COORDINATION COMPOUNDS OF MANGANESE(II) WITH 1,10 PHENANTHROLINE

III THERMAL STUDIES OF PSEUDOHALOGENATO COMPLEXES

C. F. BELL and R. E. MORCOM

School of Chemistry, Brunel University, Uxbridge, Middlesex, England

(Received October 10, 1977)

TG and DTA of the compounds $Mn(phen)_2X_2$ (where $X = CN^-, CNO^-, NCS^-$ and $NCSe^-$), $Mn(phen)(NCS)_2$, $Mn(NCS)_2$ and $Mn(NCSe)_2$ (where *phen* = 1,10 phenanthroline) are reported and discussed. Decomposition schemes are proposed based on TG and DTA results and, where possible, the analysis and properties of intermediates formed during thermal breakdown. The decomposition of thiocyanate and selenocyanate ligands is observed to lead to an apparent slight increase in sample weight. This phenomenon is discussed in relation to buoyancy changes resulting from the release of sulphur or selenium vapours.

Thermal studies of some halogenato complexes of manganese(II) with 1,10 phenanthroline (*phen*) have previously established [1] that the decomposition of $Mn(phen)_2Cl_2$ and $Mn(phen)_2Br_2$ in air proceeds by loss of one phenanthroline molecule and then on further heating by the loss of halogen and volatile decomposition products of the second phenanthroline molecule which breaks up while still coordinated to the metal. The controlled thermal decomposition of these two complexes can be exploited as a preparative method for the corresponding *mono* complexes, $Mn(phen)Cl_2$ and $Mn(phen)Br_2$.

We have previously reported [2] the spectroscopic characterization of four complexes, $Mn(phen)_2X_2$, where $X = CN^-$, CNO^-, NCS^- or $NCSe^-$ and now describe the thermal analysis of these. As an aid to the formulation of decomposition schemes for these complexes, the thermal decomposition of manganese(II) thiocyanate and selenocyanate has also been examined.

Experimental

The preparation of $Mn(phen)_2X_2$ has been described previously [2].

Manganese(II) thiocyanate, $Mn(NCS)_2$, was prepared by a procedure based on that of Flint and Goodgame [3] by reaction between anhydrous manganese(II) chloride (0.01 mol) and potassium thiocyanate (0.02 mol) in absolute ethanol (40 cm³). The mixture was refrigerated for 24 h, the precipitate of potassium chloride filtered off and dry benzene (30 cm³) added to the filtrate. The solution was filtered again to remove a small quantity of white solid and then evaporated to a

small volume in a rotary evaporator. After cooling at 0°, the product was collected, washed with ethanol and dried over calcium chloride.

Dithiocyanato mono(phenanthroline) manganese(II), Mn(*phen*) (NCS)$_2$, was prepared by adding a solution of phenanthroline (0.002 mol) in dry acetone (20 cm^3) to a solution of Mn(NCS)$_2$ (0.006 mol) in dry acetone (30 cm^3) under reflux. A yellow precipitate of Mn(*phen*) (NCS)$_2$ formed during addition. Reflux was continued for 10 minutes, then the mixture was cooled and the yellow solid filtered off, washed with acetone and heated at 60° to remove solvent. Analysis: % found: C, 46.00; N, 15.76; H, 2.60: % calc. for Mn(*phen*) (NCS)$_2$: C, 47.88; N, 15.95; H, 2.30.

Manganese(II) selenocyanate, Mn(NCSe)$_2$, was prepared by a similar method to that used for Mn(NCS)$_2$. This compound, a pale green crystalline solid when pure, is readily oxidized by air with the formation of selenium and so must be prepared under nitrogen.

Attempts to prepare a selenocyanate analogue of Mn(*phen*) (NCS)$_2$ using mole ratios Mn(NCSe)$_2$: phen between 2 : 1 and 100 : 1 always gave the *bis* complex.

Similar attempts to make a cyanato analogue were unsuccessful.

TG was performed on a TR-750 Stanton thermobalance. Simultaneous DTA and TG were carried out on a Stanton thermobalance (TR-1) fitted with a 4-range DTA attachment (STA 661) and coupled to a modified Leeds and Northrup "Speedomax" type "W" recorder (STA 662).

IR spectra between 2500 and 400 cm^{-1} were recorded for Nujol mulls using a Grubb—Parsons Spectrometer.

Magnetic susceptibility measurements were made at room temperature using a Newport Instruments' electromagnet (Type C, pole diameter 1/2 in.) powered by a Newport VR 3 d.c. supply and a Stanton balance Model SM 12/S.

Elemental analysis for C, H, N and S were carried out by Butterworth Microanalytical Consultancy Ltd. Manganese was determined by EDTA titration.

Results and discussion

The thermal decomposition of the four *bis*(*phen*) complexes has been examined at different heating rates using two different thermobalances, each of which necessitated the use of different sample weights. This work has confirmed the effect noted by Ozawa [4] that the greater the heating rate the more the TG curve is shifted laterally to a higher temperature range and also shown that the form of this curve is critically dependent on sample size for this type of compound.

The results for each complex when heated in air are shown in Figures 1 – 4. The unbroken lines refer to simultaneous TG-DTA on a sample of c. 100 mg heated at 4 deg. min^{-1} and the broken lines to TG on a sample of c. 2.5 mg heated at 2 deg. min^{-1}. These illustrate how the loss of volatile products is appreciably retarded, presumably by diffusion-controlled processes in the bulk of the solid, by the use of larger samples and more rapid heating rates. It is valuable to compare TG and

DTA results obtained on the same sample but for the formulation of probable decomposition schemes, it is preferable to use the data obtained for a small sample heated at a low rate.

Comparison of the DTA curves shows that all four complexes decompose in two or more exothermic reactions. These are not resolved on the TG and DTG curves for $Mn(phen)_2(NCO)_2$ but, in contrast, the decomposition between 300°
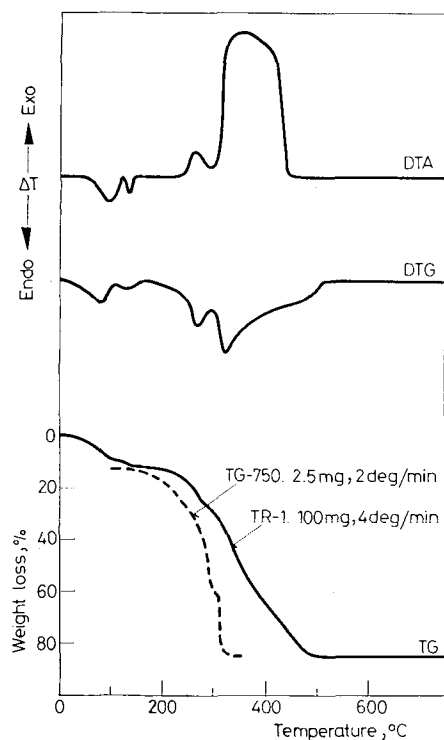

Fig. 1. Thermal decomposition of $Mn(phen)_2(CN)_2.3 H_2O$ in air

and 600° of $Mn(phen)_2(NCS)_2$ and $Mn(phen)_2(NCSe)_2$ is marked by three distinct stages of weight loss and three clearly separated exotherms. These stages can be identified, in accordance with the proposed breakdown schemes for $Mn(phen)_2Cl_2$ and $Mn(phen)_2Br_2$ [1], with volatilization of phenanthroline, decomposition of pseudohalogenato ligands, and the decomposition of coordinated phenanthroline together with oxidation of the products to volatile materials.

The first exotherm occurs very near the temperature of the first DTG peak. Using either as an indication of thermal stability, the order of stabilities of the *bis* complexes is observed to be:

$$Mn(phen)_2(CN)_2 < Mn(phen)_2(NCO)_2 < Mn(phen)_2(NCSe)_2 < Mn(phen)_2(NCS)_2$$

The final exotherm marks the burning off of decomposition products to form Mn_2O_3 from the cyanide, cyanate and selenocyanate. In the case of $Mn(phen)_2(NCS)_2$, however, there is evidence from TG that another intermediate, stable to c. 750°, precedes the formation of Mn_2O_3.

Thermogravimetry in nitrogen shows a much smaller weight loss, in every case, than that observed in air and the final large exotherm does not appear. The weight
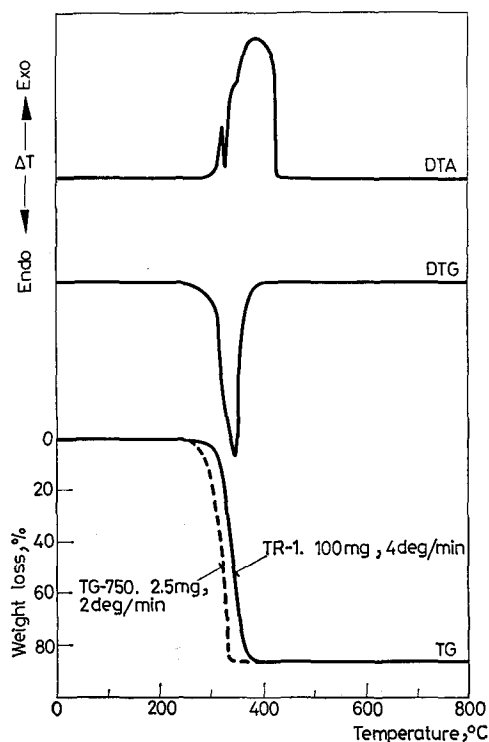

Fig. 2. Thermal decomposition of $Mn(phen)_2(NCO)_2$ in air

loss observed probably corresponds to volatilization of some phenanthroline and partial or complete conversion of the pseudohalide to volatile products. The remaining phenanthroline polymerizes to a non-volatile, nitrogen-containing char which remains virtually unaffected by further heating in the absence of air.

Dicyano bis(phenanthroline) manganese(II) trihydrate, $Mn(phen)_2(CN)_2.3\ H_2O$

This loses water of crystallization endothermically in two stages between 80° and 170°. In air, degradation to Mn_2O_3 then occurs:

$$Mn(phen)_2(CN)_2.3\ H_2O \rightarrow Mn(phen)_2(CN)_2 \rightarrow 1/2\ Mn_2O_3$$
$$11.4\ (10.4) \qquad\qquad 74.8\ (74.5)$$
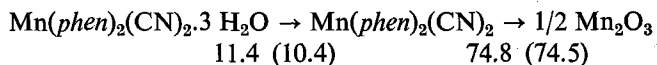
(Here, and subsequently, the figure in brackets is the theoretical percentage weight loss, that outside is the observed loss.) The inflection at 270° on the TG curve and the two exotherms at about this temperature point to the occurrence of at least two reactions but these overlap considerably and the individual stages cannot be quantified.
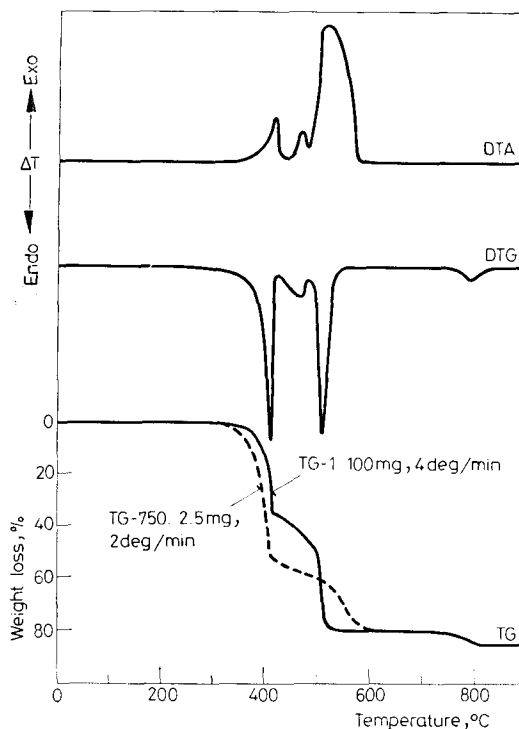

Fig. 3. Thermal decomposition of Mn($phen$)$_2$(NCS)$_2$ in air

In nitrogen, there is a sharp weight loss finishing at 350°. This amounts to 36% of sample weight and is near to that expected (38.5%) for the loss of one phenanthroline. Elemental analysis and the properties of the product indicate that the second phenanthroline molecule has decomposed and been converted largely to a non-volatile polymeric material.

Dicyanato bis(phenanthroline) manganese(II), Mn($phen$)$_2$(NCO)$_2$

In air, this compound appears to decompose completely in one stage although the slight inflection on the DTA exotherm at 345° could signify two overlapping reactions. The endotherm superimposed at 320° on the exotherm marks fusion

of the black, partly-decomposed material. The decomposition can thus be simply represented by:

$$Mn(phen)_2(NCO)_2 \rightarrow Mn_2O_3$$
$$84.8 \ (84.2)$$

In nitrogen, pyrolysis is virtually complete at 400°. By then, the compound has lost about 25% by weight. As in the case of the dicyano complex, the remaining
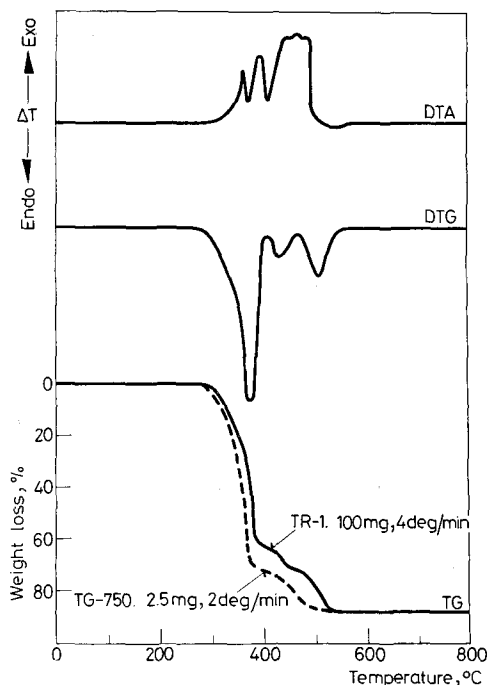

Fig. 4. Thermal decomposition of Mn(phen)₂(NCS)₂ in air

phenanthroline has degraded to non-volatile products by the time that this temperature is reached.

Dithiocyanato bis(phenanthroline) manganese(II), Mn(phen)₂(NCS)₂

The weight losses observed when this is heated in air and in nitrogen are given in Table 1. In both atmospheres, the loss at the first decomposition stage corresponds quite closely with that calculated for one phenanthroline and the conversion of coordinated thiocyanate to sulphide and volatile products according to:

$$2\,SCN^- = (CN)_2 + S + S^{2-} \tag{1}$$
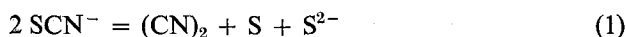
This reaction has been reported [5] for the thiocyanate complexes of transition metals with phenanthroline and bipyridyl.

The identification of the products as Mn(*phen*)S is confirmed by the presence of sulphide. There is no stage corresponding to the formation of the *mono* complex, Mn(*phen*) (NCS)$_2$, as an intermediate.

In nitrogen, decomposition virtually ceases at the sulphide stage. In air, oxidation of the remaining phenanthroline produces a second intermediate, stable between 600 and 750°. Several formulations are possible for this intermediate including $MnSO_4.MnO_2$, $MnSO_4.MnO$, MnOS and 2 $MnSO_4.Mn_2O_3$. The formation of the intermediate $MnSO_4.MnO$ has been proposed [5] in the decomposition of an isoquinoline thiocyanate complex of manganese, and an analogous nickel compound is reported [6] as being produced in the thermal breakdown of Ni(*phen*)$_2$(NCS)$_2$.
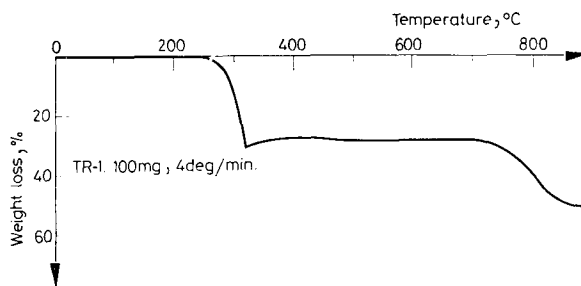

Fig. 5. Thermal decomposition of Mn(NCS)$_2$ in air

However, the product isolated between 600° and 750° from Mn(*phen*)$_2$(NCS)$_2$ not only contains sulphate, but also shows oxidizing properties. For example, it releases iodine from acidified aqueous potassium iodide. Its magneton number, calculated on the basis of a molecular weight of 115, is 4.67, well below the spin-only value of 5.92 theoretically predicted for high-spin Mn(II). Elemental analysis is consistent with its formulation as 2 $MnSO_4.Mn_2O_3$ (%found: Mn, 49.6; S, 13.2: % calc.: Mn, 47.8; S, 13.9).

Finally in air the mixed oxide/sulphate is converted to Mn_2O_3.

These conclusions are confirmed by the thermogravimetric behaviour of Mn(NCS)$_2$ in air. This is illustrated in Fig. 5 and the proposed decomposition scheme shown in Table 1 is based on the formation of 2 $MnSO_4.Mn_2O_3$ as an intermediate.

The abrupt weight loss occurring at about 300° marks decomposition of the thiocyanate ion according to Eq. (1). Near the end of this stage, the thermogravimetric trace shows that the sample weight appears to increase slightly (by about 2%). Oxidation can be ruled out as the cause of this, because similar increases are observed when this compound is heated in a nitrogen atmosphere. We believe it is an apparent rather than a real increase, probably explicable in terms

Table 1

Thermal decomposition schemes for manganese(II) thiocyanate and its *mono* and *bis* phenanthroline complexes

Compound	Weight loss (%)		
	In air	In N$_2$	Calculated
Mn(*phen*)$_2$(NCS)$_2$			
↓	51.0	52.0	49.7
Mn(*phen*)S			
↓	27.1		28.6
$\frac{1}{4}$(2MnSO$_4$·Mn$_2$O$_3$)			
↓	7.3		6.8
$\frac{1}{2}$Mn$_2$O$_3$			
Mn(*phen*)(NCS)$_2$			
↓	43.4		45.0
$\frac{1}{2}$Mn$_2$(*phen*)S$_3$			
↓	22.2		22.2
$\frac{1}{4}$(2MnSO$_4$·Mn$_2$O$_3$)			
↓	7.0		10.2
$\frac{1}{2}$Mn$_2$O$_3$			
Mn(NCS)$_2$			
↓	29.5		32.7
$\frac{1}{4}$(2MnSO$_4$·Mn$_2$O$_3$)			
↓	23.1		21.0
$\frac{1}{2}$Mn$_2$O$_3$			
Mn(NCS)$_2$			
↓		47.1	49.1
MnS			

of the temporary buoyancy change associated with the release of sulphur or cyanogen vapour. When this occurs, the gas around the sample crucible is displaced by much denser vapour so that the weight loss recorded is greater than the real value. When this vapour is swept out and replaced by the less buoyant air or nitrogen, the apparent weight of the crucible increases slightly. A similar phenomenon is observed in the thermal decomposition of Mn(NCSe)$_2$ (see below).

Dithiocyanato mono(phenanthroline) manganese(II), Mn(*phen*) (NCS)$_2$

The TG curve of this shows three clearly defined stages (Fig. 6). It starts to decompose in air at about 300°. This temperature is below that at which Mn(*phen*)$_2$(NCS)$_2$ begins to break down and this explains why Mn(*phen*)$_2$(NCS)$_2$ cannot be made by thermolysis of the *bis* complex.

The first stage is exothermic and here the thiocyanate and phenanthroline ligands decompose simultaneously. The weight loss observed (Table 1) indicates that

phenanthroline is not volatilized at this stage but converted to an involatile, polymeric product which is then oxidized exothermically to gaseous compounds in the second stage. The polymer has the approximate stoichiometry $Mn_2(phen)S_3$. At the end of the second stage, $2\ MnSO_4.Mn_2O_3$ remains and this is converted to Mn_2O_3 above 800°.
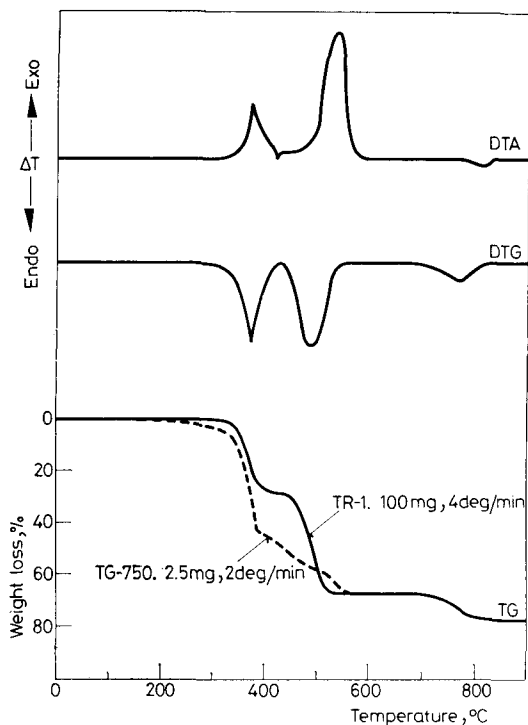

Fig. 6. Thermal decomposition of Mn(*phen*) (NCS)$_2$ in air

In nitrogen, a 60% weight loss is observed in one stage between 270° and 440°. The ligands are converted to a non-volatile product containing carbon, nitrogen and sulphur.

Differences in thermal stability between Mn(*phen*)$_2$(NCS)$_2$ and Mn(*phen*) (NCS)$_2$ may be related to structural differences between the two complexes. In Mn(*phen*)$_2$(NCS)$_2$, the thiocyanate ligand is monodentate and is bound to manganese via nitrogen [2]. Thiocyanate bound thus is characterized by two strong bands due to $\nu(C-N)$, located at 2055 and 2062 cm^{-1}. In Mn(*phen*) (NCS)$_2$ we find two bands attributable to $\nu(C-N)$ at 2092 and 2112 cm^{-1}. On this evidence, we suggest that Mn(*phen*) (NCS)$_2$ contains bridging NCS ligands because an increase in $\nu(C-N)$ for coordinate thiocyanate ligands is regarded as typical of their chang-

ing from a monodentate to a bridging function [7, 8]. This compound is probably polymeric, as appears to be the case for Mn(*phen*)Cl$_2$ and Mn(*phen*)Br$_2$ [1].

The energetics and mode of decomposition of Mn(*phen*)$_2$(NCS)$_2$ are likely to be very different from those of Mn(*phen*) (NCS)$_2$. When the former decomposes this process must involve, at least as far as the thiocyanate ligand is concerned, the breaking of Mn$-$N bonds and the formation of Mn$-$S bonds. In Mn(*phen*)(NCS)$_2$, with $-$NCS$-$ acting as a bridging ligand, the Mn$-$S bonds are already established. The *bis* complex has a mononuclear structure whereas the *mono* complex is likely to be polymeric. This is another reason why they would be expected to show different thermolytic behaviour.

Diselenocyanato bis(phenanthroline) manganese(II), Mn(*phen*)$_2$ (NCSe)$_2$

In view of strong similarities between the DTA and DTG curves for this compound and those for Mn(*phen*)$_2$(NCS)$_2$, we suggest that both decompose in similar ways. In the case of the selenium compound, the volatilization of phenanthroline, the decomposition of the pseudohalogenato ligand and the burning off of phenanthroline decomposition products occur together over quite a narrow temperature range for a small sample (the broken line in Fig. 4). From the observed weight losses, the following decomposition scheme may be adduced:
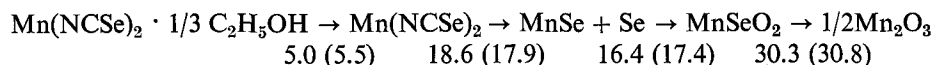
$$Mn(phen)_2(NCSe)_2 \rightarrow MnSeO_2 \rightarrow 1/2\ Mn_2O_3$$
$$75.0\ (73.5) \qquad 12.4\ (13.9)$$
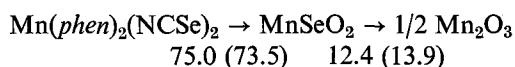
A mixed selenate/oxide analogous to 2 MnSO$_4$.Mn$_2$O$_3$ does not appear to be formed as intermediate presumably because manganese selenate would not be thermally stable.

MnSeO$_2$ also occurs as an intermediate in the thermal decomposition of solvated Mn(NCSe)$_2$ (Fig. 7). First, there is loss of ethanol of crystallization, then the selenocyanate ligand decomposes with loss of cyanogen according to:

$$2\ SeCN^- = (CN)_2 + Se + Se^{2-} \tag{2}$$

The solid loses selenium and takes up oxygen to give MnSeO$_2$ and finally this is oxidized to Mn$_2$O$_3$:

$$Mn(NCSe)_2 \cdot 1/3\ C_2H_5OH \rightarrow Mn(NCSe)_2 \rightarrow MnSe + Se \rightarrow MnSeO_2 \rightarrow 1/2Mn_2O_3$$
$$5.0\ (5.5) \qquad 18.6\ (17.9) \qquad 16.4\ (17.4) \qquad 30.3\ (30.8)$$

A number of TG runs of samples of Mn(NCSe)$_2$ in air and nitrogen atmospheres at different flow rates showed that, in some instances, the decomposition of the selenocyanate ligand caused an apparent increase in weight of $1-2\%$. Whether or not this phenomenon was observed depended on the flow rate and it therefore appeared to be related to the loss of selenium or cyanogen vapour from the sample which temporarily caused a marked change in the buoyancy of the atmosphere around the TG crucible. The TG curve for Ni(pyridine)$_4$

(NCSe)$_2$ [9] shows a similar slight increase in weight during the decomposition of Ni(NCSe)$_2$ which could be caused by the same effect.

In nitrogen, the decomposition of Mn(*phen*)$_2$(NCSe)$_2$ appears to follow the scheme:

$$\text{Mn(}phen\text{)}_2\text{(NCSe)}_2 \rightarrow \text{Mn(}phen\text{)Se}$$
$$49.2 \ (49.8)$$
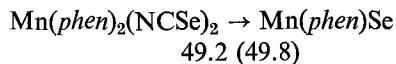
Although the stoichiometry is represented here as Mn(*phen*)Se, the properties of the product are consistent with the presence of polymeric organic material formed by phenanthroline pyrolysis. A gradual weight loss occurs at temperatures above 400°, due to the slow volatilization of phenanthroline and the remaining selenium.
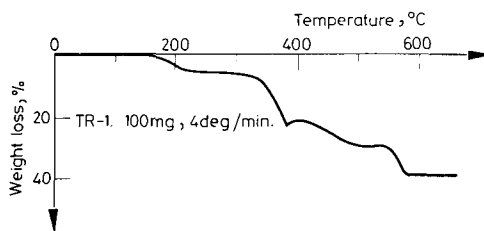

Fig. 7. Thermal decomposition of Mn(NCSe)$_2$ in air

We have not been able to prepare a *mono* complex of stoichiometry Mn(*phen*) (NCSe)$_2$, presumably because selenium is a much weaker donor than sulphur and therefore selenocyanate cannot act as a bridging ligand in the way that thiocyanate does.

*

We wish to express our thanks to Professor S. C. Bevan for helpful advice, particularly in connection with the buoyancy effect noted for thiocyanate and selenocyanate complexes.

References

1. C. F. BELL and R. E. MORCOM, J. Inorg. Nucl. Chem., 36 (1974) 3689.
2. C. F. BELL and R. E. MORCOM, J. Inorg. Nucl. Chem., 35 (1973) 1865.
3. C. D. FLINT and M. GOODGAME, J. Chem. Soc. Ser. A (1970) 442.
4. T. OZAWA, Bull. Chem. Soc. Japan, 38 (1965) 1881.
5. B. LÓRÁNT and M. BOJTOR, J. Thermal Anal., 2 (1970) 151.
6. B. LÓRÁNT and M. BOJTOR, J. Thermal Anal., 5 (1973) 379.
7. J. CHATT and L. A. DUNCANSON, Nature, 176 (1956) 997.
8. Y. Y. KHARITONOV, G. V. TSINTSADZE and A. Y. TSIVADZE, Russ. J. Inorg. Chem., 15 (1970) 204.
9. I. PORUBSZKY, Á. NÉMETH and G. LIPTAY, Thermal Analysis (Proc. of the 3rd ICTA, Davos, 1971) Vol. 2, p. 679, 1972.

RÉSUMÉ — On décrit et discute la TG et l'ATD des composés Mn(*phén*)₂X₂ (X = CN⁻, CNO⁻, NCS⁻ et NCSe⁻), Mn(*phén*) (NCS)₂, Mn(NCS)₂ et Mn(NCSe)₂ (où *phén* = 1,10 phénantroline). On propose des schémas de décomposition à partir des résultats de TG et d'ATD et, si possible, on donne l'analyse et les propriétés des produits intermédiaires formés lors de la décomposition thermique. On a observé que la décomposition des ligands de thiocyanate et de sélénocyanate entraîne une faible augmentation apparante du poids du prélèvement. On explique ce phénomène par les variations de poussée résultant du dégagement de vapeurs de soufre ou de sélénium.

ZUSAMMENFASSUNG — TG und DTA Untersuchungen der Verbindungen Mn(*phen*)₂X₂ (X = CN⁻, CNO⁻, NCS⁻ und NCSe⁻), Mn(*phen*) (NCS)₂, Mn(NCS)₂ und Mn(NCSe)₂ (*phen* = 1.10 Phenantrolin) werden beschrieben. Anhand der TG- und DTA-Ergebnisse werden Zerzetzungsschemata vorgeschlagen und wenn möglich, Analyse und Eigenschaften der im Laufe der thermischen Zersetzung entstandenen Zwischenprodukte angegeben. Es wurde beobachtet, daß die Zersetzung der Thiocyanat- und Selenocyanatliganden zu einer scheinbaren schwachen Zunahme des Probengewichts führt. Dieses Phänomen wird im Zusammenhang mit infolge der Abspaltung von Schwefel- oder Selendämpfen auftretenden Änderungen des Auftriebs diskutiert.

Резюме – Приведены и обсуждены данные ТГ и ДТА для соединений Mn(фен)₂X₂, Mn(фен) (NCS)₂, Mn(NCS)₂ и Mn(NCSe)₂, где X = CN⁻, CNO⁻, NCS⁻, NCSe⁻ и фен = 1.10-фенантролин. На основании результатов ТГ и ДТА предложены схемы разложения и, где это представлялось возможным, проведен анализ и исследованы свойства промежуточных продуктов, образующихся при термическом разложении. Разложение тиоцианатного и селеноцианатного лигандов приводит к небольшому увеличению веса образца. Это явление обсуждено на основе поплавковых изменений, возникающих в результате выделения паров серы или селена.