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Thermal analysis and vibrational spectroscopy of Mn(II)–urea–halide complexes: comparative study of the metal–ligand bond strength

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Abstract

The thermal study of Mn(II)–urea–halide complexes as a function of the metal–ligand bond strength is given. The results compared very well with those obtained from vibrational spectra. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Halogeno manganese(II) complexes; Urea complexes; Thermal analysis; Vibrational spectroscopy; Metal–ligand bond strength

1. Introduction

The study of metal-amide complexes is of great importance to the pharmaceutical and medical sciences. Over the past years certain platinum compounds, e.g. ‘cisplatin’ $Pt(NH_3)_2Cl_2$, have been used as anticarcinogenic agents. It has also been found that some Pt–urea complexes have antitumor activity [1] and biological applications [2]. More research on the biological activity of other urea complexes is needed [3]. First of all a thorough fundamental characterisation of these urea complexes is necessary. Two reviews have been published which summarize the work on urea and its complexes [3,4]. Two general studies on the structure [5] and the vibrational spectroscopy [6] of these complexes have also been published.

This is why we started with the characterization of the complexes of urea with manganese-halide salts. The synthesis, structure and vibrational characterisation of the following compounds with the general formula MnU_mX_2, where U=urea, have been described elsewhere [7]: m=1, 2, 4 for X=Cl; m=2, 4, 6 for X=Br and m=6 for X=I. As mentioned in a previous article [7] the literature on these complexes is sparse: infrared spectra, electronic spectra, paramagnetic susceptibility and powder diffraction patterns of these compounds, except for $MnUCl_2$, had been mentioned in the literature [8–10]. Only the structure of MnU_2Cl_2 had been determined by X-ray diffraction [11,12]. Literature on the thermal decomposition of these complexes was also poor: Lupin discussed the thermal decomposition of MnU_4Cl_2 in air and in Ar-atmosphere [13] and Srivastava discussed the thermal decomposition of $MnU(H_2O)_3Cl_2$ [14]. However, all these studies focussed mainly on the determination of the coordination sphere of the individual Mn–urea complexes with no thorough vibrational or thermal characterisation and no comparative study of these complexes has been published.

Previously [7] we focussed mainly on the synthesis, structure and vibrational analysis of these complexes. In this article we combine results from infrared and

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Raman spectroscopy as well as TGA- and DSC-measurements to obtain information about the relative metal–ligand bond strength. For the vibrational spectra only diagnostic bands will be discussed. The magnitude of the shift of these vibrational bands on complexation compared to the free ligand, as well as the thermal stability and the ΔH value of the corresponding decomposition processes, are, as will be shown further in this article, indicative of the metal–ligand bond strength.

2. Experimental section

Infrared spectra were recorded on a Bruker IFS 113v Fourier Transform spectrometer, using a liquid nitrogen cooled MCT detector with a resolution of 1 cm^{-1}. For each spectrum 100 scans were recorded and averaged. Far infrared spectra were recorded using a DTGS-detector with a resolution of 4 cm^{-1}. For each spectrum 250 scans were recorded and averaged. The Raman spectra were recorded on a Bruker IFS 66v interferometer equipped with a FT Raman FRA106 module and a Nd-YAG laser. For each spectrum 1000 scans with a resolution of 4 cm^{-1} were recorded and averaged.

The thermogravimetric analysis experiments and the calorimetric measurements were performed on a SDT-2960 and a DSC-2920 modules, respectively, from TA-instruments. A sample mass of approximately 15 mg was heated at a heating rate of 5°C min^{-1} in a N_2 atmosphere at a flow rate of 50 cm^3 min^{-1}.

Urea (U) and the metal salts were purchased from Aldrich with a purity higher than 99%. The syntheses of the complexes and the deuterated compounds have been described previously [7].

3. Results and discussion

3.1. Structure and thermal decomposition of Mn–urea–halide complexes

Table 1 shows the synthesized complexes (left) and the different complexes made by heating of the synthesized compounds (right). Complexes with other stoichiometries could not be prepared.

Table 1
Summary of the synthesized complexes

Synthesized complexes	Heating conditions	Thermal products
MnU_1Cl_2	–	–
MnU_2Cl_2	Up to 240°C at 5°C min^{-1}	MnU_1Cl_2
MnU_4Cl_2	Iso 150°C for 4 h	MnU_2Cl_2
	Iso 185°C for 1 h	MnU_1Cl_2
MnU_2Br_2	Up to 250°C at 5°C min^{-1}	$MnU_2Br_2{\cdot}MnBr_2$
MnU_4Br_2	Iso 150°C for 96 h	MnU_2Br_2
MnU_6Br_2	Iso 130°C for 24 h	MnU_4Br_2
	Iso 125°C for 96 h	MnU_2Br_2
MnU_6I_2	–	–

For all these complexes the Mn-atom has an octahedral coordination (Fig. 1) and urea is coordinated to the metal via the oxygen atom.

The octahedral surrounding has already been shown by previous workers by means of electronic spectra, fluorescence and X-ray powder diffraction experiments [8,9] and was confirmed previously by means of X-ray diffraction and far infrared studies [7]. The oxygen–metal bond was readily observed in the infrared and Raman spectra in that the bands corresponding to the CO– and the CN–stretching vibrations appear at, respectively, lower and higher frequency than the free ligand [7]. The opposite effect, i.e. a higher CO–stretching frequency and lower CN– stretching bands, was observed for nitrogen coordinations as in the Pt–urea complexes [6]. In the 1:6-complex, the halogens acts as counterion in contrast with the 1:4 complex where they are bound directly to the metal in the *trans* position, and with the 1:2- and 1:1-complexes where the halogen was bridged between different metal atoms [7].

MnU_6Cl_2 could not be prepared probably because the chloride ion was too small to act as a counterion to stabilize the large MnU_6^{2+} ion in contrast with the bigger bromide and iodide ions (symbiotic effect). By heating MnU_2Br_2 at 5°C min^{-1} to 250°C a stable compound was obtained with a mass loss corresponding to loss of one molecule of urea. However, if we compare the mid-infrared spectra of this compound and MnU_2Br_2 we see that these are exactly identical. This means that this compound must be $MnU_2Br_2{\cdot}MnBr_2$ and not $MnUBr_2$. Consequently $MnUBr_2$ could not be obtained either in the laboratory or by means of thermogravimetry. This compound is

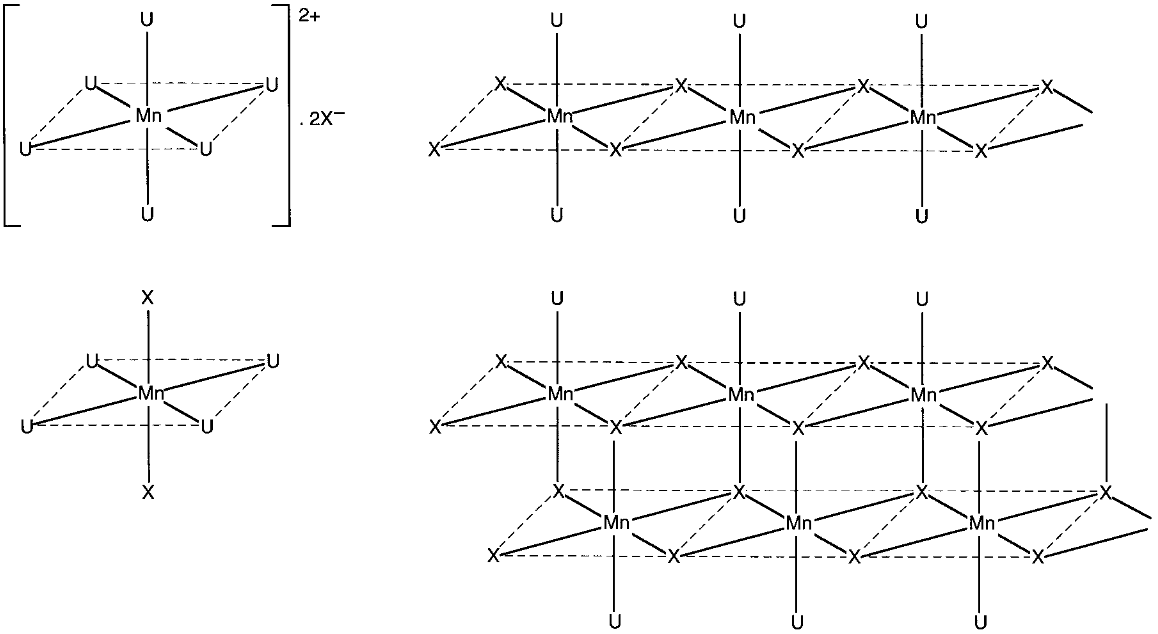

Fig. 1. Structure of MnU_6X_2 (top left), MnU_4X_2 (bottom left), MnU_2X_2 (top right) and $MnUX_2$ (bottom right).

not stable because the bromide is probably too large to bridge between three metal ions in contrast with the chloride ion. Thermal decomposition experiments on the MnU_6I_2 complex always yielded complexes in which ligand bonds were broken. Consequently we could not obtain, neither in the laboratory nor by thermal analysis any urea complex in which the iodide was bound directly to the metal due to the fact that, according to the H.S.A.B. theory [15], the iodide is too soft to bind directly to the hard manganese ion in competition with the hard oxygen atoms of the urea ligands.

Several complexes could be prepared in the laboratory as well as by the thermal decomposition (TGA) of complexes with a higher Mn–urea stoichiometry (Table 1). IR spectroscopy was used to prove that in each case products from both methods of preparation were identical. As an example Fig. 2 shows the identical infrared spectra of the $MnUCl_2$ complex prepared in the laboratory (top) and by thermogravi-

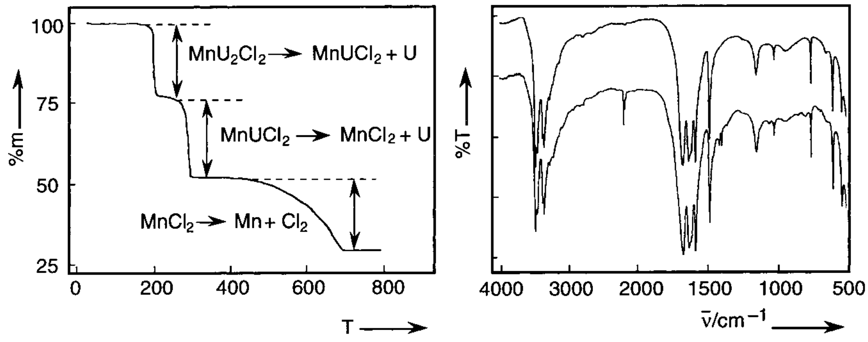

Fig. 2. Thermal decomposition of MnU_2Cl_2 at a heating rate of 5°C min^{-1}. Infrared spectrum of $MnUCl_2$ prepared in the laboratory (top) and by thermal analysis (TGA) of MnU_2Cl_2 (bottom).

metry (bottom). The sharp peak at 2200 cm^{-1} in the bottom spectrum corresponded to the nitrile vibration in the decomposition product after release of urea: NH_4OCN [16–19].

Table 1 shows that on heating the metal–ligand bond is broken and complexes with lower Mn–Urea stoichiometry are formed according to the following reaction scheme

$$MnU_6X_2 \rightarrow MnU_4X_2 \rightarrow MnU_2X_2 \rightarrow MnUX_2 \rightarrow MnX_2$$

This allowed us to perform a comparative study of the metal–ligand bond strength by means of thermal analysis, looking at the thermal stability of the different compounds and the ΔH value of the decomposition processes, in addition to vibrational spectroscopy.

As is shown on the DSC responses shown in Fig. 3, the non-polymeric complexes melt before decomposing, in contrast to that of the polymeric compounds. A shows one endotherm corresponding to the decomposition of $MnUCl_2$ to $MnCl_2$. B shows two endotherms corresponding to the thermal decomposition of MnU_2Cl_2 to $MnUCl_2$ and further to $MnCl_2$. C shows three events the first belonging to a process which does not involve any mass loss, (the melting of the complex), the second to the decomposition of MnU_4Cl_2 to MnU_2Cl_2 and then to $MnUCl_2$ and the third to the further decomposition to $MnCl_2$.

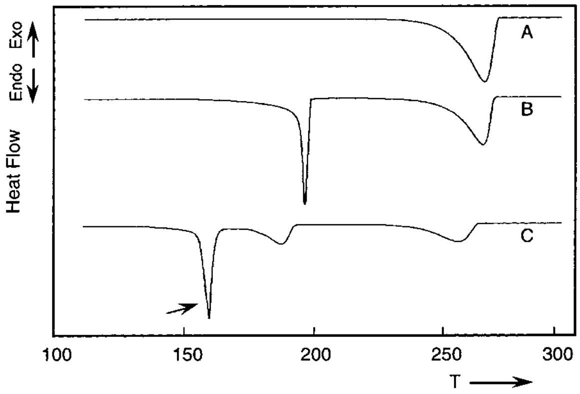

Fig. 3. DSC of $MnUCl_2$ (A), MnU_2Cl_2 (B) and MnU_4Cl_2 (C) at a heating rate of 0.5°C min^{-1} (arrow: process without mass loss, concluded from TGA measurements).

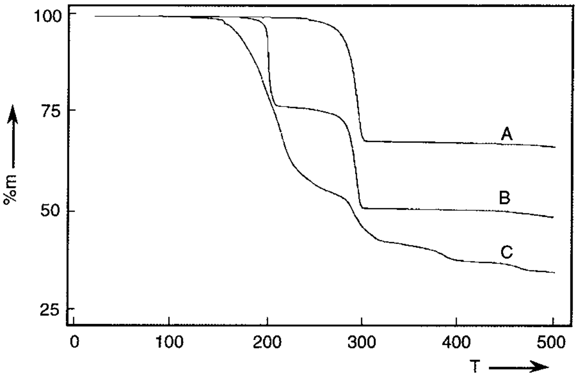

Fig. 4. Thermal decomposition of $MnUCl_2$ (A), MnU_2Cl_2 (B) and MnU_4Cl_2 (C) at a heating rate of 5°C min^{-1}.

3.2. *A comparative study of the metal–oxygen bond strength in the Mn–urea–halide complexes*

3.2.1. *Comparison of the chloride complexes*

Fig. 4 shows the increase in thermal stability from the 1:4-chloride complex to the 1:2 and then the 1:1-chloride complex. As all these complexes decompose at the metal–ligand bond, the more stable compounds would be expected to have a stronger metal–ligand bond, resulting in a lower CO stretching frequency, higher CN stretching frequencies and a lower π(C–O) mode compared to the free ligand, as well as higher metal–oxygen frequencies. Except for the CO stretching frequency this was indeed observed as can be seen in Table 2 [7].

The band with pure ν(C–O) character should be diagnostic of the metal–ligand bond strength. However, for urea and its complexes we determined and calculated for the normal compound an intensive coupling with the $\delta(NH_2)$, s-mode and for the deuterated compound with the ν(C–N), s-mode [7,20–22]. As only pure vibrations can be interpreted, they could not be compared directly with the metal–ligand bond strength. For these reasons the CO stretching vibration will not be used in further discussion. Frequencies corresponding to metal–oxygen stretching vibrations cannot be used to compare these compounds because of their different structural symmetry.

The enthalpies of decomposition, ΔH, obtained from DSC measurements, as listed in Table 3. These were in the order of the proposed stability, confirming the relative metal–oxygen bond strength differences

Table 2
Infrared and Raman frequencies of urea and the Mn-halide complexes (cm^{-1})

	Urea		$[MnCl_2U_4]$		$[MnCl_2U2]$		$[MnCl_2U]$		$[MnU_6]Br_2$		$[MnBr_2U_4]$		$[MnBr_2U_2]$		$[MnU_6]I_2$	
	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman
ν_{as} (C–N)	1466	1466	1471	1470	1477	1478	1487	1503	1478	1477	1478–1494	1491	1473–1478	1478	1476	1477
ν_s (C–N)	1003	1010	1011	1017	1018	1018	1024	1026	1017	1018	1018	1023	1018	1018	1018	1018
π(C–O)	790	790	778	788	777	779	760	761	777	776	777	–[b]	777	777	773	782
ν_{as} (C–N)[a]	1485	1485	1504	–	1509	–	1521	–	1501	–	1514	–	1507	–	1501	–
π(C–O)[a]	778	778	770	777	73	775	755	753	768	766	765	765	763	765	763	764

[a] Deuterated complexes.

[b] – Too weak to be observed.

Table 3
ΔH values for $MnUCl_2$, MnU_2Cl_2 and MnU_4Cl_2 (kJ mol^{-1})

	ΔH_{melt}	$\Delta H_{1:4\rightarrow1:2}$	$\Delta H_{1:2\rightarrow1:1}$	$\Delta H_{1:1\rightarrow MnX_2}$
$MnUCl_2$	–	–	–	132
MnU_2Cl_2	–	–	110	145
MnU_4Cl_2	99	116	110	134

already concluded from the vibrational spectra and the thermal stability measurements.

The relative metal–oxygen bond strength can be explained from the structure of these complexes (Fig. 1). The number of bridged halogen atoms increases in the order 1:4-, 1:2- and 1:1-chloride complex. The electron density is concentrated more between the metal and the directly bonded urea molecules, with a stronger metal–oxygen bond in the 1:1- than in the 1:2- and the 1:4-chloride complex as a consequence.

3.3. Comparison of the bromide complexes

The 1:2-bromide complex was more stable than the 1:4- and the 1:6-bromide complex (Fig. 5). However, vibrational shifts show (Table 2) that the metal–oxygen bond strengths are comparable for these compounds [7]. Again frequencies corresponding to metal–oxygen stretching vibrations were not considered because of the different structural symmetries of these compounds.

DSC measurements (Table 4) also suggested a weaker metal–urea bond in the 1:4 than in the 1:2-bromide complex: 160 kJ mol^{-1} was required to release two urea molecules compared to 114 kJ mol^{-1} for one urea molecule confirming the relative thermal stabilities. The results of the decomposition of the 1:6-bromide complex are difficult to interprete due to a relatively high amount of decomposition products of released urea molecules influencing the experimental ΔH value.

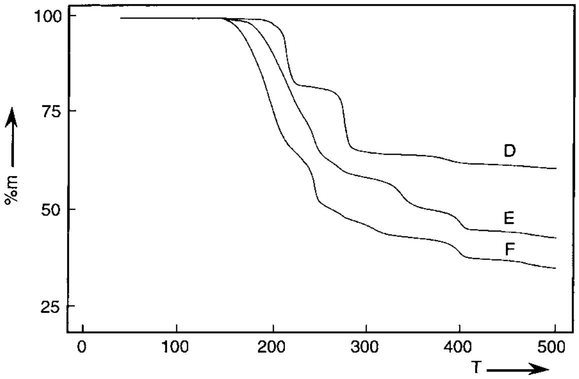

Fig. 5. Thermal decomposition of MnU_2Br_2 (D), MnU_4Br_2 (E) and MnU_6Br_2 (F) at a heating rate of 5°C min^{-1}.

Consequently, as the metal–oxygen bond strength seems to be comparable, differences in lattice energy must be at the origin of the different thermal stability of these compounds.

3.4. Comparison of the chloride and the bromide complexes

Fig. 6 shows that the 1:4-bromide complex is more stable than the 1:4-chloride complex. Vibrational spectral shifts show (Table 2) that this relative thermal stability is produced from stronger metal–oxygen bond in the 1:4 bromide compared to the 1:4-chloride complex. The same conclusion can also be drawn from the manganese–oxygen frequencies [7]: as in the far-infrared spectra the manganese–oxygen vibrations shift to higher wavenumber on halogen substitution of the chloride through a bromide atom, i.e. from 234, 213 and 184 cm^{-1} to 249, 232 cm^{-1} and a shoulder on the lower frequency side of the band at 203 cm^{-1}, assigned to the metal–bromide stretching vibration, respectively, a stronger metal–oxygen bond can be considered for the 1:4-bromide complex. In the

Table 4
ΔH values for MnU_2Br_2, MnU_4Br_2 and MnU_6Br_2 (kJ mol^{-1})

	ΔH_{melt}	$\Delta H_{1:6/4\rightarrow1:2}$	$\Delta H_{1:2\rightarrow1:1}$	$\Delta H_{1:1\rightarrow MnBr_2}$
MnU_2Br_2	–	–	114	123
MnU_4Br_2	43	160	130	
MnU_6Br_2	59	475	203	

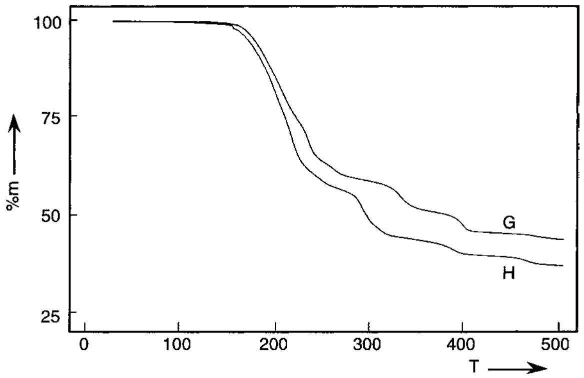

Fig. 6. Thermal decomposition of MnU_4Br_2 (G) and MnU_4Cl_2 (H) at a heating rate of 5°C min^{-1}.

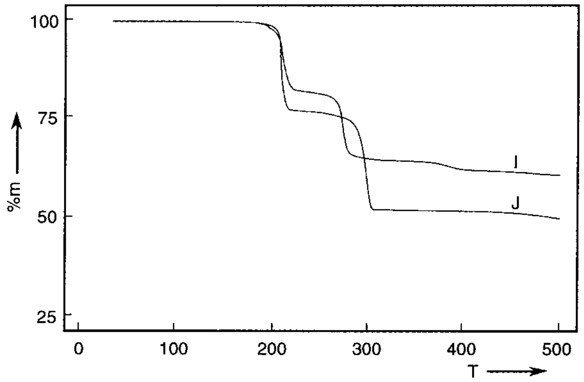

Fig. 7. Thermal decomposition of MnU_2Br_2 (I) and MnU_2Cl_2 (J) at a heating rate of 5°C min^{-1}.

Raman spectra the bands corresponding to the metal–oxygen vibrations also shift to higher wavenumber on halogen substitution of the chloride through a bromide atom, i.e. from 241, 187 and 160 cm^{-1} for the chloride complex to 259, 201 and 160 cm^{-1}, respectively, for the bromide complex, also indicating a stronger metal–oxygen bond for the bromide complex.

DSC measurements also indicate a stronger metal–urea bond in the 1:4 bromide than in the 1:4-chloride complex (Table 5) confirming the results from the vibrational spectra and the relative thermal stabilities.

The difference in metal–oxygen bond strength can be explained from the differences in the electronegativities of chloride and a bromide atom. The chloride atom, which is more electronegative than the bromide atom, attracts the electrons from the metal relatively more, resulting in a lower electron density between the metal and urea, and consequently a weaker metal–oxygen bond.

The thermal stability of the 1:2-bromide and chloride complexes appears to be comparable (Fig. 7). Vibrational spectral shifts show (see, Table 2) that the metal–oxygen bond strength is comparable as well as confirming the relative thermal stabilities. The same conclusion can also be drawn from the metal–oxygen vibrations [7]: in the far-infrared and in the Raman spectra the manganese–oxygen vibrations give rise to bands at 272 and 222 cm^{-1}, respectively, for both the chloride and the bromide complexes.

As it is shown in Table 6 the energy to break one metal–urea bond in the 1:2 chloride and 1:2 bromide complex is also comparable confirming the results from the vibrational shifts and the relative thermal stabilities. The energies needed for the further decomposition of these compounds can not be compared because they decompose to 1:1 complexes with different molecular structures ($MnUCl_2$ versus $MnU_2Br_2{\cdot}MnBr_2$).

Considering the electronegativity difference between a chloride and a bromide atom, one could expect a small difference in metal–oxygen bond strength as well. As the halogen atoms in the 1:2 complexes are bridged (Fig. 1), this influence is minimized probably because of the longer metal–halogen bond in the 1:2 compared to the 1:4 complex.

Table 5
ΔH values for MnU_4Cl_2 and MnU_4Br_2 (kJ mol^{-1})

	ΔH_{melt}	$\Delta H_{1:4\rightarrow1:2}$	$\Delta H_{1:2\rightarrow1:1}$	$\Delta H_{1:1\rightarrow MnX_2}$
MnU_4Cl_2	99	116	110	134
MnU_4Br_2	43	160	130	

Table 6
ΔH values for MnU_2Cl_2 and MnU_2Br_2 (kJ mol^{-1})

	$\Delta H_{1:2\rightarrow 1:1}$	$\Delta H_{1:1\rightarrow MnX_2}$
MnU_2Cl_2	110	145
MnU_2Br_2	114	123

3.5. *Comparison of the bromide and the iodide complexes*

The thermal stability of the 1:6 bromide and iodide complexes is comparable as can be seen from Fig. 8.

Vibrational spectral shifts also indicate (Table 2) comparable metal–oxygen bond strengths confirming the relative thermal stabilities. As the far infrared and the Raman spectra of these compounds are identical [7], a comparable metal–oxygen bond strength can be considered as well from the metal–oxygen frequencies.

DSC results of the 1:6-bromide and 1:6-iodide complex (Table 7) cannot be compared because the two complexes decompose in a different way. These results are also difficult to interprete due to a relatively high amount of decomposition products.

As the halogen only occurs as a counterion in these 1:6-complexes (Fig. 1) and consequently exhibits no direct influence on the electron distribution around the metal, a comparable metal–oxygen bond could be expected.

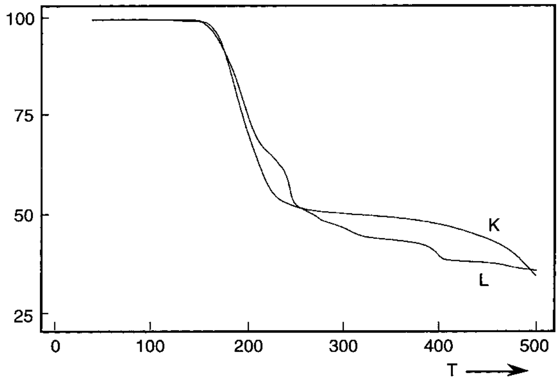

Fig. 8. Thermal decomposition of MnU_6I_2 (K) and MnU_6Br_2 (L) at a heating rate of 5°C min^{-1}.

Table 7
ΔH values for MnU_6Br_2 and MnU_6I_2 (kJ mol^{-1})

<table>
<tr><th></th><th>ΔH_{melt}</th><th>$\Delta H_{1:6\rightarrow 1:2}$</th><th>$\Delta H_{1:1\rightarrow MnX_2}$</th></tr>
<tr><td>MnU_6Br_2</td><td>59</td><td>475</td><td>203</td></tr>
<tr><td>MnU_6I_2</td><td>63</td><td colspan="2">479</td></tr>
</table>

4. Conclusions

We have shown that on heating the Mn–urea–halide complexes the metal–ligand bond is broken and thus complexes with a lower Mn–urea stoichiometry are formed according to the following reaction scheme

$$MnU_6X_2 \rightarrow MnU_4X_2 \rightarrow MnU_2X_2 \rightarrow MnUX_2 \rightarrow MnX_2$$

This allowed us to perform a comparative study of the metal–ligand bond strength by means of thermal analysis, looking at the thermal stability of the different compounds and the enthalpy of the decomposition processes, in addition to vibrational spectroscopy. This study showed that the 1:1-chloride complex is thermally more stable than the 1:2- and the 1:4-chloride complexes caused by a stronger metal–oxygen bond in the 1:1- than in the 1:2- and the 1:4-chloride complexes. A stronger metal–oxygen bond also explains the bigger thermal stability of the 1:4-bromide compared to the 1:4-chloride complex. In the case of the 1:2-bromide and chloride complexes the thermal stability as well as the metal–oxygen bond strength are comparable. Although the metal–oxygen bond strength is comparable in the case of the bromide complexes the 1:2-bromide complex is thermally more stable than the 1:4-and the 1:6-bromide complex. Differences in lattice energy are probably responsible for these differences in thermal stability. Only very small differences in thermal stability and metal–oxygen bond strength are observed between the 1:6-bromide and 1:6-iodide complexes.

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