	78.10
	(30.89)	(2.57)	(9.83)	(13.07)	(7.49)	(24.89)	
[Fe(fthH)(dipic)]Cl	36.40	2.26	10.46	14.13	8.07	8.94	40.42
	(36.15)	(2.25)	(10.54)	(14.02)	(8.03)	(8.90)	
[Fe(fthH)(picH)NO_3]$(NO_3)_2$	26.18	2.18	16.42	10.92	6.29	–	80.02
	(26.04)	(2.17)	(16.57)	(11.01)	(6.31)		
[Fe(fthH)(dipic)]NO_3	33.64	2.10	13.10	13.03	7.47	–	39.26
	(33.89)	(2.11)	(13.18)	(13.14)	(7.53)		
[Fe(fthH)(picH)H_2O]·$(ClO_4)_2$	25.84	2.55	8.23	11.11	6.27	–[a]	78.90
	(26.09)	(2.57)	(8.30)	(11.04)	(6.32)		

[a] Not estimated.

TABLE 2

Thermogravimetric measurements of Fe(II) and Fe(III) mixed coordination complexes

Complex	TG		
	Temp. range (°C)	%Loss	
		Found	Calc.
[Fe(fthH)(picH)H_2O]SO_4	150–160	4.50	4.47
	175–190	34.75	35.00
	450–460	60.88	60.35
[Fe(fthH)(dipic)]	180–190	45.90	45.47
	480–500	55.50	55.98
[Fe(fthH)(picH)H_2O]Cl_2	150–160	4.80	4.76
	175–190	37.70	37.32
	450–470	58.20	57.72
[Fe(fthH)(picH)I]I	175–190	43.08	43.48
	450–460	72.90	72.20
[Fe(fthH)(picH)Cl]Cl_2	175–190	28.60	28.79
	450–470	62.00	62.61
[Fe(fthH)(dipic)]Cl	180–190	41.74	41.42
	450–470	59.40	59.85
[Fe(fthH)(picH(NO_3)]$(NO_3)_2$	175–190	27.50	27.27
	480–500	65.00	64.58
[Fe(fthH)(dipic)](NO_3)	180–190	38.50	38.83
	470–500	62.00	62.41
[Fe(fthH)(picH)H_2O]$(ClO_4)_2$	150–160	3.60	3.56
	175–190	28.10	27.87
	470–490	68.00	68.42

by an exothermic peak (at about 210 °C) in the DT curve takes place in all the complexes at 190 °C when picolinic/dipicolinic acid is eliminated. In the end, thiohydrazide is also lost at about 400 °C and cleavage of the metal–ligand bond takes place. An endothermic peak is seen in the DTA thermogram at about 430 °C. The results of thermal analysis are presented in Table 2.

IR spectra

In the IR spectra of mixed complexes, thioamide bands I and II, occurring at 1530 and 1305 cm^{-1} in the thiohydrazide, show positive shifts of 30–40 cm^{-1} while band IV, seen at 810 cm^{-1} as a sharp band, is shifted to a low frequency band (770–780 cm^{-1}). These observations show that the sulphur of the thioamide group is involved in bond formation with the metal [8,9]. The bands characteristic of a primary amino group [10] show negative shifts of the order of 15–25 cm^{-1} in all the complexes, indicating coordination through its nitrogen atom. The coordination through the nitrogen atom [11] is further evidenced by a slight negative shift of 10–15 cm^{-1} in the

$\delta(NH_2)$ (deformation band) occurring at 1630 cm^{-1} in the ligand. The ligand shows strong bands at 610 and 590 cm^{-1}, assigned to furan ring-deformation modes [11]. These bands show a red shift of 20–30 cm^{-1} on complexation, indicating metal–ligand bonding through the furyl oxygen atom.

The C–C, C=N and ring stretching absorptions present at 1600–1400 cm^{-1} in the spectrum of picolinic/dipicolinic acid are shifted to higher frequency bands (1630 vs, 1605, 1485 cm^{-1}) in the complexes which suggests the donation of electrons from the ring nitrogen to the metal.

The shifting of the 1650 and 1520 cm^{-1} bands of the picolinic acid ligand to lower frequency (about 1640 and 1510 cm^{-1}) and the shifting of the 1590 cm^{-1} band to higher frequency (about 1600 cm^{-1}) suggest the coordination of the metal through the carboxylic acid moiety.

In the spectra of mixed complexes with dipicolinic acid (as co-ligand), the $\nu_{as}(COO)$ and $\nu_s(COO)$ bands show a negative shift of about 40 cm^{-1} and the band due to $\delta(OH)$ is not detectable, indicating the involvement of oxygen atoms of deprotonated OH groups in coordination, and eliminating the possibility of the participation of the carbonyl oxygen atom [12].

In the spectra of Fe(II) sulphate, Fe(II) chloride and chlorate complexes, two bands at 3470 cm^{-1} and 830–840 cm^{-1} are observed, which are assumed to be due to the presence of coordinated water molecules. Some non-ligand bands exist at 350–370, 300–320 and 460–470 cm^{-1} in the spectra of complexes which may be assigned to ν_{M-N}, ν_{M-S} and ν_{M-O} vibrations. In the iodo complex of Fe(II) and the chloro complex of Fe(III) with picolinic acid, a band at 210–220 cm^{-1} is observed which may be due to ν_{M-X} (X = I, Cl). In the perchlorate complex, the strong ν_3 band and a strong ν_4 band appear at about 1085 and 620 cm^{-1}, indicating tetrahedral symmetry and non-coordination of perchlorate [11,12]. The presence of the ν_3 band around 1355 cm^{-1} in the nitrate complexes shows that ionic nitrate (D_{3h}) is present in these complexes but in the nitrate complex of Fe(III) with picolinic acid as co-ligand, two NO stretching bands at 1420 and 1308 cm^{-1} also exist, showing the presence of unidentate coordination of the nitrate group. In the spectrum of the Fe(II) sulphate complex, one stretching band (ν_3) at about 1135 cm^{-1} is observed indicating T_d symmetry of the ionic sulphate.

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