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A THERMAL DECOMPOSITION STUDY OF SOME NICKEL(II)THIOUREACHLORIDE COMPLEXES

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TG/DTA and Thermal Degradation Mass spectrometry (TDMS) data are presented for a series of nickel(II)thiourea chloride complexes: NiL_4Cl_2: L = thiourea or methyl-, dimethyl-, tetramethyl-, di-*n*-butyl, naphthyl-, ethylene- or allylthiourea. Two different thermal decomposition mechanisms are proposed for these complexes, and it is apparent that the thermal decomposition mechanism adopted by a particular complex depends on the structure of the relevant thiourea ligand and not on the nature of the halide ligand or on the existence of geometrical isomerism for these complexes.

Thermoanalytical data for metal complexes of the urea ligand family are sparse. Khattab et al. [1] have established the thermal decomposition mode of urea by TG and DTA. The thermoanalytical data are consistent with biuret as the major decomposition product. Owens et al. [2] have reported a complex two-step decomposition pathway for sym-dichlorobis(2,4,6-trichlorophenyl)urea as derived by TG, DSC and thermal degradation mass spectrometry. Eight major decomposition products were identified including chlorine and ammonium chloride. Srivastava et al. [3] have reported a two-step thermal decomposition pathway for triaquadichloroureamanganese(II) by TG and DTA, involving initial loss of urea from the complex and subsequent decomposition of urea to ammonia and cyanic acid. Airoldi et al. [4] have reported thermochemical, metal-oxygen bond energies, as derived by conventional solution calorimetry, for a series of tetramethylurea metal halide complexes $M(tmu)_2X_2$: M = Zn, Cd or Hg; X = Cl, Br or I. An attempt is made to correlate the thermodynamic data with infrared C—O and C—N stretching frequencies of the substituted urea ligand and the "softness" of the halide ligand.

For thiourea, Jona and Sramko [5] have proposed a two-step decomposition based on TG data, involving ammonium thiocyanate and guanidine thiocyanate as

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intermediates and melam thiocyanate as residue. Shapiro et al. [6] have investigated the thermal fragmentation of a series of 1-substituted,3-phenyl-2-thioureas by mass spectrometry. Deuterium labelling of these compounds enabled general decomposition mechanisms to be proposed.

Jona and Sramko [7] have reported a TG and DTA study of a series of nickel(II) thiourea halide complexes and conclude that thiourea and halide ligands are lost in two steps with NiS formed as residue. A significant aspect of this study is that the thermal decomposition mechanism of these complexes is independent of the nature of the halide ligand. Bailey and Tangredi [8] have reported a very detailed TG study of a wide variety of transition metal, substituted thiourea chloride complexes including dichlorotetra(dimethylthiourea)-nickel(II). The gaseous decomposition products were identified by infrared spectroscopy and mass spectrometry and for all complexes include dimethylthiourea, methylisothiocyanate and hydrogen chloride. It is apparent from this work that complexed and free thiourea thermally decompose via different mechanisms. Venkappayya and Brown [9] have reported a DSC study of some metal diphenylthiourea halide complexes: $M(dpt)_2X_2$ M = Co(II), Zn(II) or Cd(II); X = Cl or Br. For each complex, three endotherms are revealed (nitrogen atmosphere) corresponding to melting and a two-step thermal decomposition. Spitsyn et al. [10] have reported a TG study of several Mo(III) and Mo(V) thiourea halide complexes, which indicates that the primary decomposition involves loss of thiourea from the parent complex. Adi and Murty [11] have reported a TG study of several dioxouranium(IV) thiourea halide complexes which further supports the loss of thiourea during the thermal decomposition of transition metal thiourea halide complexes. Thermal analysis data for non-transition metal thiourea complexes appears to be limited to the series of complexes $MBi(SCN)_2(tu)_2$: M = Li, Na, K, Rb, Cs or NH_4 as reported by Ladzinska-Kulinska [12]. A general thermolysis reaction for these complexes is reported for decomposition in air involving nitrogen, water, sulphur dioxide and carbon dioxide as gaseous products and bismuth metal, bismuth(III)-sulphide and alkali metal sulphate as residues.

Finally, several calorimetric studies have been reported for transition metal thiourea complexes [13–15] and for $[Bi(tu)_3](ClO_4)_3$ in aqueous solution [16], which collectively reveal a scarcity of thermodynamic data for complexes containing metal-sulphur bonds.

This paper presents a preliminary TG/DTA study of thiourea and some substituted thioureas and a detailed thermal analysis study of several nickel(II)thiourea chloride complexes. The relevant thermal decomposition mechanisms for these complexes, proposed on the basis of TG data, have been confirmed using Thermal Degradation Mass Spectrometry (TDMS).

Experimental

The trans-nickel(II)thiourea chloride complexes were synthesized according to the general procedure of Singh et al. [17] or modifications thereof given by Carlin and Holt [18], Bailey et al. [19] or Furlani et al. [20], which involve refluxing a 2 : 1 mole ratio of the thiourea with nickel chloride hexahydrate in ethanol for at least one hour followed by recrystallization of the green to brown product from ethanol with subsequent vacuum drying. Yields vary from 50–90%. Hexa-aquanickel(II) chloride was obtained from BDH Chemicals (AnalaR Grade) and thioureas were obtained from Aldrich Chemical Co. U.K.

Trans-Dichlorotetrakis(thiourea)nickel(II): Ni(Tu)$_4$Cl$_2$
Yield 90%: m.p. 224–226 (Lit. [14] 225–226 °C); $\mu = 3.19$ B.M.
Calcd. forNi[SCN_2H_4]$_4$$Cl_2$: C, 11.06; H, 3.71; N, 25.81;
Found: C, 11.12; H, 3.67; N, 25.47%.

Trans-Dichlorotetrakis(N-methylthiourea)nickel(II): Ni(MTu)$_4$Cl$_2$
Yield 51%: m.p. 144–156 °C; $\mu = 3.17$ B.M.
Calcd. for Ni[$SC_2N_2H_6$]$_4$$Cl_2$: C, 19.62; H, 4.90; N, 22.87;
Found; C, 19.16; H, 4.68; N, 24.56%.

Trans-Dichlorotetrakis(N,N'-dimethylthiourea)nickel(II) Ni(DMTu)$_4$Cl$_2$
Yield 65%: m.p. 134–135 °c; $\mu = 2.81$ B.M.
Calcd. for Ni[$SC_3N_2H_3$]$_4$$Cl_2$: C, 26.36; H, 5.86; N, 20.50;
Found: C, 26.21; H, 6.01; N, 20.11%.

Trans-Dichlorotetrakis(N,N'-di-n-butylthiourea)nickel(II): Ni(DBTu)$_4$Cl$_2$
Yield 94%: m.p. 62.8–63.5 °C; $\mu = 3.03$ B.M.
Calcd. for Ni[$SC_9N_2H_{20}$]$_4$$Cl_2$: C, 48.93; H, 9.13; N, 12.69;
Found: C, 48.63; H, 8.94; N, 12.18%.

Trans-Dichlorotetrakis (1-naphthyl-2-thiourea) nickel(II): Ni(NAPTu)$_4$Cl$_2$
Yield 66%: $\mu = 2.87$ B.M. (Lit. [18] 2.89 B.M., 298 K)
Calcd. for Ni[$SC_{11}N_2H_{10}$]$_4$$Cl_2$: C, 56.35; H, 4.27; N, 11.95;
Found: C, 56.92; H, 4.32; N, 11.54%.

Trans-Dichlorotetrakis(ethylenethiourea)nickel(II): Ni(ETu)$_4$Cl$_2$
Yield 64%: m.p. 182–184 °C; $\mu = 2.96$ B.M. (Lit. [18] 2.98 B.M., 258 K).
Calcd. for Ni[$SC_3N_2H_6$]$_4$$Cl_2$: C, 26.75; H, 4.46; N, 20.81;
Found: C, 26.49; H, 4.78; N, 21.31%.

Trans-Dichlorotetrakis(1,1,3,3-tetramethylthiourea)nickel(II): Ni(TMTu)$_4$Cl$_2$
Yield 71%: m.p. 80–82 °C
Calcd. for Ni[$SC_5N_2H_{12}$]$_4$$Cl_2$: C, 36.48; H, 7.30; N, 17.03;
Found: C, 32.63; H, 7.41; N, 15.10%.

Trans-Dichlorotetrakis(allylthiourea)nickel(II): Ni(ALTu)$_4$Cl$_2$
Yield 58%: m.p. 64–65 °C; $\mu = 3.36$ B.M.
Calcd. for Ni[SC$_4$N$_2$H$_8$]$_4$Cl$_2$: C, 32.30; H, 5.38; N, 18.84;
Found: C, 32.07; H, 5.18; N, 18.62%.

Cis-nickel(II) thiourea chloride complexes were synthesized according to the procedure given by Carlin and Holt [18] which involves refluxing the corresponding trans isomer in ethanol for 48 hours.

Cis-dichlorotetrakis(thiourea) nickel(II): cis-Ni(Tu)$_4$Cl$_2$
m.p. 216–218 °C; $\mu = 3.61$ B.M.
Calc. for Ni[SCN$_2$H$_4$]$_4$Cl$_2$: C, 11.06; H, 3.71; N, 25.81;
Found: C, 10.85; H, 3.57; N, 25.66%.

Cis-dichlorotetrakis(ethylenethiourea)nickel(II): cis-Ni(ETu)$_4$Cl$_2$
m.p. 188–190 °C; $\mu = 3.27$ B.M. (Lit. [18] 3.29 B.M., 260 K)
Calc. for Ni[SC$_3$N$_2$H$_6$]$_4$Cl$_2$: C, 26.75; H, 4.46; N, 20.81;
Found: C, 26.52; H, 4.38; N, 20.63%.

Microanalysis data were obtained from AMDEL Microanalytical Service, Melbourne, Australia.

Melting points were obtained using a Mettler FP2 Hot-Stage Microscope system. Magnetic moments at ambient temperature were determined (± 0.05 B.M.) using a Mettler Gouy Balance with a Varian: Type V2901 regulated magnetic power supply. Corrections for diamagnetism were made using the appropriate magnetic susceptibility constants [21], and the following diamagnetic corrections were adopted: H, −2.93; C, −6.00; S, −15.00; Cl, −20.10; Ni(II), −11.00; N (open chain), −5.57; N (ring), −4.61; N (monoamide), −1.54; N (diamide, unide), −2.11.

TG/DTA was obtained using a Rigaku–Denki (Thermoflex) Thermal Analysis System (Type 8085), platinum crucibles, a sample mass in the range 5–10 mg, a heating rate of 10 deg min^{-1} and a dynamic dry nitrogen atmosphere. Alumina was used as the thermally inert reference for DTA. X-ray powder patterns were obtained using a Phillips PW1002 X-ray generator and a Weissenberg camera.

Thermal degradation mass spectrometry (TDMS) primarily involved use of a JEOL (JMS-D100) Mass Spectrometer in the electron impact mode and an ionisation voltage of 74 eV. Programmed heating of the sample over the temperature range ambient −400°, within the ionisation chamber, was effected using a JEOL direct probe temperature control: Type MS–DPT01. The TDMS profile is the Total Ion Current *vs.* sample temperature plot. Mass spectra were recorded at appropriate stages throughout the analysis. Thus, TDMS reveals the number and temperature range of the decomposition steps and the nature of the decomposition products.

Results and discussion

Prior to presentation of thermal analysis data for the nickel(II)thiourea chloride complexes, TG/DTA data are given (Table 1) and discussed for the parent thioureas. The TG/DTA profile for thiourea is presented in Fig. 1. For thiourea, Jona and Sramko [5] have proposed the following very complicated, essentially two-step, thermal decomposition mechanism, involving partial conversion of thiourea to ammonium thiocyanate, followed by reaction of thiourea with

Table 1 TG and DTA data for thioureas

	M.P., °C	Thermal stability upper limit, °C	Decomposition endotherms (peak temp.), °C	Total mass loss	Residue mass, %
TU	175–178	197	195 244	97.05	2.95
MTU	119–121	182	130 236	100.00	—
DMTU	60–62	170	75 244	100.00	—
DBTU	63–65	178	74 248	100.00	—
TMTU	75–77	116	92 188	100.00	—
ALTU	70–72	172	80 238	95.38	4.62
ETU	197–200	243	218 334	95.10	4.90
NAPTU	190–192	190	186 190	93.42	6.58

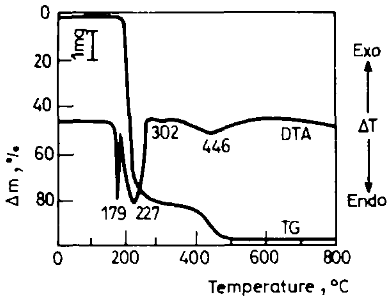


Fig. 1 TG/DTA profiles of thiourea

ammonium thiocyanate to give guanidine thiocyanate, which converts at ~270° to melam thiocyanate which remains as an involatile residue:

$$24CS(NH_2)_{2(S)} \rightarrow 6CS(NH_2)_2 + 18NH_4SCN$$

$$6CS(NH_2)_2 + 18NH_4SCN \rightarrow 6CH_5N_3 \cdot HSCN + 3(NH_4)_2CS_3 + 9NH_4SCN$$

$$6CH_5N_3 \cdot HSCN \rightarrow C_6H_9N_{11} \cdot HSCN_{(S)} + 2NH_3 + 5NH_4SCN$$

The present TG data are consistent with this mechanism, since the calculated overall mass loss for a melam thiocyanate residue is 97.05% compared to 96.88% obtained. Also, a two-step decomposition is noted (Fig. 1).

For substituted thioureas, a single decomposition step is apparent from the relevant TG profiles and two endotherms are revealed from DTA (Table 1). The first DTA endotherm is not associated with mass loss. Thus corresponds to the melting point. The second endotherm is broad and dominant and the corresponding temperature range corresponds to that for approximately total mass loss. Thus, it is apparent that the thermal decomposition mechanism of substituted thioureas is different from that of thiourea.

In the context of interpretation of the derived thermal data for nickel(II) thiourea chloride complexes, it is necessary to review the available structural data for these complexes. X-ray crystallographic data have been published for $Ni(TU)_4Cl_2$ [22] and $Ni(ETU)_4Cl_2$ [23] as prepared by the standard method [17], and may be summarised as NiL_4Cl_2 existing as hexacoordinated nickel units in which the four coordinated sulphur atoms are in a plane above the nickel atom with the two chlorine atoms occupying the axial (trans) positions. All four Ni—S bond lengths are equal (2.464 Å) but the two chlorine atoms occupy non-equivalent positions at 2.40 and 2.54 Å distant from nickel. Thus, trans-distorted octahedral complexes result from the standard synthetic procedure. For the series of complexes presently studied, this stereochemistry is indirectly confirmed by the magnetic moment data which are within the range accepted (2.8–3.4 B.M.) [24] for trans-distorted octahedral nickel(II) complexes.

It is possible, on the basis of TG data, to separate the nickel(II) thiourea chloride complexes into two series, designated Type I and Type II. TG/DTA profiles for Type I and Type II complexes are reproduced in Figs 2 and 3, respectively and the essential data are summarised in Tables 2 and 3, respectively. X-ray powder diffraction data [25] for residues obtained from thermal analysis are summarised in Table 4.

It is apparent that all complexes decompose in two steps. In general, the DTA profiles of these complexes exhibit four endotherms, the first of which is not associated with a corresponding mass loss and represents melting of the complex.

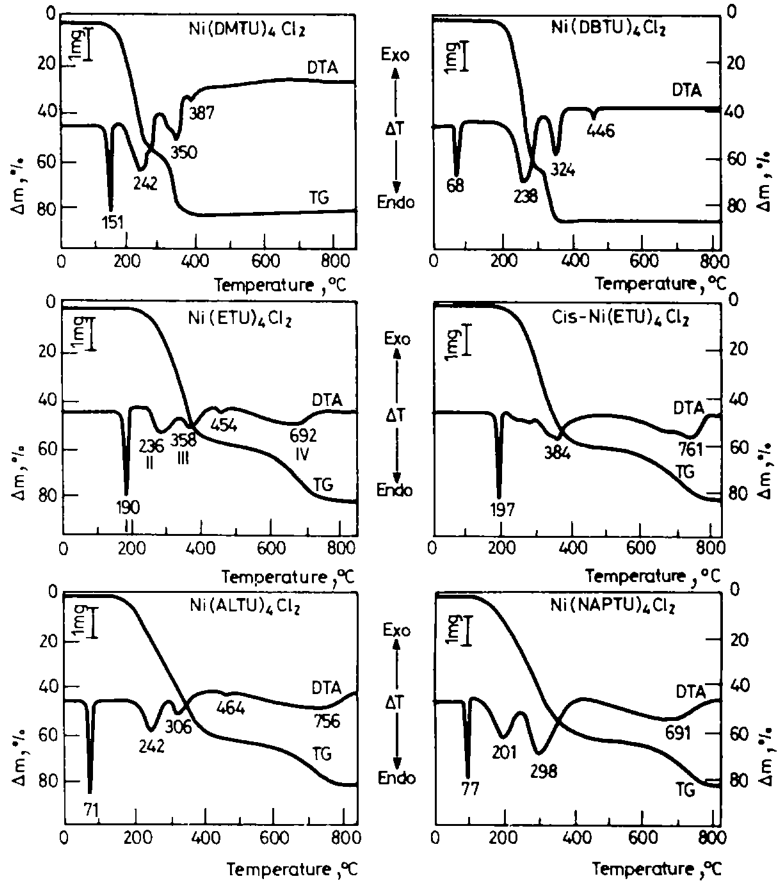


Fig. 2 TG/DTA profiles of type I complexes

The following two endotherms are associated with the first decomposition step of the complex and the fourth endotherm is associated with the second decomposition step of the complex. The X-ray powder patterns of all residues obtained from thermal analysis, characterise these as αNiS [25].

Type I complexes exhibit thermal stability up to about 200°. The TG data for these complexes are consistent with the loss of three thiourea ligands in the first decomposition step and a residue of nickel(II) sulphide. Thus a generalised thermal decomposition mechanism for Type I complexes is proposed as:

$$\mathrm{NiL_4Cl_{2(S)}} \xrightarrow{200\text{–}400^\circ} \underset{\text{intermediate}}{[\mathrm{NiLCl_{2(S)}}]} \xrightarrow{400\text{–}800^\circ} \underset{\text{residue}}{\alpha\mathrm{NiS_{(S)}}}$$

where L = DMTU, DBTU, ETU, ALTU or NAPTU.

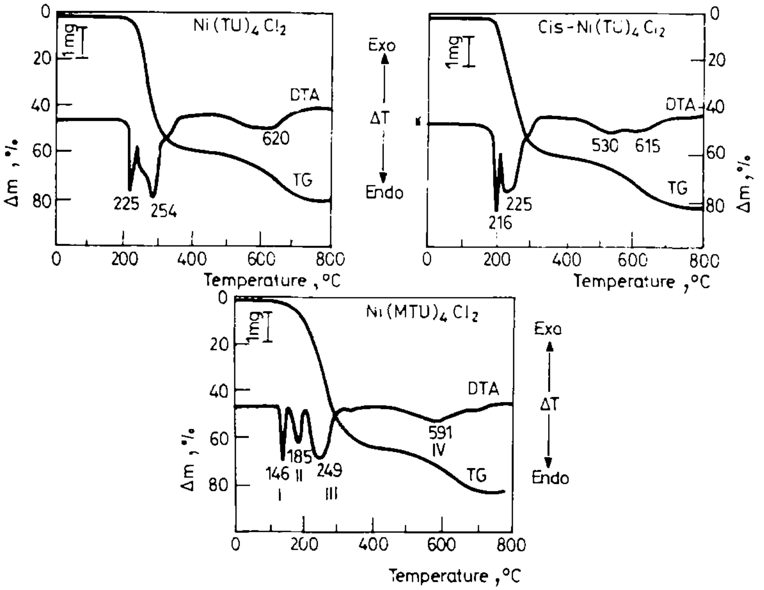


Fig. 3 TG/DTA profiles of type II complexes

Further, the extent of the plateau at 400° in the TG of these complexes, suggests that the intermediate has a finite lifetime. This thermal decomposition mechanism implicitly suggests that both halogen ligands are lost in the second decomposition step and in this respect, this mechanism is in contradiction to that proposed by Sramko et al. [7] which suggested that for these types of complexes, halogen is lost in both decomposition steps.

The TG/DTA data for cis- and trans-Ni(ETU)$_4$Cl$_2$ are very similar, which indicates that geometrical isomerism has no direct influence on the thermal decomposition mechanism of nickel(II)thiourea chloride complexes.

Type II complexes generally exhibit higher thermal stability than Type I complexes. The TG data for these complexes are consistent with the loss of three thiourea ligands and hydrogen chloride in the first decomposition step and a residue of nickel(II) sulfide. Thus, a generalised thermal decomposition mechanism for Type II complexes is proposed as:

$$\mathrm{NiL_4Cl_{2(S)}} \xrightarrow{170\text{–}400^\circ} \underset{\text{intermediate}}{[\mathrm{NiLCl}]_{(S)}} \xrightarrow{400\text{–}750^\circ} \underset{\text{residue}}{\alpha\mathrm{NiS}_{(S)}}$$

where L = TU or MTU.

Further, the extent of the plateau at 400°C, in the TG of these complexes, suggests that the intermediate is not associated with a finite lifetime. This thermal decomposition mechanism implicitly suggests that one halogen ligand is lost in each

Table 2 TG and DTA data for Type I Complexes

Complex[a]	Thermal stability upper limit, °C	Formation temp. of intermediate & residue, °C	Mass loss, %	
			Found (TG)	Theoretical
$Ni(DMTU)_4Cl_2$	178	270	56.5	57.20
		440	83.7	83.38
$Ni(DBTU)_4Cl_2$	190	300	64.2	63.99
		450	87.5	89.71
$Ni(ETU)_4Cl_2$	260	426	58.5	56.94
		800	85.0	83.14
cis-$Ni(ETU)_4Cl_2$	212	430	59.0	56.94
		800	83.5	83.14
$Ni(ALTU)_4Cl_2$	192	400	61.0	58.64
		800	83.0	84.72
$Ni(NAPTU)_4Cl_2$	105	555	64.0	64.64
		810	84.0	86.98

Complex[a]	DTA endotherms, °C			
	I (peak temp.)	II (range)	III (range)	IV (range)
$Ni(DMTU)_4Cl_2$	151	178–292	300–365	—
$Ni(DBTU)_4Cl_2$	68	190–295	310–370	—
$Ni(ETU)_4Cl_2$	190	260–324	335–430	450–760
cis-$Ni(ETU)_4Cl_2$	197	212–300	305–425	470–810
$Ni(ALTU)_4Cl_2$	71	192–290	300–385	505–830
$Ni(NAPTU)_4Cl_2$	97	105–240	245–405	410–820

[a] Trans isomer except where otherwise indicated

decomposition step of the complex and in this respect, this mechanism is consistent with that proposed by Sramko et al. [7] for these types of complexes.

Since Sramko et al. [7] proposed the same thermal decomposition mechanism for NiL_4Cl_2 and NiL_4Br_2, it is inferred that the nature of the halogen ligand has no influence on the thermal decomposition mechanism of these complexes and hence it is concluded that the structure of the thiourea ligand is the controlling mechanism factor.

Rationalisation of Type I and Type II thermal behaviour of nickel(II) thiourea chloride complexes is based exclusively on the magnitude of the inductive effect of the *R*-group substituents of the thiourea ligand. It is necessary to propose an imine structure for the intermediate formed during decomposition of Type II complexes

Table 3 TG and DTA data for Type II complexes

Complex[a]	Thermal stability upper limit, °C	Formation temp. of intermediate & residue, °C	Mass loss, %	
			Found (TG)	Theoretical
$Ni(TU)_4Cl_2$	230	420	59.2	60.77
		815	80.5	79.09
cis-$Ni(TU)_4Cl_2$	225	380	60.5	60.77
		800	82.0	79.09
$Ni(MTU)_4Cl_2$	155	405	62.0	63.30
		800	82.0	81.48

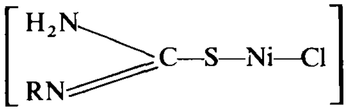
Complex[a]	DTA endotherms, °C			
	I (peak temp.)	II (range)	III (range)	IV (range)
$Ni(TU)_4Cl_2$	225	230–285	440–720	—
cis-$Ni(TU)_4Cl_2$	216	225–315	420–725	—
$Ni(MTU)_4Cl_2$	146	155–190	200–340	430–750

[a] Trans isomer except where otherwise indicated

Table 4 X-ray powder diffraction data for a typical residue obtained from thermal analysis of nickel thiourea chloride complexes

Residue: d(Å), *I*	2.95 vs, 2.58 s, 1.97 s, 1.72 m, 1.51 s, 1.46 m, 1.42 s, 1.34 m, 1.21 w, 1.05 s
αNiS: d(Å), *I*[b]	2.96 vs, 2.58 s, 1.97 s, 1.71 m, 1.52 s, 1.48 m, 1.42 s, 1.33 m, 1.21 w, 1.05 s

[b] From Ref. 25.



Inductive(+ I) effects of alkyl groups decrease markedly with increase in carbon chain length and thus, for the series of thiourea ligands presently considered, thiourea and methylthiourea are associated with the greatest overall inductive electronic effects. Type II thermal behaviour is associated with those complexes incorporating thiourea ligands of relatively large inductive electronic effects. It follows that, for Type II complexes, loss of halogen in the primary decomposition step and concomitant stabilisation of an imine intermediate is assisted by a strong + I electronic shift from the terminal *R*-groups of the thiourea ligand toward the metal centre.

Type II thermal behaviour is further supported by crystallographic data for $Ni(TU)_4Cl_2$ [22], which indicate strong hydrogen-bonding between one thiourea ligand and one chlorine ligand, effecting a distorted octahedral structure with unequal Ni—Cl bond lengths. Thus, loss of one chloride ligand preferentially in the first decomposition step is assisted by intramolecular hydrogen bonding in the lesser substituted complexes.

In addition to having a relatively low inductive (+I) effect, bulky *R*-group substituents such as dibutyl-, allyl-, naphthyl-, are associated with a steric effect which further decreases the effective inductive effect of these groups. As a consequence, Type I thermal behaviour is associated with those complexes incorporating thiourea ligands of relatively small inductive electronic effects. It follows that, for Type I complexes, loss of halogen in the primary decomposition step is not favoured, since there is no assisting transmitted electronic effect from the associated thiourea ligands.

For NiL_4Cl_2 complexes, two different thermal decomposition mechanisms have been proposed and rationalised in terms of the intrinsic structure of the thiourea ligand. Type I thermal behaviour has not been identified previously and hence it is necessary to provide further justifications for this mechanism which appears to be adopted by a majority of these complexes.

Thermal degradation mass spectrometry [26] has been applied recently to assist in the derivation of thermal decomposition mechanisms of metal complexes [27, 28].

TDMS profiles for Type I and Type II complexes are reproduced in Figs 4 and 5, respectively. Decomposition temperatures are relatively low for all complexes due to the vacuum medium. For all complexes, two major peaks are apparent and consistent with a two step decomposition. Interpretation of the mass spectra obtained at strategic stages of the programmed heating of the complexes is assisted on the basis of published mass spectra [29, 30] for thiourea, methylthiourea, dimethylthiourea, dibutylthiourea, allylthiourea, ethylenethiourea and naphthylthiourea.

For Type I complexes, the first TDMS peak (100–250°) corresponds to the loss of the thiourea ligand as confirmed by the presence of intense peaks in the associated mass spectra corresponding to the ions $[R_1R_2NCSNR_3R_4]^+$ (molecular ion), $[R_1R_2NCS]^+$, $[R_3R_4NCS]^+$, $[R_1R_2N]^+$ and $[R_3R_4N]^+$. The presence of the molecular ion confirms intact loss of the thiourea ligand. No chlorine-containing product is apparent from mass spectra taken during the first decomposition step. The second TDMS (250–400°) corresponds to the further loss of the thiourea ligand and hydrogen chloride. A much reduced intensity of the thiourea molecular ion is apparent in mass spectra taken during the second decomposition step which suggests significant in situ decomposition of the remaining thiourea ligand above

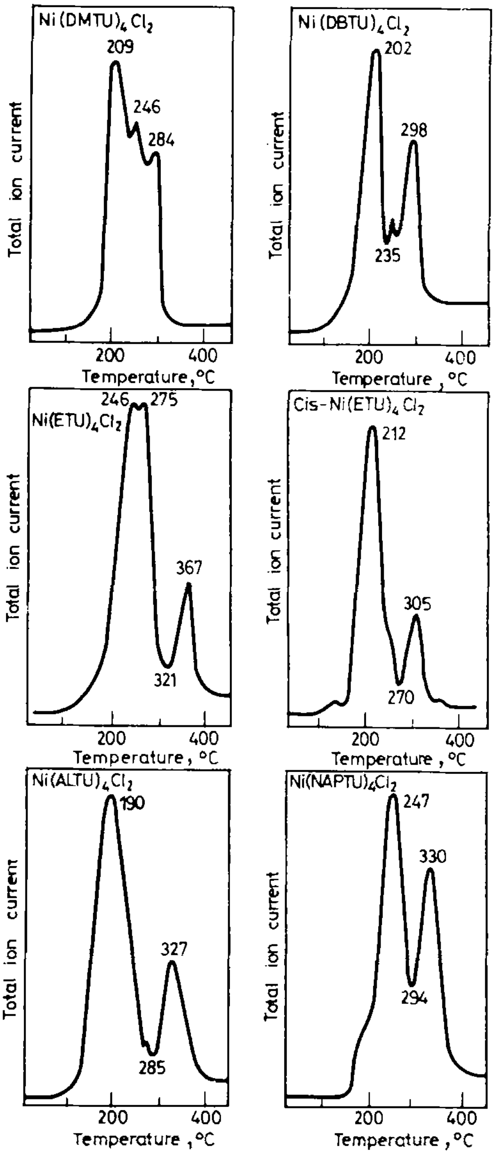


Fig. 4 TDMS profiles of type I complexes

250°. Hydrogen chloride is confirmed by the presence of intense peaks in the associated mass spectra at *m/z* 35, 36, 37, 38. For Type II complexes, the TDMS peaks are in the range 150–300 and 310–400°, respectively. The associated mass spectra confirm the loss of the thiourea ligand and hydrogen chloride in both decomposition steps.

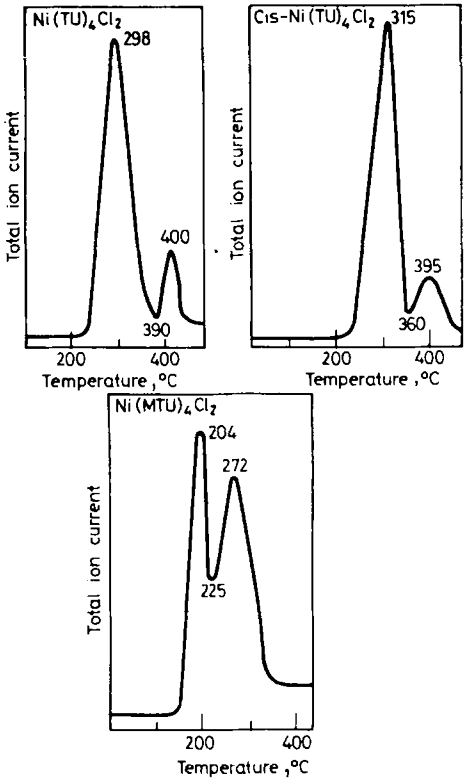


Fig. 5 TDMS profiles of type II complexes

Thus the TDMS data in general are in excellent agreement with the TG data and it is therefore concluded that nickel thioureachloride complexes decompose by one of a possible two thermal decomposition mechanisms and that the thermal decomposition mechanism adopted depends exclusively on the structure of the thiourea ligand and not on the nature of the halide ligand or on the existence of geometrical isomerism for these complexes.

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Zusammenfassung — Durch TG, DTA und thermodegradative Massenspektrometrie (TDMS) von Nickel(II)-thioharnstoff-chlorid-Komplexen, NiL_4Cl_2 (L = Thioharnstoff oder Methyl-, Dimethyl-, Tetramethyl-, Di-*n*-butyl-, Naphthyl-, Vinyl- oder Allylharnstoff), erhaltene Daten werden angegeben. Zwei verschiedene Mechanismen werden für die thermische Zersetzung vorgeschlagen. Es ist offensichtlich, daß der Mechanismus, nach der die thermische Zersetzung eines gegebenen Komplexes verläuft, von der Struktur des relevanten Thioharnstoffliganden und nicht von der Natur des Halidliganden oder vom Vorliegen einer geometrischen Isomerie abhängt.

Резюме Представлены данные ТГ/ДТА и масс-спектрометрии термического распада для ряда комплексов производных мочевины и хлорида никеля общей формулы NiL_4Cl_2, где L = мочевина, метил-, диметил-, тетраметил-, ди-н-бутил-, нафтил-, этилен- и аллилмочевина. Предложены два различных механизма их термического разложения. Угтановлено, что механизм термического разложения каждого отдельного комплекса определяется структурой соответствующего производного мочевины и не зависит от природы галоида и геометрической изомерии комплексов.