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THE THERMAL BEHAVIOR OF DITHIOOXAMIDE LIGANDS AND THEIR NICKEL COMPLEXES

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ABSTRACT

The thermal behavior of substituted dithiooxamide ligands and their nickel complexes has been studied with differential scanning calorimetry and thermogravimetry. The thermal products were analyzed by mass spectral and IR techniques. The mechanism of the thermal decomposition of both the free ligands and metal complexes precludes the clean thermal formation of the polymeric nickel complexes from the neutral ligand derivatives, $Ni(LH_2)_2Br_2$.

INTRODUCTION

Continuing our interest in exploring the chemistry of dithiooxamide (DTO) ligands [1,2], we have studied the thermal behavior of the free ligands in order to make comparisons with that of their nickel complexes. Previous reports on thermal processes of related DTO metal complexes [3-6] suggest that the polymeric nickel complex $\{Ni(LH)\}_n$ might be prepared via thermal loss of HBr and excess ligand from the dibromobis(DTO) complex, $Ni(LH_2)_2Br_2$. We have found that, in general for the nickel complexes, the polymers are not formed cleanly. The reasons this occurs are related to the interesting thermal behaviour of the free ligands which, apparently, has not previously received attention.

The substituted DTO ligands (structures **1-7** below) and their nickel complexes were studied by differential scanning calorimetry (DSC), thermo-

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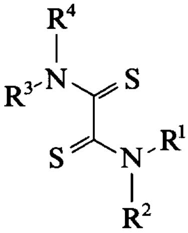
gravimetry (TG), differential thermal analysis (DTA) and mass spectrometry (MS).



1 $R_1 = R_2 = R_3 = R_4 = H$ (DTO)
2 $R_1 = R_3 = -CH_2C_6H_5, R_2 = R_4 = H$
3 $R_1 = -CH_2C_6H_5, R_2 = R_3 = R_4 = H$
4 $R_1 = -CH_2C_6H_5, R_3 = p\text{-}OCH_3\text{-}C_6H_4, R_2 = R_4 = H$
5 $R_1 = -C_6H_5, R_2 = R_3 = R_4 = H$
6 $R_1 = -CH_2CH_3, R_2 = R_3 = R_4 = H$
7 $R_1 = -CH_3, R_2 = R_3 = R_4 = H$

EXPERIMENTAL

Synthesis of the ligands

DTO (**1**) (Aldrich Chemical Co.) was recrystallized from hot ethanol containing activated charcoal. Ligand **2** was prepared according to ref. 7. Ligands **3**–**6** were prepared as described previously [2].

Synthesis of $Ni(LH_2)_2Br_2$

The complexes were prepared by known methods [8–11]. Details concerning conditions and characterization are described elsewhere [12].

Synthesis of $\{Ni(LH)\}_n$

The polymeric complex of ligand **3** was prepared by mixing methanolic solutions of the free ligand with nickel acetate (10% excess) at room temperature. The product was separated and washed repeatedly with methanol, and dried in vacuo for 3 days.

Thermal techniques

DSC and TG analyses were run at heating rates of 10 °C min^{-1} (except where noted), controlled by a DuPont Instruments 9900 computer/thermal analyzer under nitrogen purge (50 ml min^{-1}). DSC samples were run on a

DuPont model 912 dual sample DSC (3–5 mg, closed pan) calibrated with indium standards. TG samples (10–15 mg) were run on a DuPont model 951 TGA. DuPont DSC, TG and DSC purity software programs were used for all thermal data calculations.

Mass spectral analyses were recorded on an HP5995A GC/MS. Samples were put into a melting-point capillary tube which was then placed in the direct insertion probe. The probe was positioned in the spectrometer's source and heated at 10 °C min^{-1}. The volatile components were subjected to ionizing bombardment at 70 V in the electron impact mode.

RESULTS

The results, summarized in Table 1, are discussed in detail below.

Free ligands

Dithiooxamide (1)

The DSC shows two endothermic transitions which are consistent with the occurrence of two melting points. However, TG (Fig. 1) combined with MS shows that these transitions are due to DTO sublimation complicated by simultaneous decomposition. This complex process peaks at 230 °C and is then followed by slow loss of residue. Unlike all of the other ligands

TABLE 1

Results of thermal studies on free ligands

Ligand	m.p. [a] (°C)	TG [b] (°C)	MS
1 DTO	220.6	138–300, 90.1%	DTO + decomp
2 Di-benzyl DTO	111.5 99.9% pure [c] possible *cis–trans*	200–400, 92.9%	DTO + decomp
3 Benzyl DTO	87.0	145–275, 61.2%	DTO + decomp
4 Benzyl-methoxy-benzyl DTO	90.7	200–520, 84.5%	DTO + decomp
5 Phenyl DTO	96.9% pure 101.0 98.7% pure	150–300, 81.6%	DTO only
6 Ethyl DTO	80.3 100% pure	100–220, 100.0%	DTO only
7 Methyl DTO	124.1	80 –165, 45.0% 165–210, 50.4%	

[a] Melting point peak temperature determined via DSC.

[b] Weight loss limits determined between minima in DTA curves: the remaining weight loss in these samples continues at gradual rate.

[c] Purity as determined by DuPont DSC purity analysis software and confirmed with elemental analysis.

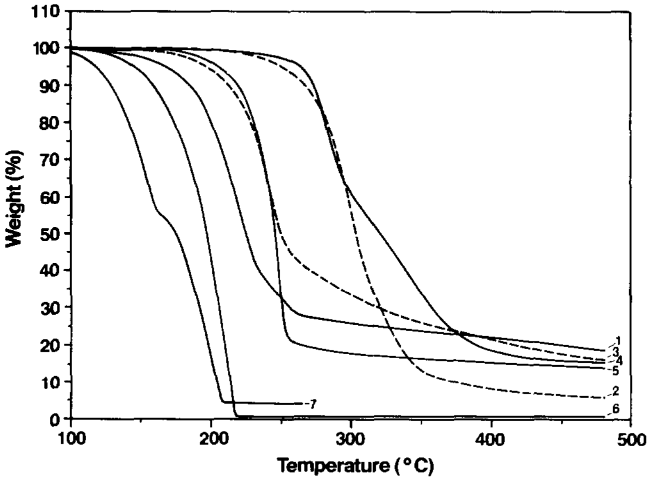


Fig. 1. TG curves for the free dithiooxamide ligands.

reported below, the apparent melting point for DTO (230 °C) is characterized by volatization combined with a decomposition process beginning at temperatures as low as 110 °C. Further, as much as a 60% weight loss accompanies the attaining of the DSC melting-point temperature. By 250 °C, the end of the apparent melting range, 90% is lost. All of the other DTOs sublime and/or decompose at temperatures well beyond their melting points.

Dibenzyl dithiooxamide (2)

DSC also shows two melting point endotherms, similar to the DTO DSC, but the two-phase weight loss in the TG occurs at a much higher temperature and demonstrates that the endotherms occur without weight loss. The smaller endotherm could be the result of an impurity; however, elemental analysis and spectral properties indicate that the purity of the compound is quite high. This suggests the possibility that crystallization of this material during the purification process may produce polymorphic solids. This might arise from a mixture of separately crystallized *cis* and *trans* isomers. In such a case, melting the sample would be expected to equilibrate the mixture to the most stable isomer and, thereafter, a second heating cycle in the DSC would find only the one isomer leading to a single melting point: this is what was found.

Monobenzyl dithiooxamide (3)

Above the single melting point of this compound, TG and MS also show volatility combined with decomposition. However, the peak decomposition is 60 °C lower than that observed for compound (**2**).

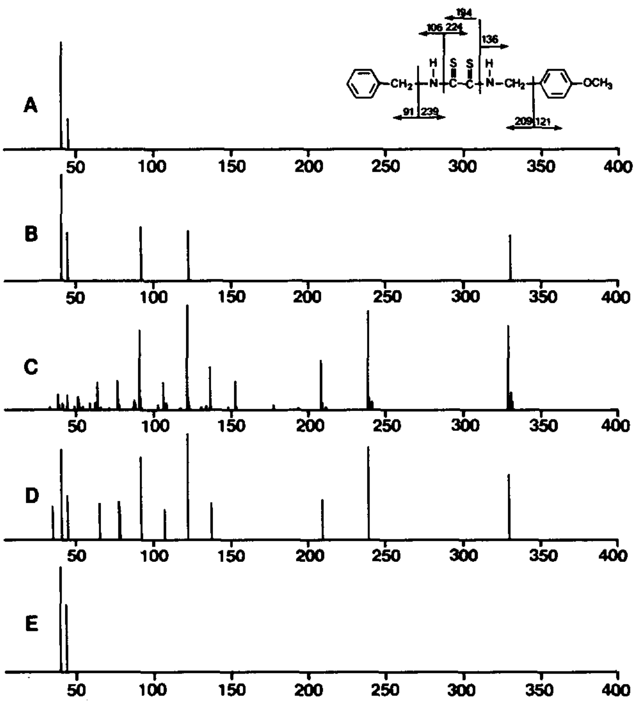


Fig. 2. Mass spectral analysis of the heating process for benzyl-methoxy-benzyl dithiooxamide. Spectra at the following times t: A, $t = 0$; B, $t = 5$ min; C, $t = 10$ min; D, $t = 15$ min; E, $t = 20$ min.

Benzyl methoxybenzyl dithiooxamide (4)

The thermal behavior parallels that of the other DTOs, but the thermal stability is found to be lower than that of **2** and greater than that of **3**.

The results of the mass spectral analysis of the heating process for this ligand are typical of the free ligands and are shown in Fig. 2, where A is the spectrum observed at $t = 0$; B, at 5 min; C, at 10 min; D, at 15 min; and E, at 20 min. At zero time, only spectrometer gases are observed ($m/e = 40$ and 44). After 5 min of heating three peaks are observed which are related to the fragmentation of the ligand at $m/e = 91$ (49%), 121 (45.1%) and 330 (43%). After 10 min, a complete mass spectrum is present in which all fragments of the ligand are observed. The interpretation is the same as that reported for similar ligands [12]. As the time of heating continues, some peaks are lost until after 20 min all of the ligand peaks have disappeared; this is consistent with the decomposition of the ligand in this time span.

Monophenyl dithiooxamide (5)

DSC for compound **5** shows a single melting point at 101° C and TG shows a deceptively simple sublimation/decomposition weight loss process; MS, however, demonstrates that the apparently simple TG weight loss is a mixture of sublimation and decomposition, yet even at high temperatures a substantial residue remains.

Monoethyl dithiooxamide (6)

The TG and MS of this ligand are unlike those of any of the other DTOs. This ligand has a single volatilization transition with no sign of decomposition. Compared to DTO itself, the melting point drops by about 140 ° C; it sublimes cleanly without decomposition, and the sublimation temperature is lower by about 20 ° C. All of this is caused by the simple replacement of a hydrogen with an ethyl group. Higher molecular weight monoalkyl DTOs do not exhibit the same simple sublimation pattern. Their sublimation temperatures are closer to those of monoaryl DTOs, but their thermal stabilities are much lower.

Monomethyl dithiooxamide (7)

Compared to the monoethyl DTO, the thermal behavior of the monomethyl DTO is surprisingly complex. Two main weight losses occur (DTA shows peaks at 150 and 200 ° C), resulting in a 3.9% residue.

$Ni(LH_2)_2Br_2$ complexes

The results summarized in Table 2, are discussed in detail below.

*Nickel complex of **1***

The DSC of unsubstituted $[Ni(LH_2)_2Br_2]$ is deceptively simple: two apparent "melting points" are followed by decomposition. On the other hand, the TG is deceptively definitive (Fig. 3). While the first weight loss can be clearly attributed to one mole of H_2O (3.98% theory; 4.02% found) and correlates well with the elemental analyses, the following weight losses are not as clear cut. The second weight loss is cleanly separated from both the preceding water loss and the succeeding weight loss at 400 ° C, and is equivalent to the first DSC "melting point" endotherm transition at 284 ° C. However, no clear assignment of this transition can be made because of the convoluted loss of not only HBr and free ligand but also of ligand decomposition products, as revealed by the mass spectral results. This transition which constituted a 53.05% loss in weight, which calculates to 240.32 a.m.u., could represent 2 moles of ligand or, alternatively, a sum of one and a half DTOs and one HBr. Clearly, we cannot assign a structure to the erstwhile intermediate implied by these results. In contrast, the sum of the two main TG losses leave an NiS residue at the point where the temperature has reached 700 ° C (20.04 calc.; 17.50% found).

*Nickel complex of **2***

For this compound, the dibenzyl derivative, the DSC is quite complex. The transition at 192.5 ° C appears to be a melting point that leads directly

TABLE 2

Results of thermal studies on $Ni(LH_2)_2Br_2$

Ligand	DSC (°C)	TG [a] (°C)	Wt. loss	MS
1 DTO	284.0 + 355.3	150–220	4.0%	HBr, DTO, S2
		220–340	53.1%	
		340–490	20.1%	
2 di-benzyl DTO	192.6	80 –225	13.1%	HBr + DTO
		225–306	20.4%	
		306–394	24.0%	
		394–545	13.8%	
3 Benzyl DTO	214.7 exotherm	50 –120	4.6%	HBr + DTO
		120–237	16.1%	
		237–280	10.7%	
		280–334	11.0%	
4 Benzyl-methoxy-benzyl DTO	192.7	145–215	12.6%	HBr + DTO
		215–445	34.8%	
5 Phenyl DTO	250 exotherm	170–300	30.6%	HBr + DTO
		300–465	27.4%	
6 Ethyl DTO	229 endotherm	130–300	46.5%	HBr + DTO
	304/348 main endotherm	300–400	26.9%	
7 Methyl DTO	250 exotherm	140–300	54.6%	
		300–450	10.6%	
Results of studies on $\{Ni(LH)\}_n$ (**8**)				
Benzyl DTO	290.2 exotherm	250–350	25.1%	no HBr
		350–500	10.5%	

[a] Weight loss limits determined between minima in DTA curves: the remaining weight loss in these samples continues at gradual rate.

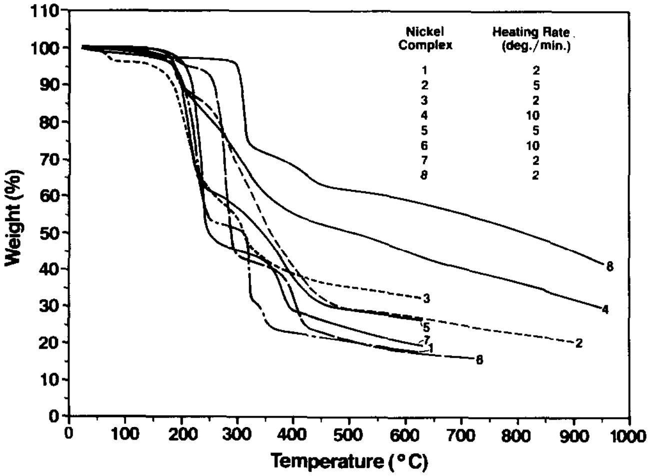


Fig. 3. TG curves for the nickel complexes of dithiooxamide ligands.

into thermal decomposition (197.3 ° C). The new species then undergoes a similar transition at 389.2–404.3 ° C. TG shows that 0.5 mole of water is lost by 150 ° C. This is followed by a complicated series of weight losses (at least 5) that cannot be separated. MS shows that both HBr and free ligand are lost during the thermal decomposition. A final NiS residue would constitute only 11.07% of the original weight, but this complex is still decomposing at 800 ° C and a 25% residue remains at that point.

The comparison of the TG of the free ligand with that of this nickel complex is revealing. Since the free ligand is not lost until about 300 ° C, the comparison suggests that the first main transition may involve HBr loss: theory, 9.79%; found, 13.10%. MS reveals that HBr loss occurs essentially simultaneously with sublimation and decomposition of the free ligand.

Nickel complex of ***3***

Not surprisingly, the DSC of the monobenzyl derivative is virtually identical to that of the complex of **2**. The TG, however, shows differences, not the least of which is the absence of water. The onset temperatures compare well (theory for one HBr, 9.22%; found, 12.46%), but the subsequent decomposition, while as complicated, is very different, and even at 900 ° C decomposition is still occurring (29.8% residue still remaining versus 10.32% calculated for NiS). For formation of the polymer, there should be a 44.24% weight loss: by 440 ° C the loss is about 46%.

Nickel complex of ***4***

The DSC shows a small phase change at about 100 ° C which precedes a single decomposition exotherm (214.7 ° C), followed by a changing baseline due to decomposition and weight loss. The DTA suggests that there are several transitions, the first of which might be expected to involve water: it shows a peak temperature of 75 ° C with the slower heating rate of 2 ° C min^{-1}. However, it calculates to a molar mass of 29.4, possibly indicating more than one mole of water or a higher molecular weight solvent. The next peak corresponds to the DSC exotherm at 225 ° C.

It is intriguing to note that the transitions marked on Fig. 3 approximately account for 2HBr and one ligand. This suggests that a polymer might be produced by about 500 ° C. The MS shows that such materials are lost. Finally, NiS should give a residue of 14.19% in this case but weight loss is still occurring past 700 ° C (still more than 35 wt.% remaining). Both the peak rate for free ligand volatilization (at 240 ° C) and analogy with the complexes noted above suggest that the first decomposition peak involves loss of HBr as indicated by the MS results.

Nickel complex of ***5***

The DSC results correlate reasonably well with those obtained with TG. The exotherm centered at 240 ° C is consistent with the first weight loss peaking at about 220 °C. The sum of the first two main weight losses correlates well with the MS results and the expectation that losses of two moles of HBr plus one mole of ligand should produce the polymer.

Nickel complex of ***6***

The 239 °C exotherm in the DSC data for this complex correlates well with the first minor weight loss in the TG. The complex shows no water loss via TG, and the first main weight loss, corresponding to about 47%, is reasonably close to the theoretical value for loss of one HBr and one ligand. Unlike all of the other DTO complexes and consistent with the unique character of the free ethyl substituted ligand, this complex attains its final weight by 600 °C (theoretical for NiS, 17.6%; found, 18.6%). We presume that this is because of the greater thermal stability and higher volatility of this unique ligand.

Investigation of the $Ni(LH_2)_2Br_2$ complex, where LH_2 is **6**, revealed that it decomposes into the free ligand which occurs after 15 min of heating. The molecular ion of the complex could only be detected using FAB techniques.

Nickel complex of 7

While the DSC reveals no definable transitions, the TG appears to be simple in showing only two well-separated weight changes. Its thermal decomposition, however, is similar to all of the other complexes in that no clear product is formed.

Neutral nickel complex ***8****, $[Ni(LH)]_n$*

The DSC results for the polymeric complex of ligand **3** are deceptively simple. The single main transition at 290 °C correlates well to the main weight loss in the TG centered at 300 °C. The TG of the corresponding monomeric complex (at the slower heating rate of 2 °C min^{-1}) gives a weight loss pattern above 300 °C which is reminiscent of this polymer. As expected, the polymer is more stable than the monomeric complexes.

DISCUSSION

In agreement with the related studies of Desseyn and co-workers [3–6], the nickel–DTO complexes investigated here generally form an intermediate complex during the thermal conversion of monomeric $Ni(LH_2)_2Br_2$ to polymeric $\{Ni(LH)\}_n$. However, we have found that while plateaus do occur during the thermal conversion, those features are DTO-type and heating rate dependent and they are not reliable indicators of pure polymer formation. With the exception of ethyl DTO (**6**), this can be traced to the behavior of the free ligands; they do not undergo simple sublimation. Under nitrogen, these substituted DTOs generally decompose and sublime simultaneously.

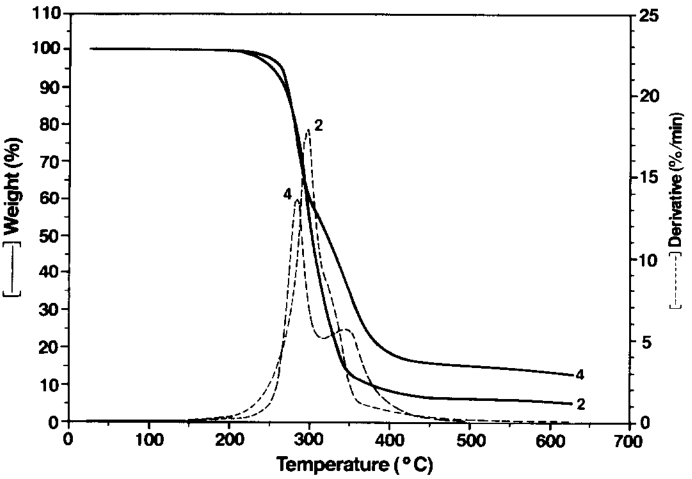


Fig. 4. Integral and derivative TG curves for two free ligands.

Furthermore, when the ligands decompose they leave non-volatile residues, even at high temperatures. Slower heating rates help to separate the thermal transitions but fail both to eliminate the decomposition and to yield pure polymer.

The nature of the free ligand decomposition products has not been established. This can be best illustrated by the results of TG studies of two similar DTOs, **2** and **4**, the dibenzyl and benzyl-*p*-methoxybenzyl derivatives, respectively. Neither compound sublimes cleanly, and, considering their similarities, their mixed decomposition/sublimation behaviors are surprisingly different. As shown in Fig. 4, thermolysis of **4** is characterized by a two-phase process while the same treatment of **2** produces an apparent single phase process at a much lower temperature. Decomposition has been confirmed for both cases and consequently, the metal complexes should not be expected to yield clean intermediates during thermolysis. On this basis it is surprising that the palladium complexes have been reported to form pure polymer upon heating of the monomeric complexes [4–6]. In conclusion, the thermal decomposition of $Ni(LH_2)_2Br_2$ complexes is not an attractive route for preparing the pure nickel DTO polymers.

Since the volatilization/decomposition processes for the free ligands generally occur at temperatures much higher than their melting points, the results of the DSC and TG studies on these free ligands cannot be said to correlate. In contrast, the DSC and TG results on some of the monomeric nickel complexes do correlate, at least for the first one or two thermal transitions. As illustrated in Fig. 3, the DSC of the nickel complex of **4**, for example, reveals the initial small weight loss associated with the presence of solvent, and the first major loss, an exothermic decomposition (2HBr + ligand) to the polymer precursor. Subsequent DSC phase changes cannot be interpreted due to the weight loss and closely spaced thermal conversions.

What can be said concerning the decomposition mechanism of the monomeric $Ni(LH_2)_2Br_2$ complexes is that, other than solvent loss in the appropriate cases, the first and only well separated step in most of the complexes is loss of HBr. The HBr is observed by mass spectrometry and its loss is consistent with the weight loss calculations in the TG, limited only by the closeness of the subsequent weight loss transitions.

The intermediate nickel complex must then undergo rearrangement to lose the additional mole of HBr and one mole of the DTO ligand. The processes associated with the subsequent loss of the combination of HBr and ligand are invariably complex and yield complicated TG and DTA curves that resist analysis. While the eventual formation of NiS from all of the complexes is likely, the complex mixture of thermal decomposition products prevent any attempt at analysis.

The unique character of ethyl-substituted DTO, ligand **6**, can be rationalized in part by the low molecular weight of the ligand, when compared to other substituted DTOs, and by the reduced extent of hydrogen bonding, when compared to DTO itself. While the DTA of the nickel complex also shows the same complicated thermal decomposition as the other complexes, this is the only complex that is completely converted to the NiS product at a moderate temperature.

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