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STRUCTURAL AND THERMAL ANALYSIS OF SILICON ISOTHIOCYANATES COMPLEXES OF Fe(III) AND Mn(II)

A. Syngollitou-Kourakou and *I. Tossidis*

DEPT. OF GENERAL AND INORGANIC CHEMISTRY,
ARISTOTELIAN UNIVERSITY, P.O. BOX 135, THESSALONIKI 54006, GREECE

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New complexes of Fe(III) and Mn(II) with $R_xSi(NCS)_{4-x}$ as ligands have been prepared and characterized. The structure of the new compounds are discussed on the basis of their spectroscopic (IR and UV-Vis), magnetic susceptibility and thermal data.

Very little has yet been reported on the nucleophilic reactivity of silicon isothiocyanates of the type $R_xSi(NCS)_{4-x}$ [1–4]. $(CH_3)_3SiNCS$ shows nucleophilic behaviour [4] and has been reported to be a —HNCS donor [5]. Recently, $(CH_3)_2Si(NCS)_2$ and $(CH_3)_3SiNCS$ have been employed as ligands to prepare complexes with $PdCl_2$ [6]. The structure and donor capacities of silicon isothiocyanate products have also been described [7]. It has been reported that, when treated with BuLi and $(CH_3)_xSi(NCS)_{4-x}$, several tetrahydroquinoline products exhibited antiulcer and antisecretory activity and, accordingly were used as pharmaceutical intermediates [8]. It has also been described that $Si(NCS)_4$ reacts with some silyl esters to give products with antibacterial activity [9].

As a continuation of our previous work on complexes with alkylsilicon isothiocyanates as ligands, we present here results on the preparation of eight novel complexes of Fe(III) and Mn(II) with $(CH_3)_xSi(NCS)_{4-x}$, where $x=0$, 1, 2 and 3. Their IR and electronic spectra, together with the thermal properties of the Fe(III) complexes, are also reported and discussed.

Experimental

a) Preparation of the complexes

The ligands were prepared by published methods [10, 11]. Their complexes were synthesized in a similar way, and the following example is representative.

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In a three-necked flask equipped with a magnetic stirrer, a reflux condenser and a separatory funnel, 2 mmole of metal chloride was dissolved in 50 ml CCl_4. The ligand $Si(NCS)_4$ (2.2 mmole), dissolved in 50 ml CCl_4, was added slowly via the separatory funnel, under continuous stirring, with cooling of the three-necked flask in an ice-bath. The coloured mixture which was produced was refluxed for 3 h, affording a residue, which was filtered off, washed with dry ethanol and dry ether, and dried under vacuum above P_2O_5 for 24 h.

b) Physical measurements

Infrared spectra were recorded in the region 4000–250 cm^{-1} on a Perkin–Elmer 467 spectrophotometer, using KBr pellets. Electronic spectra were obtained on a Perkin–Elmer Hitachi 200 spectrophotometer, in the solid state, with Nujol mulls. The elemental analysis of C, H and N was performed on a Perkin–Elmer 240 elemental analyser. The metal determinations were carried out by published methods [12].

The thermal decomposition was studied on a Mettler TA 2000 system at a heating rate of 6 deg/min, in the temperature region 25–900° for all the complexes, with a sample mass of 20–40 mg and α-Al_2O_3 as reference. The measurements were performed in a dynamic atmosphere of nitrogen. The chart speed was maintained at 5 mm/min and the same platinum crucible was used throughout the experimental work.

Results and discussion

Iron(III) chloride and manganese(II) chloride react with $Si(NCS)_4$, $(CH_3)_3SiNCS$, $(CH_3)_2Si(NCS)_2$ and $(CH_3)Si(NCS)_3$ in CCl_4 solution to produce coloured complexes which are not air stable, and which are insoluble in the common organic solvents. This indicates that they are polymeric in nature. The new compounds were found to correspond to the general types $R_xSi(NCS)_{4-x} \cdot yMX_2$ or $R_xSi(NCS)_{4-x} \cdot yMX_3$, where $x = 0, 1, 2$ and 3 and $y = 4, 3, 2$ and 1, regardless of the amount of the ligand.

Analytical and infrared data are listed in Table 1, and are based on the data reported previously for the ligands [11, 12]. All the complexes show bands in the regions 2130–2050 cm^{-1}, 700–720 cm^{-1} and 450–430 cm^{-1}, which are assigned to the ν(C—N), ν(C—S) and ν(NCS) vibrations, respectively. From the positions of the above bands, especially the bands at 2115 and 2090 cm^{-1} for the Fe(III) complexes, it is believed [6, 13] that the ligands are coordinated to the metal ions through nitrogen rather than sulfur atoms, as expected to be found in thiocyanate polymer complexes of Fe(III).

Table 1 Analytical and infrared data for the silicon isothiocyanate complexes of Fe(III) and Mn(II)

Compounds	C, %	H, %	N, %	Fe, %	Mn, %	ν(C–N)	ν(C–S)	ν_{as}(Si–C)	ν_{sym}(Si–C)	δ(NCS)	ν(M–N) ν(M–S)
I $(CH_3)_3SiNCS \cdot FeCl_3$	16.80	10.00	4.30	19.80		2110vs	2090w	730m	708w	637vs	430m	380w
	(16.37)	(9.07)	(4.77)	(19.02)								
II $(CH_3)_2Si(NCS)_2 \cdot 2FeCl_3$	8.90	1.08	5.80	22.30		2115s	2095s	720m	715m	640s	445w	375w
	(9.63)	(1.21)	(5.61)	(22.31)								300m
III $CH_3Si(NCS)_3 \cdot 3FeCl_3$	6.05	0.50	5.92	23.10		2112s	2090s	730m	700m	660s	455m	293w
	(6.82)	(0.42)	(5.96)	(23.79)								298m
IV $Si(NCS)_4 \cdot 3FeCl_3$	5.90		8.10	23.10		2110s	2095s	720m	710m	655m	430m	300m
	(6.43)		(7.49)	(22.43)								290m
V $(CH_3)_3SiNCS \cdot MnCl_2$	18.80	3.70	5.10		22.00	2130s	2085s	720m	700m	650s	440m	340m
	(18.69)	(3.52)	(5.44)		(21.37)							280s
VI $(CH_3)_2Si(NCS)_2 \cdot 2MnCl_2$	13.20	1.72	7.08		31.70	2125m	2060m	735m	705m	640vs	435s	330m
	(13.53)	(1.70)	(7.88)		(30.94)							287s
VII $CH_3Si(NCS)_3 \cdot 3MnCl_2$	8.15	0.48	7.40		28.60	2130s	2090s	740m	690m	645s	450m	340m
	(8.07)	(0.50)	(7.06)		(27.70)							285m
VIII $Si(NCS)_4 \cdot 4MnCl_2$	6.00		7.20		29.60	2125m	2050s	745m	690w	630s	430s	350m
	(6.29)		(7.33)		(28.77)							280m

Table 2 Solid state magnetic moments and electronic spectra of the new silicon isothiocyanate complexes of Fe(III) and Mn(II)

Compunds	μ_{eff}(BM)[a]		Band maxima			
I $(CH_3)_3SiNCS \cdot FeCl_3$	5.90	45.0[b]	38.5	25.0sh	22.0	12.0
II $(CH_3)_2Si(NCS)_2 \cdot 2FeCl_3$	5.92	44.8	39.0	24.6	21.7	11.8
III $(CH_3)Si(NCS)_3 \cdot 3FeCl_3$	5.89	44.8	38.8	24.8 sh	21.8	11.9
IV $Si(NCS)_4 \cdot 3FeCl_3$	5.90	44-7	38.0	25.0 sh	22.0	12.0
V $(CH_3)_3SiNCS \cdot MnCl_2$	5.90	45.0	37.5	27.3	25.8	20.0
VI $(CH_3)_2Si(NCS)_2 \cdot 2MnCl_2$	5.89	44.7	38.0	27.0	26.0	19.0
VII $(CH_3)Si(NCS)_3 \cdot 3MnCl_2$	5.91	44.8	38.5	28.1	26.6	18.9
VIII $Si(NCS)_4 \cdot 4MnCl_2$	5.92	45.1	39.0	28.0	26.2	19.1

[a] = measured at room temperature, [b] = ν/kK.

All the studied complexes have spectral bands (Table 2) in the typical pseudo-octahedral range, which are in good agreement with those of known octahedral and pseudo-octahedral complexes of the analogous isothiocyanate complexes [14, 15].

The TG and DTA curves reveal that most of the new complexes decompose in three stages, all of them endothermic. Thermal decomposition curves are given in Figs 1–4, while the TG weight loss data and DTA peak temperatures are presented in Table 3.

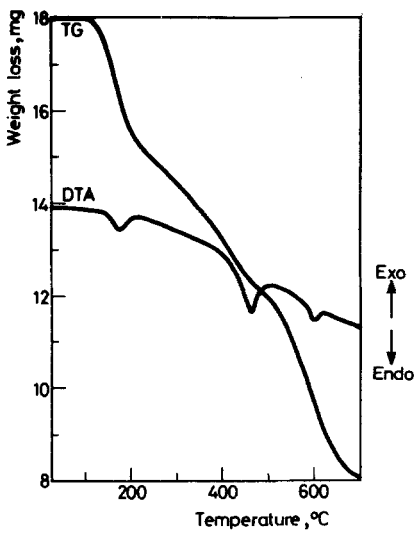

Fig. 1 Thermoanalytical curves for $(CH_3)_3SiNCS \cdot FeCl_3$ in nitrogen

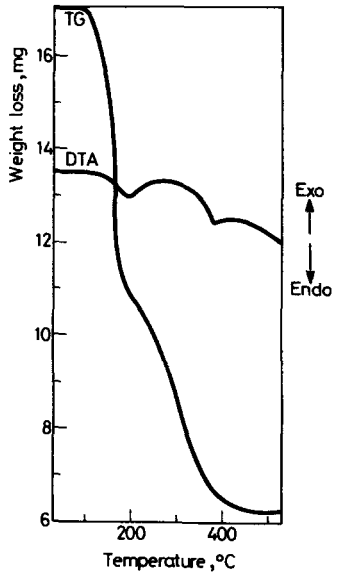

Fig. 2 Thermoanalytical curves for $(CH_3)_2Si(NCS)_2 \cdot 2FeCl_3$ in nitrogen

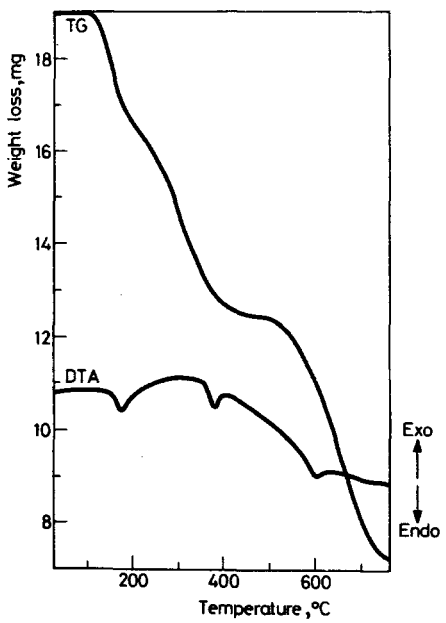

Fig. 3 Thermoanalytical curves for $CH_3(NCS)_3 \cdot 3FeCl_3$ in nitrogen

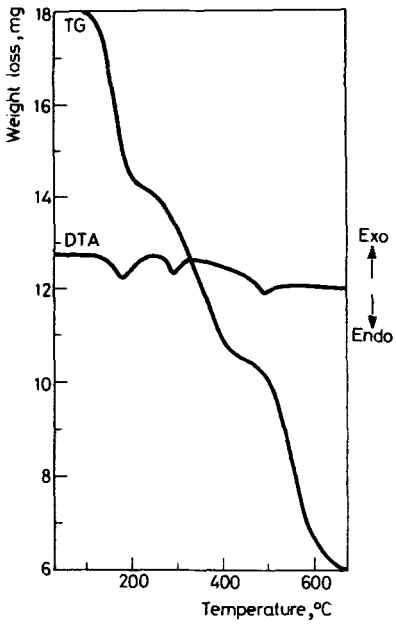

Fig. 4 Thermoanalytical curves for $Si(NCS)_4 \cdot 3FeCl_3$ in nitrogen

Table 3 Thermoanalytical results (TG/DTA) of the silicon isothiocyanate complexes of Fe(III) and Mn(II)

Complex	DTA peak temp., C	Stage	TG temp. range, °C	Mass loss, %	Evolved moiety	
					formula	mass calcd., %
I $(CH_3)_3Si(NCS) \cdot FeCl_3$	170 (−)	a	110–210	14.8	$3CH_3$	15.36
	460 (−)	b	210–500	18.6	SiNC	18.45
	600 (−)	c	500–680	22.4	2Cl	23.94
		residue	>700	44.2	FeSCl	41.93
II $(CH_3)_2Si(NCS)_2 \cdot 2FeCl_3$	190 (−)	a	100–200	35.8	$(CH_3)_2Si(NC)_2$ + +2Cl	36.31
	380 (−)	b	200–450	27.6	4Cl	28.44
		residue	>500	36.6	Fe_2S_2	35.26
III $CH_3Si(NCS)_3 \cdot 3FeCl_3$	180 (−)	a	110–200	12.7	CH_3SiN_3	12.13
	380 (−)	b	200–450	21.2	3C + 3Cl	20.25
	600 (−)	c	500–750	28.1	6Cl	30.24
		residue	>750	38.0	Fe_3S_3	37.38
V $Si(NCS)_4 \cdot 3FeCl_3$	180 (−)	a	110–230	21.2	$(SCN)Si(NC)_3$	21.98
	290 (−)	b	230–420	20.0	4Cl	18.98
	490 (−)	c	460–650	25.2	5Cl	23.73
		residue	>650	33.6	Fe_3S_3	35.31

(−): endothermic, (+): exothermic peak.

Characteristic thermal decomposition features of the studied compounds

1. $(CH_3)_3SiNCS \cdot FeCl_3$

This complex decomposes in three steps, the first two being consecutive. All the decomposition stages are endothermic, as is seen from the corresponding DTA curve. Subsequently, as the temperature is raised, the complex decomposes further and finally yields a residue of {FeSCl}.

2. $(CH_3)_2Si(NCS)_3 \cdot 2FeCl_3$

The thermal decomposition of this complex takes place in only two stages, which are endothermic in nature, as shown by two endothermic peaks, at 190° and 380°, in the DTA curve. When the sample is heated to above 500°, it leaves $\{Fe_2S_2\}$ as residue.

3. $CH_3Si(NCS)_3 \cdot 3FeCl_3$

The thermal degradation of this complex occurs in three well-separated stages, with three endothermic peaks in the DTA curve (180°, 380° and 600°). It leaves $\{Fe_3S_3\}$ as final residue.

4. $Si(NCS)_4 \cdot 3FeCl_3$

When heated in a dynamic nitrogen atmosphere, this complex decomposes in three steps; the decomposition processes are accompanied by three endothermic peaks, at 180°, 290° and 490°. The end-product is $\{Fe_3S_3\}$.

Conclusions

The available thermal data allow the suggestion that the thermal decompositions of the Fe(III) complexes begin at rather low temperature (110°) with partial removal of the ligands. The TG curves of all the complexes show decompositions occurring in three well-defined steps, all of them endothermic in nature. The first step indicates the removal of organosilicon species, except in the case of complex I. The final residue in all the studied decompositions is a compound containing iron and sulfur. This implies that the M—S bond is more thermally stable than the C—S bond.

On the basis of the above arguments, the following decomposition mechanism is proposed:

$$(CH_3)_{4-x}Si(NCS)_x \cdot yFeCl_3 \rightarrow \{(CH_3)_{4-x}Si(NC)_x\} + \{yFeCl_3 \cdot xS\}$$

$$\{yFeCl_3 \cdot xS\} \rightarrow 3y\,Cl + \{Fe_yS_x\}$$

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Zusammenfassung — Es wurden neue Fe(III)- und Mn(II)-Komplexe mit Liganden der Formel $R_xSi(NCS)_{4-x}$ hergestellt und beschrieben. Bei der Diskussion der Struktur dieser neuen Verbindungen wurden spektroskopische (IR, UV), thermische Daten und Daten über die magnetische Suszeptibilität verwendet.

Резюме — Получены и охарактеризованы новые комплексы трехвалентного железа и двухвалентного марганца с лигандами $R_xSi(NCS)_{4-x}$. Структура новых соединений обсужден на основе их спектарьлных данных (ИК спектроскопия, абсорбционная спектроскопия в УФ- и видимой области), данных по магнитной восприимчивости и термических данных.