Thermochimica Acta, 85 (1985) 67–70
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THERMAL ANALYSIS OF $M(LH_2)_2X_2$ COMPLEXES WITH PLANAR DITHIO OXAMIDES $M = Pt, Pd, Ni; X = Cl, Br, I.$

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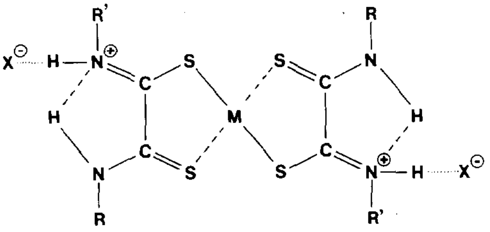
ABSTRACT

In this study we compared the thermal decompositions and the presence of stable intermediates for $M(LH_2)_2X_2$ complexes with LH_2 is a planar dithiooxamide and X = Cl, Br, I. The difference in thermal decomposition can be explained with the H.S.A.B. theory.

EXPERIMENTAL

Planar dithio oxamides such as $H_2NCSCSNH_2$ (DTO), $CH_3HNCSCSNH_2$ (MDTO) and $CH_3HNCSCSNHCH_3$ (DMDTO) generally give $M(LH_2)_2X_2$ complexes in acid media when a ligand solution in acetic acid is added dropwise to a M^{2+} solution in HX. The LH_2 : M ratio must be 2 : 1 (ref. 1,2). $M(DTO)_2I_2$ could not be formed. The precipitates are separated and washed with acetic acid to remove unreacted products and the access of X^- counterions. The structure consists of $M(LH_2)_2^{2+}$ dications and X^- anions interacting through hydrogen bonds. For some $M(LH_2)_2I_2$ compounds, the molecular formula contains 2 HI in addition. The ligands coordinate through sulfur (ref. 3.) (fig. 1.).



and other mesomeric forms

Fig. 1. The structure of $M(LH_2)_2X_2$

The thermal measurements are recorded with a Du Pont R90 thermal analyser equipped with a 951 TGA balance in a N_2 gas flow (50 ml/min). Sample sizes of 7.5 - 15. mg and heating rates of 1°C, 5°C, 10°C and 20°C/min are used as the

0040-6031/85/$03.30

heating rate may determine whether or not successive reactions can be separated (ref. 4).

RESULTS

The $M(LH_2)_2X_2$ complexes do not decompose by a simple deprotonation of the LH_2 ligands by the X^- anions to form $M(LH)_2$ and 2HX. However, this could be expected as this deprotonation was already observed for the $Pd(LH_2)_2X_2$ complexes at room temperature. When $Pd(LH_2)_2X_2$ was pressed in a NaF matrix we obtained, due to the strong electronegativity of fluorine, $Pd(LH)_2$, $NaHF_2$ and NaX. (ref. 5) according to the reactions :

$$\begin{array}{lcl} M(LH_2)_2X_2 + 2NaF & \longrightarrow & [M(LH_2)_2F_2] + 2NaX \\ [M(LH_2)_2F_2] & \longrightarrow & M(LH)_2 + 2HF \\ 2HF + 2NaF & \longrightarrow & 2NaHF_2 \end{array}$$

The first step is a halide exchange in approximately hundred fold excess of NaF. The $Pd(LH_2)_2F_2$ compound was not stable due to the exceptionally strong N^+- H....F^- associations, resulting in the formation of $Pd(LH)_2$ and in the elimination of HF. The HF is then captured by NaF forming $NaHF_2$.

The decomposition is much more complicated and depends strongly on the nature of the metal M^{2+} and on the counterion X^-. We can divide the 24 coordination compounds into 3 main categories according to the 3 metals : Pt, Pd and Ni.

No stable intermediates are obtained for the $Pt(LH_2)_2X_2$ complexes. All decompose to Pt in a curve with inflections but without a plateau. Decomposition begins little above room temperature but the maximum weight loss occurs between 250°C and 300°C, e.g. $Pt(MDTO)_2Br_2$ (fig. 2).

The $Pd(LH_2)_2X_2$ curves indicate in some cases a stable intermediate. $Pd(LH_2)_2I_2$.2HI looses the DMDTO ligand and 2HI between 120°C and 190°C and forms $Pd(DMDTO)_1I_2$ (th -44.3%, exp -42.5%). The reaction is confirmed by the infrared spectrum of the 1:1 compound. This intermediate product is stable in the 190°C - 250°C region. $Pd(DMDTO)_2Cl_2$ decomposes between 120°C and 240°C to form an intermediate that starts decomposing immediately. $Pd(MDTO)_2Cl_2$ gives a curve inflection at 240°C without a distinct plateau. Until now we cannot assign a stoichiometric compound to the curve inflections of both compounds, but the infrared spectra of both intermediates reveal that undissociated LH_2 is still present.

The $Ni(LH_2)_2X_2$ complexes form in all cases intermediates during the decomposition. The most occurring intermediate is the $(NiL)_m$ polymer. This polymer is formed for $Ni(DTO)_2Br_2$, $Ni(MDTO)_2Cl_2$, $Ni(MDTO)_2Br_2$, $Ni(MDTO)_2I_2$.2HI and $Ni(DMDTO)_2I_2$.2HI. The heating rate has no influence on the chain length of the polymer. The experimental and calculated weight loss for infinite chain length are compared in table 1. The difference between the experiment and the calculated value must be due to short polymer chains because the infrared and far-infrared spectra of the $(NiL)_m$ compounds are, with exception of the $[Ni(DMDTO)]_m$ polymer, the same as the spectra obtained for the $[NiL]_m$ polymers prepared in alkaline media. These compounds also exist with short chains of about 5 units. The different spectrum obtained for the $[Ni(DMDTO)]_m$ polymer prepared by thermal methods in comparison with the compound prepared in alkaline solution is due to an additional coordination of H_2O in the latter compound (ref. 2).

TABLE 1
Weight loss for the thermal preparation of $(NiL)_m$ from $Ni(LH_2)_2X_2$.

Compound	Weight loss [%]	Cal. weight loss for infinite chain length [%]
$Ni(DTO)_2Br_2$	59.5	61.5
$Ni(MDTO)_2Cl_2$	48.5	52.0
$Ni(MDTO)_2Br_2$	55.0	60.8
$Ni(MDTO)_2I_2.2HI$	71.0	77.2
$Ni(DMDTO)_2I_2.2HI$	73.5	76.3

The TG curves in which the same $(Ni(MDTO))_m$ polymer is formed for the 3 Ni-MDTO complexes are presented in fig. 3. Instead of weightpercentage versus temperature the average molecular weight versus temperature is shown. This implies that the plateaus of the 3 curves coincide. The 3 remaining $Ni(LH_2)_2X_2$ compounds, $Ni(DTO)_2Cl_2$, $Ni(DMDTO)_2Cl_2$ and $Ni(DMDTO)_2Br_2$ show a decomposition curve with a distinct plateau, but further analysis must reveal the molecular formula of these intermediates.

DISCUSSION

The absence of stable intermediates for $Pt(LH_2)_2X_2$ and the presence of few intermediates for $Pd(LH_2)_2X_2$ and much more for $Ni(LH_2)_2X_2$ can be explained by the theory of Hard and Soft Acids and Bases (H.S.A.B.) (ref. 6). This theory implies that a strong bonding is formed between the "soft" Pt^{2+} metal and the "soft" sulfur part of the ligand through which the coordination occurs. This strong bond between Pt and S is the reason why the first weight loss is due to the decomposition of the ligand and not to the separation of a complete ligand unit. Therefore no stable $Pt-LH_2$ combination is obtained during the decomposition. Pd^{2+} is less "soft". Therefore the bond between Pd and LH_2 is less stable and stable $Pd-LH_2$ combinations are obtained during some of the thermal decompositions. Ni is a borderline metal according to the H.S.A.B.theory. This implies that the Ni-sulfur bond is not very stable and the $Ni(LH_2)_2X_2$ complexes tend to decompose by breaking the weakest link, between Ni and the ligand and stable Ni-ligand combinations, as the $(NiL)_m$ polymers are formed for which the release of one ligand is combined with the deprotonation of the remaining coordinated ligand.

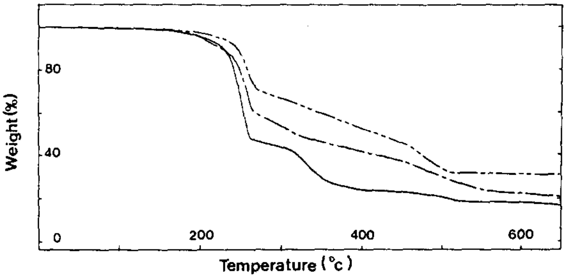


Fig. 2. Thermal decomposition curves of $M(MDTO)_2Br_2$
M = Ni (———), Pd (—-—), Pt (—--—) (heating rate 5°C/min).

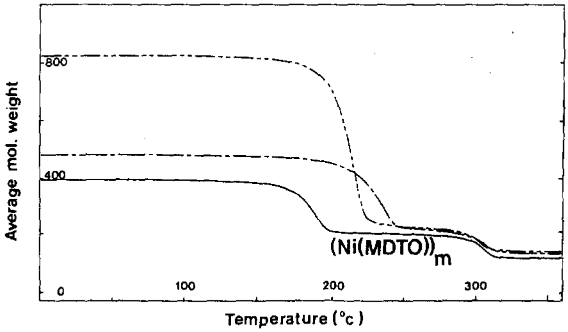


Fig. 3. Thermal decomposition curves of $Ni(MDTO)_2X_2$
X = Cl (———), Br (—-—), I (—--—) (heating rate 1°C/min).

ACKNOWLEDGEMENTS

The authors wish to thank J. Janssens and G. Thijs for technical assistance.

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