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# Thermal analysis of some Au(III) and Cu(I) dithiooxamide complexes

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## Abstract

Planar dithiooxamides form stable complexes with Au(III)- and Cu(I)-ions. The neutral $Au(LH)X_2$ ($LH_2$=RHNCSCSNHR)-complexes decompose without forming any intermediate. The ionic $A[Au(L)_2]$ (A=Li, Na, K) are mainly stabilized by the lattice forces. In the $[Au(LH_2)Br_2]Br$-complex the release of 1HBr per molecule occurs in two steps to form the more stable $Au(LH)Br_2$. The neutral $Cu(LH_2)_2X$ (X=Cl, Br, I) decompose to form the more stable $Cu(LH_2)X$. The $Cu(LH_2)X$-complexes disproportionate to form $(CuL)_x$ polymers, Cu, ligand and HX. The $Cu(CH_3HNCSCSNHCH_3)I$ shows the formation of a stable $Cu_4(CH_3HNCSCSNHCH_3)I_4$ and the ligand at 200°C. © 1998 Elsevier Science B.V.

*Keywords:* Au-complexes; Cu-complexes; Dithiooxamides; TG

## 1. Introduction

Planar dithiooxamides ($LH_2$=RHNCSCSNHR; R=H, alkyl) form neutral $Au(LH)X_2$ (X=Cl, Br, I)-complexes in acid media and ionic $A[Au(L)_2]$ (A=Li, Na, K)-complexes in strong alkaline media. The synthesis, the complete vibrational analysis and molecular structures of these complexes have recently been published [1]. The Cu(I)-complexes formed in acid media are described as $Cu(LH_2)X_1$ (X=Cl, Br, I). These compounds generally appear as binuclear complexes with bridging halogens and the ligands in the S-*cis* structure. For some complexes infrared spectra indicate a S-*trans* conformation for the ligand in a polymeric structure. $Cu(H_2NCSCSNH_2)Cl$ exhibits terminal metal–halogen bonds and a trigonal coordination, while the $Cu(H_2NCSCSNH_2)Br$ and all $Cu(LH_2)I$ appear in a tetrahedral coordination with bridging halogens [2].

In acetonitrile Cu(I) can also form $Cu(LH_2)_2X$ (X=Cl, Br), the ligands appear in the S-*cis* configuration exhibiting a $CuS_4$ coordination and a very weak terminal Cu–halogen. A very unusual six coordination with bridging halogens is less possible from the vibrational spectra [3].

Complexes can decompose at the ligand or by breaking the metal–ligand bond. For compounds with strong metal–ligand bonds we can expect a decomposition for the ligand; the breaking of the metal–ligand bond occurs for complexes with rather weak metal–ligand bonds. The Au(III)-complexes form strong metal–sulfur bonds as can be observed from the high $\nu$Au–S≈400 $cm^{-1}$ in the infrared spectra [1]. The Cu(I)-complexes form weaker metal–ligand bonds with the $\nu$Cu–S appearing in the 300 $cm^{-1}$ region [2]. The different metal–ligand bond strengths can result in a different thermal behaviour of these

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complexes. Some typical examples are discussed in this article.

## 2. Experimental

The compounds under investigation have been synthesized according to the literature data [1–3]. The infrared spectra were recorded on a Bruker IFS 113v F.T. spectrometer. The thermal analysis was performed on T.A. Instruments S.D.T. 2960 and T.G.A. 2950. All experiments were performed under dry nitrogen atmosphere (50 ml/min) and 5°C/min was the heating rate. $H_2S$ was identified by passing the evolved gas through an $AgNO_3$ solution, forming a black $Ag_2S$ precipitate.

The solid compounds formed at the end of the oven tube were all identified by infrared spectroscopy as pure ligands, as these planar dithiooxamides exhibit strong intramolecular hydrogen bonds and all sublime at higher temperatures [4]. The formation of acids was proved by passing the evolved gas through water and measuring the change in pH.

## 3. Results and discussion

### 3.1. The Au(III)-complexes

The most important data for the thermal decomposition of the Au(III)-complexes are summarized in Table 1.

It can be mentioned that none of the complexes at this heating rate (5°C/min) displayed a real plateau, indicating an intermediate was observed. The 'mass loss plateau' and 'temperature plateau' indicate the points where the most important mass loss ended.

The TG curves for the A[Au(DMDTO-2H)$_2$]-complexes are given in Fig. 1. It is very remarkable that the Li-complexes appeared thermally more stable than the Na- or K-compounds. The same sequence was (Table 1) observed for the DEDTO-complexes. However, the latter appeared to be less stable than the DMDTO-complexes. This is due to the different stability of the ligands as the decomposition of the complex occurs first at the ligand and not at the

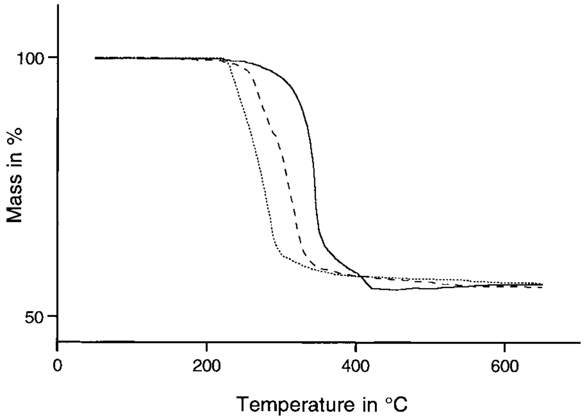

Fig. 1. The TG curves for the A[Au(DMDTO-2H)$_2$]-complexes. A=Li (———); A=Na (- - -); A=K (· · ·).

Table 1
Data for the thermal decomposition of Au(III)-complexes with planar dithiooxamides (5°C/min)

| Complex | Ti (°C) | Exp. mass loss | Theor. mass. loss for pure gold | Remaining products [a] |
|---|---|---|---|---|
| Li[Au(DMDTO-2H)$_2$] | 275 | −44 | −60.3 | Au$^0$ and Li salts |
| Na[Au(DMDTO-2H)$_2$] | 250 | −44 | −61.6 | Au$^0$ and Na salts |
| K[Au(DMDTO-2H)$_2$] | 230 | −44 | −62.7 | Au$^0$ and K salts |
| Li[Au(DEDTO-2H)$_2$] | 135 | −57 | −64.3 | Au$^0$ and Li salts |
| Na[Au(DEDTO-2H)$_2$] | 110 | −57 | −65.4 | Au$^0$ and Na salts |
| K[Au(DEDTO-2H)$_2$] | 100 | −57 | −66.3 | Au$^0$ and K salts |
| Au(DMDTO-H)Cl$_2$ | 165 | −55 | −52.5 | Au$^0$ |
| Au(DMDTO-H)Br$_2$ | 200 | −60 | −60.9 | Au$^0$ |
| Au(DMDTO)Br$_2$]Br | 150 | −65 | −66.3 | Au$^0$ |

[a] Characterisation of salts see text.
DMDTO=$CH_3HNCSCSNHCH_3$; DEDTO=$C_2H_5HNCSCSNHC_2H_5$.

metal–ligand bond. A decomposition at the metal–ligand bond should result in the formation of pure ligand which, then, could be identified at the oven tube as a sublimed compound. Infrared spectra of the remaining product clearly showed the presence of KNCS, indicating the decomposition of the ligand, due to the strong Au–S bonds.

The fact that the Li-complexes appeared as the most stable compounds is in contradiction with the principle of symbiosis as formulated by Basolo [5].

A possible explanation for the high stability of the Li-compounds could be ascribed to the stronger ion pair in the Li-compounds, the attractive forces between the two types of ions in the lattice then become weaker for Na- and K-compounds.

The [Au(DMTO)$Br_2$]Br appears with two covalent Au–Br groups and one bromide counter ion, strongly hydrogen bonded with the NH of the secondary thioamide group.

The $\nu$NH for this complex was observed as a very broad band with a maximum at 2690 $cm^{-1}$ indicating very strong $N^+$–H- - -$X^-$ hydrogen bonding, similar to the ammonium type of hydrogen bonding. This strong hydrogen bonding stabilizes the complex. This complex starts to decompose at 150°C to form pure $Au^0$ as given in Fig. 2. The isothermal at 100°C for this compound gave a weight loss of ca. 14%, probably corresponding to one mole of HBr. This formation of HBr clearly occurs in two steps. The first step is the release of half a mole of HBr resulting in a stable intermediate with minimum formula $\{[Au_2(LH_2)(LH)Br_4]Br\}_n$. The second step is the formation of the stable Au(LH)$Br_2$, characterised by the typical intramolecular $\nu$(N–H$\cdots$N) at 3206 $cm^{-1}$ [6]. The overall reaction is given in Fig. 3. As shown in Table 1, the neutral Au(III)-complexes all decompose to form the pure metal. The ionic compounds also form the pure metal and other residual products exhibiting C–C≡N groups and NCS-ions, as observed from the nitrile frequencies in the infrared spectra [7].

### 3.2. The Cu(I)-complexes

Table 2 contains the summarized data for the thermal degradation of some Cu(I)-complexes with dithiooxamides. The data for the Cu–halides, formed during the decomposition are also included.

For CuBr the mass loss is completely due to the sublimation and vaporisation of this compound, with a very low melting point of 492°C [8]. CuCl (430°C) and CuI (602°C) also have very low melting points, but here only partial mass loss is observed; this resulting mass corresponds exactly to the formation of Cu(II)O. This is confirmed by the far-infrared spectra of the remaining product. The oxidation is due to small amounts of oxygen, still present in the T.A. equipment. This phenomenon has already been observed with the same type of instrumentation [9]. So

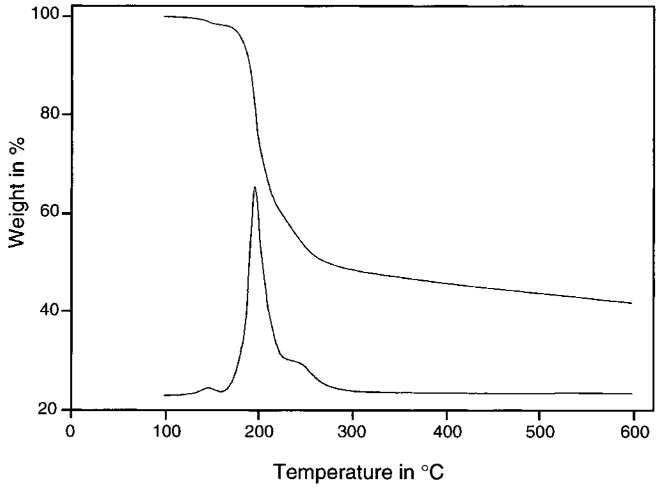

Fig. 2. The TG and DTG curves for [Au(DMDTO)$Br_2$]Br.

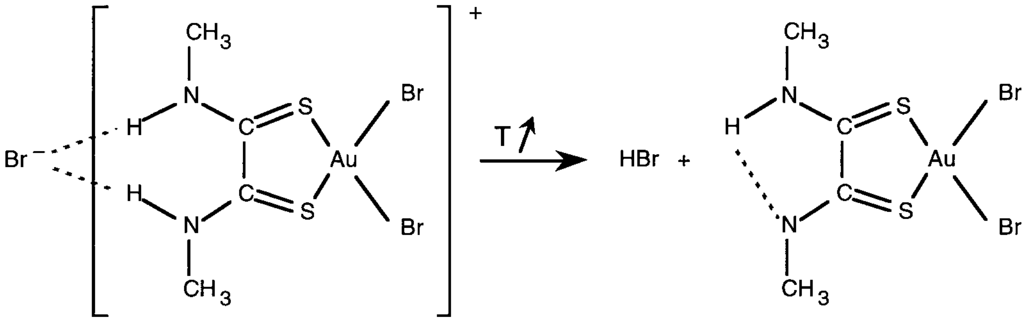

Fig. 3. The reaction scheme for the formation of $Au(LH)Br_2$.

Table 2
Data for the thermal decomposition of Cu(I)-complexes with planar dithiooxamides (5°C/min)

| Complex | Ti (°C) | Exp. mass loss | Theor. mass. loss for pure CuO | Rest products |
|---|---|---|---|---|
| Cu(DTO)Cl | 165 | −64 | −63.7 | CuO |
| Cu(MDTO)Cl | 100 | −66 | −65.9 | CuO |
| Cu(DMDTO)Cl | 135 | −68 | −67.8 | CuO |
| Cu(DTO)Br | 130 | −69 | −69.8 | CuO |
| Cu(MDTO)Br | 125 | −81 | −71.4 | CuO |
| Cu(DMDTO)Br | 120 | −87 | −72.7 | CuO |
| Cu(DTO)I | 175 | −70 | −74.4 | CuO |
| Cu(MDTO)I | 140 | −75 | −75.5 | CuO |
| Cu(DMDTO)I | 140 | −82 | −76.5 | CuO |
| $Cu_4(DMDTO)I_4$ | 205 | −68 | −65 | CuO |
| $Cu_2(DMDTO)Cl_2$ | 175 | −47 | −55 | CuO |
| $Cu(DMDTO)_2Cl$ | 110 | −80 | −79.9 | CuO |
| $Cu(DEDTO)_2Cl$ | 100 | −83 | −82 | CuO |
| $Cu(DMDTO)_2Br$ | 105 | −87 | −81.9 | CuO [a] |
| $Cu(DEDTO)_2Br$ | 100 | −86 | −84 | CuO [a] |

[a] See text (sublimation of CuBr).
DMDTO=$CH_3HNCSCSNHCH_3$; DEDTO=$C_2H_5HNCSCSNHC_2H_5$.

the sublimation for CuBr only seems to occur faster than the oxidation.

The resulting mass of the Cu-compounds indicates that in most cases the complexes decompose to form Cu(II)O. For some iodo-complexes however, we observed the formation of the intermediate CuI, further oxidized to Cu(II)O.

This oxidation is also responsible for the unusual TG curve obtained for Cu(DMDTO)Cl where at 350°C a minimum mass is reached, on further heating the mass again increases until it finally decreases again, reaching the same level as observed at 350°C. This behaviour is also observed in the decomposition of $CuC_2O_4$ in the presence of small traces of oxygen [9].

The TG and DTG curves for the $Cu(DEDTO)_2Cl$ and $Cu(DEDTO)Cl_2$ are given in Fig. 4. $Cu(DEDTO)_2Cl$ decomposed with a weight loss that corresponds to one ligand to form Cu(DEDTO)Cl. This is clearly shown in Fig. 4 where the dotted curves are the TG and DTG of the Cu(DEDTO)Cl-complexes. This was not observed for the DMDTO-complexes as the Cu(DMDTO)Cl already started to decompose at 135°C, at this temperature. A loss of weight of ca. 5% was observed for the $Cu(DMDTO)_2Cl$-compound.

Fig. 5 gives the TG curves for several chloro-complexes with DMDTO as ligand. The different compounds show a similar profile in their decomposition, forming a stable compound ca. 200°C, followed by an increase in mass in the 400–600 region. The loss of

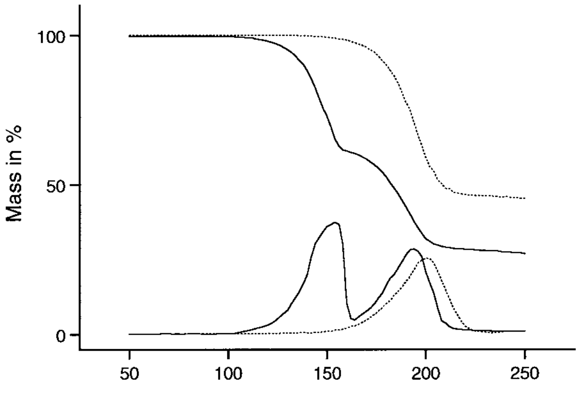

Fig. 4. The TG and DTG curves of Cu(DEDTO)$_2$Cl (———) and Cu(DEDTO)Cl (· · ·).

weight at 200°C corresponds to 1.5 ligand and 1HCl for Cu(DMDTO)$_2$Cl; 0.5 ligand and 1HCl for Cu(DMDTO)Cl and 2HCl for Cu$_2$(DMDTO)Cl$_2$.

The stable product formed at 200°C for all compounds is identified as the Cu(II)-polymer as given in Fig. 6 [10], characterised in the vibrational spectra by the absence of the NH modes.

The decomposition of the Cu(DMDTO)$_x$Cl$_x$-complexes are all very similar and can be given as follows:

$$2x\mathrm{Cu(DMDTO)_2Cl} \rightarrow [\mathrm{Cu(DMDTO-2H)}]_x + 3x\mathrm{DMDTO} + 2x\mathrm{HCl} + x\mathrm{Cu}^0$$

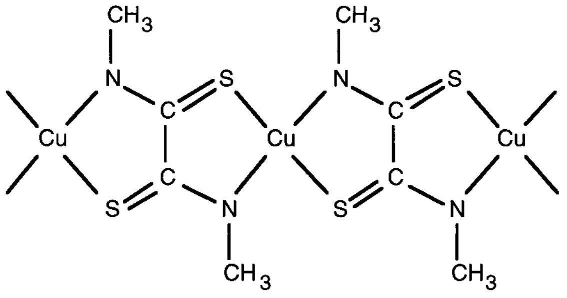

Fig. 6. Geometry of the Cu-polymer [Cu(DMDTO-2H)]$_n$.

$$2x\mathrm{Cu(DMDTO)Cl} \rightarrow [\mathrm{Cu(DMDTO-2H)}]_x + x\mathrm{DMDTO} + 2x\mathrm{HCl} + x\mathrm{Cu}^0$$

$$x\mathrm{Cu_2(DMDTO)Cl_2} \rightarrow [\mathrm{Cu(DMDTO-2H)}]_x + 2x\mathrm{HCl} + x\mathrm{Cu}^0$$

Some of the ligands deprotonate to form polymers, identical to the polymers formed by deprotonation in alkaline medium with Cu(II) [9].

The formation of solid AgCl, and the lowering of the pH by dissolving the gas in water is a clear indication of the formation of HCl. The solid, formed at the end of the oven tube by the decomposition of Cu(DMDTO)$_2$Cl and Cu(DMDTO)Cl has been identified by infrared as the pure ligand.

For all reactions we have the disproportionation:

$$2\mathrm{Cu(I)}_{\mathrm{monomer}} \rightarrow \mathrm{Cu(II)(polymer\ form)} + \mathrm{Cu}^0$$

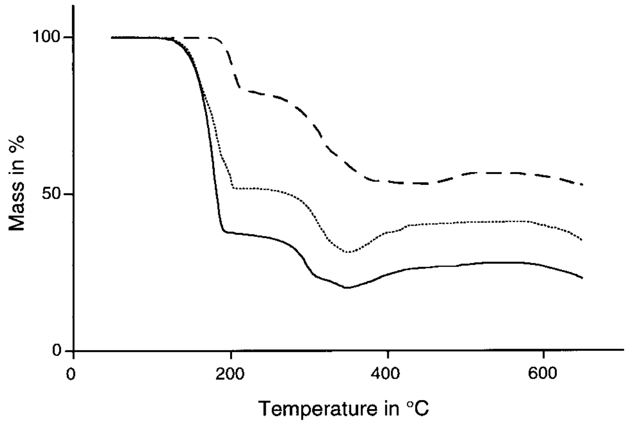

Fig. 5. The TG curves of Cu$_2$(DMDTO)Cl$_2$ (- - -), Cu(DMDTO)Cl (· · ·) and Cu(DMDTO)$_2$Cl (———).

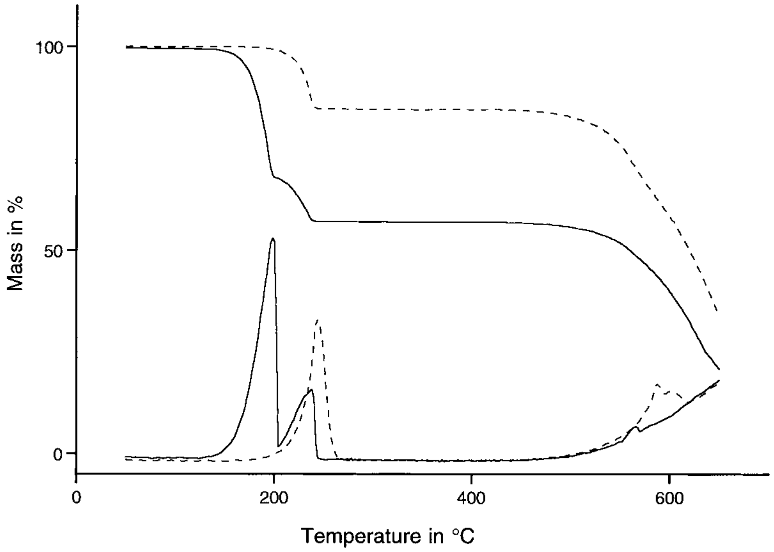

Fig. 7. The TG and DTG curves of Cu(DMDTO)I (———) and $Cu_4(DMDTO)I_4$ (- - -).

Fig. 7 gives the TG and DTG curves for Cu(DMDTO)I and $Cu_4(DMDTO)I_4$. The decomposition of Cu(DMDTO)I occurs in three steps. The first step is a loss of weight of ca. 32% i.e. 3/4 of the ligand and the second step gives a loss of weight of 11.5% (1/4 of the ligand). The last step is the oxidation from CuI to CuO

The IR spectrum of the stable intermediate formed after the first step is identical to the $Cu_4(DMDTO)I_4$ formed in the laboratory [11].

By the decomposition of Cu(DMDTO)I some pure ligand is formed at the oven tube, so the reaction can be given as follows:

$$4Cu(DMDTO)I \rightarrow 3DMDTO + Cu_4(DMDTO)I_4$$

$Cu_4(DMDTO)I_4$ appears as layers of CuI and layers of the ligand in the stable S-*trans* form [11].

Regarding the stability of these complexes it is obvious that the iodo-complexes are all more stable than the chloro- and bromo-compounds. To some extent the structure of the complexes plays a role in the greater stability (i.e. for the DMDTO-complexes), but mainly the very strong soft–soft interactions in the Cu–I have their influence. This is confirmed by the fact that the decomposition of all iodo-complexes occurs through the formation of CuI, while CuCl and CuBr salts are not always formed.

## 4. Conclusion

The Au(III)-complexes decompose without forming any intermediates, while the Cu(I)-complexes all decompose by releasing some ligand and forming new complexes.

This is due to the strong metal–ligand bonds in the Au-complexes ($\nu$Au–S$\approx$400 cm$^{-1}$) compared with the weaker bonds in the Cu-complexes ($\nu$Cu–S$\approx$300 cm$^{-1}$).

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