J. inorg. nucl. Chem., 1974, Vol. 36, pp. 3689–3694. Pergamon Press. Printed in Great Britain.

CO-ORDINATION COMPOUNDS OF MANGANESE(II) WITH 1:10 PHENANTHROLINE—II

THERMAL STUDIES OF HALOGENATO COMPLEXES AND PROPERTIES OF MONO-COMPLEXES

C. F. BELL and R. E. MORCOM

School of Chemistry, Brunel University, Kingston Lane, Uxbridge, Middlesex

(*Received* 14 *January* 1974)

Abstract—The decomposition of four dihalogenato complexes of manganese(II) and 1:10 phenanthroline has been studied by thermogravimetry and differential thermal analysis. Intermediate decomposition products have been isolated and characterized spectroscopically. Experimental conditions are described for the preparation of the *mono* complexes Mn(phen)X_2 (X = Cl, Br or I) and evidence for their structures is presented.

INTRODUCTION

We have previously reported[1] studies on some *bis*(1:10 phenanthroline) complexes of manganese(II). Work on these has been extended using thermogravimetry and differential thermal analysis and we now report the thermal behaviour of some halogenato complexes and the properties of the intermediate products of their decomposition. The latter include the *mono* complexes, Mn(phen)X_2, where X = Cl or Br. The corresponding iodo complex, Mn(phen)I_2, cannot be obtained by the thermal decomposition of a higher complex but we have prepared it by an alternative route. Although a product of stoichiometry Mn(phen)F_2 has been isolated, this appears to be a mixture rather than a pure compound.

Although Mn(phen)Cl_2 and Mn(phen)Br_2 have been previously reported [2]–[6], this appears to be the first time they have been identified as products of the controlled thermal breakdown of *bis* complexes. We have found no previous reference to Mn(phen)I_2. The stereochemistry around manganese in all three compounds has been inferred from their vibrational and ESR spectra.

Table 1. Analytical data for manganese complexes

Compound		Per cent Mn	C	H	N	H_2O
Mn(phen)$_2$F$_2$. 6H$_2$O . $\frac{1}{2}$DMF	Calc.	9·18	51·2	5·27	10·55	18·1
	Found	8·98	51·07	4·83	10·75	18·6
Mn(phen)$_2$F$_2$. 2H$_2$O	Calc.	11·23	58·85	4·13	11·45	7·4
	Found	11·54	57·73	4·06	11·47	8·3
"Mn(phen)F$_2$"	Calc.	20·11	52·77	2·95	10·26	
	Found	19·71	53·49	2·98	10·13	
Mn(phen)Cl$_2$	Calc.	17·95	47·1	2·63	9·16	
	Found	17·85	47·14	2·91	9·16	
Mn(phen)Br$_2$	Calc.	13·91	36·49	2·04	7·09	
	Found	13·64	36·35	2·26	7·20	
Mn(phen)I$_2$	Calc.	11·24	29·48	1·65	5·73	
	Found	11·18	30·16	1·83	6·41	
"Mn(phen)$_{3/4}$Cl$_2$"	Calc.		41·4	2·3	8·05	
	Found		42·2	1·8	8·76	
"Mn(phen)$_{3/4}$Br$_2$"	Calc.		30·9	1·7	6·0	
	Found		30·8	2·7	6·2	

Similar studies on *bis*(1:10 phenanthroline) complexes of manganese(II) which contain pseudohalide ligands will be reported later.

EXPERIMENTAL

Bis complexes were prepared as reported previously[1]. The identity of the two solvates of difluoro*bis*(1:10 phenanthroline)manganese(II) was established by elemental analysis and by Karl–Fischer determinations of their water content (Table 1).

Preparation of mono *complexes by thermal methods*

A product of composition Mn(phen)F_2 was isolated by heating Mn(phen)$_2$$F_2$ in air at 200°C to constant weight. Its magnetic moment, assuming a formula weight corresponding to Mn(phen)F_2, was found to be 5·86 B.M. at 23°C. Mn(phen)Cl_2 was prepared by a modification of Broomhead and Dwyer's method[2] and also by heating Mn(phen)$_2$$Cl_2$ in air at 310°C to constant weight. Mn(phen)Br_2 was made by heating Mn(phen)$_2$$Br_2$ in air at 345°C to constant weight and also by heating this *in vacuo* to 250°C over P_2O_5.

Preparation of mono *complexes in non-aqueous solvents*

Dichloro(1:10 *phenanthroline*)*manganese*(II). The preparation of this was attempted using Broomhead and Dwyer's method[2], (viz. the reaction of anhydrous manganese(II) chloride and phenanthroline in a 1:1 molar ratio in anhydrous dimethylformamide). Unlike the compound described by these workers, our product did not contain DMF of solvation and elemental analysis showed that its composition approximated to Mn(phen)$_{1\cdot25}$$Cl_2$. Thermogravimetric analysis was consistent with the breakdown scheme:

$$\mathrm{Mn(phen)_{1\cdot25}Cl_2} \xrightarrow{350\text{–}420^\circ\mathrm{C}} \mathrm{Mn(phen)Cl_2} \xrightarrow{450\text{–}690^\circ\mathrm{C}} \tfrac{1}{2}\mathrm{Mn_2O_3}$$

Table 2. Thermal decomposition schemes

Compound	Temp. range (°C)	Weight loss (%) Obs.	Calc.
(a) Mn(phen)$_2$$F_2$. $6H_2O$. $\frac{1}{2}$DMF			
↓	70–95	15·5	18·1
(b) Mn(phen)$_2$$F_2$. $2H_2O$			
↓	100–130	6·8	6·1
(c) Mn(phen)$_2$$F_2$			
↓	200–305	28·7	30·1
(d) Mn(phen)$_2$$F_2$/Mn$F_2$			
↓	305–340	31·3	30·1
(e) MnF_2			
↓	460–520	4·4	2·3
(f) $\frac{1}{2}Mn_2O_3$			
(a) Mn(phen)$_2$$Cl_2$			
↓	300–420	36·9	37·0
(b) Mn(phen)Cl_2			
↓	430–520	9·6	9·3
(c) "Mn(phen)$_{3/4}$$Cl_2$"			
↓	530–690	38·4	37·5
(d) $\frac{1}{2}Mn_2O_3$			
(a) Mn(phen)$_2$$Br_2$			
↓	370–460	31·6	31·3
(b) Mn(phen)Br_2			
↓	475–520	8·8	7·8
(c) "Mn(phen)$_{3/4}$$Br_2$"			
↓	530–700	46·8	47·1
(d) $\frac{1}{2}Mn_2O_3$			
(a) Mn(phen)$_4$$I_2$. $3H_2O$			
↓	50–70	1·5	1·7
(b) Mn(phen)$_4$$I_2$. $2H_2O$			
↓	125–155	4·0	3·4
(c) Mn(phen)$_4$$I_2$			
↓	240–300	33·4	33·6
(d) Mn(phen)$_2$$I_2$			
↓	320–430	53·8	54·5
(e) $\frac{1}{2}Mn_2O_3$			
(a) Mn(phen)I_2			
↓	230–400	48·3	48·9
(b) Mn(phen)O			
↓	410–620	35·9	35·2
(c) $\frac{1}{2}Mn_2O_3$			

$$\%\ \text{weight loss}\ \begin{cases}\text{Theoret.} & (12\cdot8) \qquad (64\cdot7)\\ \text{Observed} & 13\cdot2 \qquad 65\cdot0\end{cases}$$

(Here and subsequently when comparing weight losses, the figure in brackets always refers to the theoretical value for the decomposition shown.)

The i.r. spectrum of $Mn(phen)_{1\cdot25}Cl_2$ showed it to be a mixture of $Mn(phen)_2Cl_2$ and $Mn(phen)Cl_2$. Similar mixtures were obtained using greater relative quantities of phenanthroline for reaction with $MnCl_2$.

The *mono* compound was isolated in the pure state by reaction between 1 mole of $MnCl_2$ and 0·75 mole of phenanthroline in dry DMF. It was identified by i.r. spectroscopy, elemental analysis and thermogravimentry:

$$\mathrm{Mn(phen)Cl_2} \xrightarrow[74\cdot4(74\cdot2)]{450\text{–}690^\circ\mathrm{C}} \tfrac{1}{2}\mathrm{Mn_2O_3}.$$

Dibromo(1 : 10 *phenanthroline*)*manganese*(II). When a reaction mixture of 1 mole of $MnBr_2$ and 1 mole of phenanthroline in dry DMF was used, the product was $Mn(phen)_2Br_2$. When this was heated *in vacuo* to 250°C over P_2O_5, the weight loss of 30·9 per cent showed conversion to $Mn(phen)Br_2$ had occurred (theory = 31·3 per cent).

Diiodo(1 : 10 *phenanthroline*)*manganese*(II). Reaction between MnI_2 and phenanthroline in a 1 : 1 molar ratio in dry DMF gave $Mn(phen)_2I_2$.

The *mono* complex was obtained as follows by the modification of a published method[5].

A solution of anhydrous manganese(II) iodide (1 mole) in dry acetone under reflux was treated with a solution of 1 : 10 phenanthroline (0·4 mole) in acetone. During the addition yellowish-green crystals were formed. After cooling and filtering, the crystals were washed with dry acetone and dried at 45°C under vacuum.

$Mn(phen)I_2$ turns brown gradually in air because of the slow formation of iodine. It has a magnetic moment of 5·84 B.M. at 23°C.

Apparatus

I.R. spectra between 400 and 40 cm^{-1} were measured as wax discs by PCMU, Harwell, using a Beckman Interferometer FS 720 coupled to a FTC 100 wave-analyzer. Raman spectra of powdered solids were recorded on a "Spex" Ramalab Laser-Raman spectrometer using light of wavelengths 514·5 and 568·2 nm for irradiation. Data and assignments are summarized in Table 2.

Thermogravimetric analyses were performed on a Stanton TR-01 thermobalance and differential thermal analyses on a "Standata" 6–25. Comparative TG and DTA were performed on a Stanton TR–1 thermobalance fitted with a 4-range DTA attachment (STA 661) and coupled to a modified Leeds and Northrup "Speedomax" type "W" recorder (STA 662). Wherever possible, intermediate decomposition products were isolated and TG and DTA performed as aids to the interpretation of the thermal breakdown of their parent compounds.

Magnetic susceptibility measurements were made using a Newport Instruments' electromagnet (Type C, pole dia. $\frac{1}{2}$ in.) powered by a Newport VR 3 d.c. supply and a Stanton balance, Model SM 12/S. ESR spectra of powdered solids were recorded on a Varian E3 X-band electron spin resonance spectrometer operating at 9·5 GHz and using silica sample tubes of 3 mm i.d.

Analysis

Analyses for carbon, hydrogen and nitrogen were carried out by the National Physical Laboratory Analytical Services, Teddington, Middlesex. Manganese was determined by EDTA titration. The water content of hydrated compounds was determined by Karl–Fischer titration. Analytical data are summarized in Table 1.

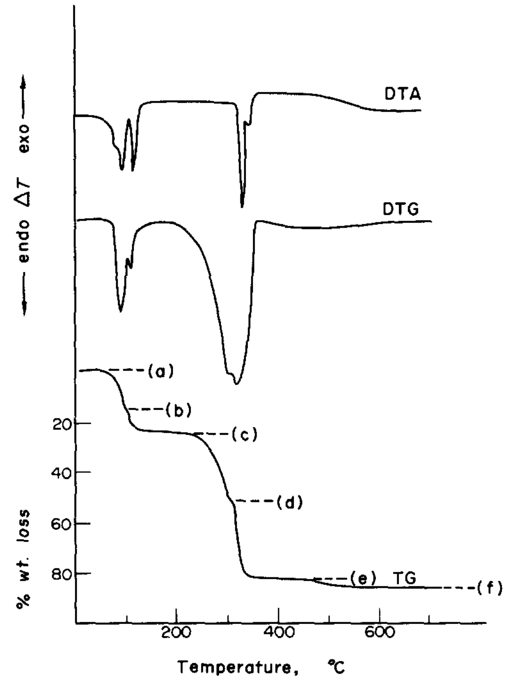

Fig. 1. Thermal decomposition of $Mn(phen)_2F_2 . 6H_2O . \frac{1}{2}DMF$.

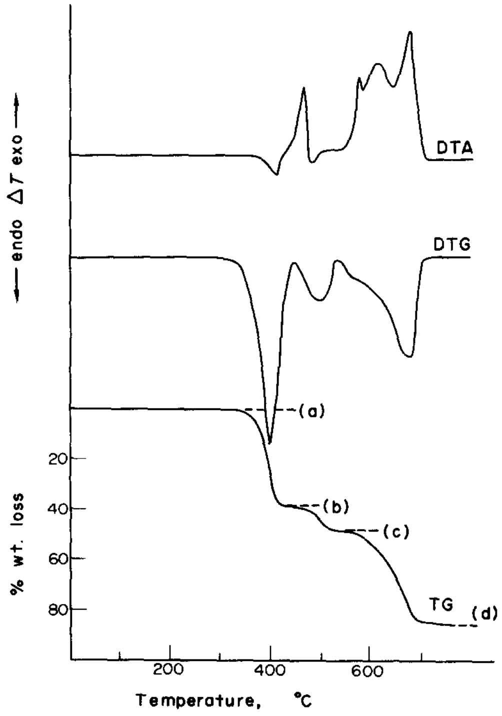

Fig. 2. Thermal decomposition of $Mn(phen)_2Cl_2$.

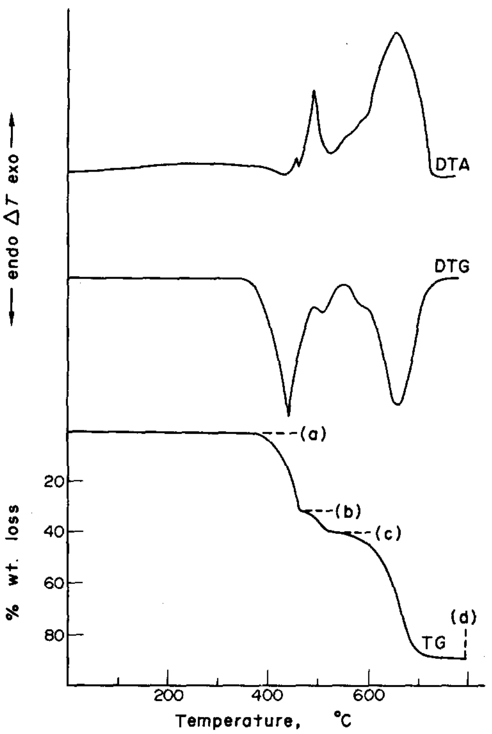

Fig. 3. Thermal decomposition of $Mn(phen)_2Br_2$.

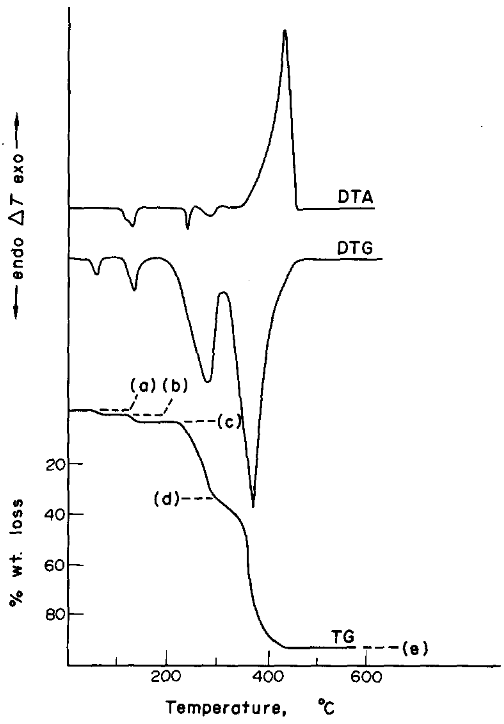

Fig. 4. Thermal decomposition of $Mn(phen)_4I_2 . 3H_2O$.

RESULTS AND DISCUSSION

Thermal decomposition

TG, DTG and DTA curves for five manganese complexes in air are plotted in Figs. 1–5. The corresponding decomposition schemes are summarized in Table 2.

Fluoro complexes

The anhydrous *bis* complex does not appear to decompose to an intermediate *mono* complex. Although the thermogram (Fig. 1) shows an inflection at 305°C, indicative of a two-stage decomposition, the weight losses between 200° and 340°C do not correspond exactly with the consecutive loss of two phenanthroline molecules. Attempts to isolate a complex of stoichiometry $Mn(phen)F_2$ have resulted only in the production of mixtures, identified spectroscopically, of $Mn(phen)_2F_2$ and MnF_2.

Chloro and bromo complexes

The most interesting feature of the decomposition of $Mn(phen)_2Cl_2$ and $Mn(phen)_2Br_2$ is the unusual behaviour of the intermediate *mono* complexes. Both melt with decomposition, $Mn(phen)Cl_2$ between 425° and 445°C, and $Mn(phen)Br_2$ at about 460°C. The changes in the molten material are very similar to those observed during the decomposition of $Co(phen)_2Cl_2$ and $Co(phen)_2Br_2$[7].

When $Mn(phen)_2Cl_2$ is heated at 510°C to constant weight, the product, "$Mn(phen)_{3/4}Cl_2$", is a black solid which has a distinctive metallic sheen. Its i.r. spectrum shows two broad regions of appreciable absorption, 1700–950 and 640–605 cm^{-1}, together with weak maxima at 725, 855, 1376, 1450 and 1610 cm^{-1}. It is quite different from that of coordinated phenanthroline and shows marked similarities to the spectra of pyrolytic chars obtained from such polycyclic aromatic compounds as anthracene[8]. This stage is believed to represent breakdown of coordinated phenanthroline. Thus it occurs very near to the temperature (432°C) reported[9] for the decomposition of phenanthroline in a condensed phase. Also significant in this context is the observation that when phenanthroline is carbonized by heat treatment at 600°C, the product retains most of the nitrogen initially present[10]. We conclude therefore that, at about 440°C, phenanthroline in the *mono* complex is converted to a polymeric graphite-like material which still contains much of the original nitrogen. This could be incorporated in the polycyclic fused ring systems of which the polymer is presumably composed[10].

The final stage (Fig. 2, (c)–(d)) represents the burning off of phenanthroline decomposition products, loss of chlorine and conversion to Mn_2O_3. All three changes appear to involve oxygen because the broad exothermic region is absent when DTA is performed under nitrogen.

The decomposition of $Mn(phen)_2Br_2$ follows a very similar pattern and an intermediate product of composition approximating to "$Mn(phen)_{3/4}Br_2$" has been isolated and characterized spectroscopically.

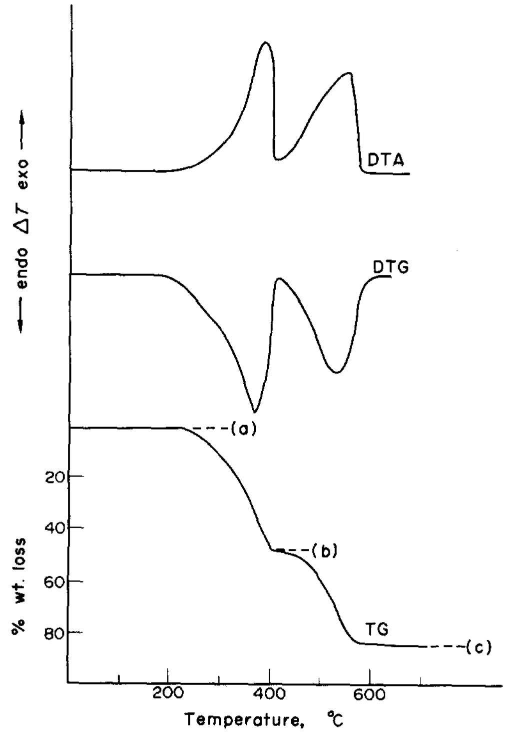

Fig. 5. Thermal decomposition of $Mn(phen)I_2$.

Iodo complexes

The anhydrous *tetrakis* complex is believed to undergo decomposition endothermically at 240°C to a mixture of the *bis* complex and free phenanthroline:

$$Mn(phen)_4I_2(s) \rightarrow Mn(phen)_2I_2(s) + 2\ phen(l).$$

Above 190°C, thermal decomposition of the *tetrakis* complex follows the same course as that of a mixture of phenanthroline and the *bis* complex.

DTA curves for samples in air and nitrogen are virtually identical up to 350°C indicating that the decomposition processes below this temperature do not involve oxidation.

TG and DTA show clearly that there is no prospect of isolating a diiodo *mono* (phenanthroline) complex by thermal methods. Thermal studies on the *mono* complex reveal that it begins to decompose at a much lower temperature than the *bis* complex.

To summarize our results, the order of thermal stability of the *bis* complexes (as signified by the lowest temperature at which weight loss begins) is:

$$\text{fluoro} \ll \text{chloro} < \text{iodo} \approx \text{bromo}$$

and of the *mono* complexes is:

$$\text{iodo} \ll \text{chloro} < \text{bromo}.$$

In the case of the fluoro, chloro and bromo *bis* complexes, decomposition starts with the loss of phenanthroline. In the case of the iodo *bis* complex, loss of phenanthroline and iodine occurs together whilst for the iodo *mono* complex, iodine is lost first and phenanthroline driven off subsequently.

It is of interest to note that we have been able to prepare two *mono* complexes by careful control of the temperature of decomposition of the appropriate *bis* complex. There appears to be no reason why analogous *mono* complexes should not be formed during the decomposition of higher phenanthroline complexes of other transition metals like cobalt[7], and nickel and iron[11].

Structures of mono *phenanthroline complexes*

The i.r. and Raman spectra below 400 cm^{-1} of $Mn(phen)Cl_2$, $Mn(phen)Br_2$ and $Mn(phen)I_2$ are summarized in Table 3. Our i.r. data confirm those reported previously[5] for the chloro and bromo complexes. Comparison of the spectra of the three compounds shows some bands whose frequency becomes progressively lower as the mass of the halogen, X, increases whilst the remaining bands show little or no variation. The former bands are therefore assigned to vibrations involving Mn—X bonds. These assignments are generally quite close to those made[1] for the corresponding *bis* complexes, $Mn(phen)_2X_2$.

Hayward[6] concluded from the X-band ESR spectra of $Mn(phen)Cl_2$ and $Mn(phen)Br_2$ that these have polymeric structures containing octahedrally coordinated manganese. According to him, polymeric complexes of manganese(II) give a single line spectrum at $g_{eff} = 2$. Zero-field splitting is not observed probably because the manganese atoms, linked by halogen bridges, undergo magnetic interaction so that all spectral lines are broadened to give one resultant line at $g_{eff} = 2$.

We have confirmed Hayward's results for $Mn(phen)Cl_2$ and $Mn(phen)Br_2$ and have observed that the spectrum of $Mn(phen)I_2$ is also a single line at $g_{eff} = 2$. These compounds are therefore believed to be polymeric with structures based on "$Mn(phen)X_4$" units, in which each halogen acts as a bridge between two manganese atoms.

The *bis*(pyridine) complexes of manganese(II) halides, $Mnpy_2X_2$, are also believed to be polymeric[12], their structures being composed of infinite chains of octahedral "$Mnpy_2X_4$" units in which the pyridine molecules are *trans* to one another. However, the *mono* phenanthroline complexes cannot have this type of structure because the two nitrogen donor sites must be *cis* to one another in the coordination shell of manganese.

Molecular models show that one possible mode of linking manganese atoms by bridging halogens results in a helical arrangement of metal atoms with each phenanthroline chelated so that its molecular plane lies at right angles to the helical axis.

In view of the similarity in far-i.r. spectra between $Mn(phen)Cl_2$ and $Mn(phen)Br_2$ and their respective bipyridyl analogues, $Mn(bipy)Cl_2$ and $Mn(bipy)Br_2$ [13], there seems little doubt that the latter also contain octahedral manganese and are similarly polymeric.

Table 3. The vibrational spectra of Mn(phen)X_2 complexes (X = Cl, Br and I): frequencies in cm^{-1}

	Mn(phen)Cl_2		Mn(phen)Br_2		Mn(phen)I_2		
	I.R.	R	I.R.	R	I.R.	R	Assignment
	282s	283s	281s	283s	282s	281s	
	264sh	267w	262m	268vw	258m	269w	
		252w		251w		251m	
	242vs	241w					ν(Mn–Cl)
			209vs	206sh			ν(Mn–Br)
					201s	200m	ν(Mn–I)
	182sh	185m		189w, sh			
			168·5s	167w, sh	166s	168s	
	160s	160s					Mn–Cl bend
	154sh			151s			
	138sh		136sh		140vw	142s	
			126s	125m			Mn–Br bend
	118sh	121vw	118s				
					112m	111sh	Mn–I bend
	101w	100w					
			97·5sh				
					95m	89s	Mn–I bend
Limit	40	80	40	110	40	70	

CONCLUSIONS

Of the four dihalogenato *bis*(phenanthroline) manganese(II) compounds whose thermal breakdown in air has been examined, $Mn(phen)_2Cl_2$ and $Mn(phen)_2Br_2$ have similar decomposition routes to Mn_2O_3 via the corresponding *mono* complex and then a complex containing a polymer derived from phenanthroline. $Mn(phen)_2I_2$ also decomposes to Mn_2O_3 but, as it is more stable thermally than $Mn(phen)I_2$, the latter is not formed as an intermediate. $Mn(phen)_2F_2$ loses phenanthroline in two stages but the *mono* complex does not appear to exist as such.

The three *mono* complexes studied appear to have polymeric structures in which octahedral coordination of manganese is preserved by the bridging action of the halogen atoms.

Acknowledgements—We thank Professor S. C. Bevan for much helpful discussion and advice on thermal analysis, Dr. K. A. K. Lott for assistance in measuring the ESR spectra, Dr. D. N. Waters for help in measuring the Raman spectra, and PCMU, Harwell, for the measurements of far i.r. spectra.

REFERENCES

1. R. E. Morcom and C. F. Bell, *J. inorg. nucl. Chem.* **35**, 1865 (1973).
2. J. A. Broomhead and F. P. Dwyer, *Aust. J. Chem.* **14**, 250 (1961).
3. H. A. Goodwin and R. N. Sylva, *Aust. J. Chem.* **18**, 1743 (1965).
4. A. Syamel, *J. Ind. chem. Soc.* **44**, 989 (1967).
5. R. E. Wilde, T. K. K. Srinivasan and S. N. Ghosh, *J. inorg. nucl. Chem.* **35**, 1017 (1973).
6. P. J. Hayward, Thesis for D.I.C., Imperial College, London University, 1968.
7. D. M. Palade, E. S. Il'ina and G. V. Chudaeva, *Z. Neorg. Khim.* **18**, 1292 (1973).
8. R. A. Friedel, *Proc. of the 4th Conf. on Carbon*, p. 321 Pergamon Press, Oxford (1960).
9. I. B. Johns, E. A. McElhill and J. O. Smith, *J. chem. Engng Data* **7**, 277 (1962).
10. L. G. Isaacs, *Carbon* **8**, 1 (1970).
11. K. Akabori, H. Matsuo and Y. Yamamoto, *J. inorg. nucl. Chem.* **35**, 2679 (1973).
12. M. Goldstein and W. D. Unsworth, *Inorg. chim. Acta* **4**, 342 (1970).
13. J. S. Strukl and J. L. Walter, *Spectrochim. Acta* **27A**, 223 (1971).