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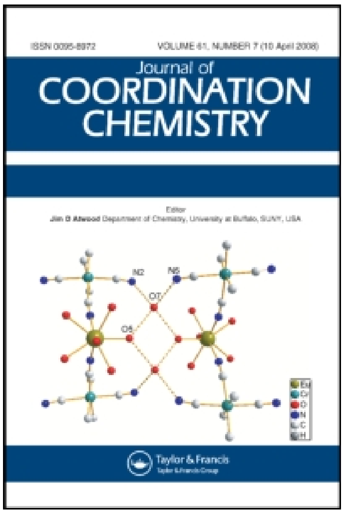

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THERMAL DECOMPOSITION OF NEODYMIUM AMIDE COMPLEXES

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The decomposition of $NdCl_3L$ ($L = N,N$-dimethylformamide [DMF] or N,N-dimethyacetamide [DMA]) compounds has been investigated by thermogravimetric and differential thermal analysis (TGA and DTA) coupled with Fourier transform infrared (FTIR) spectroscopy. When heated in air, the $NdCl_3L$ compounds decompose by a mechanism involving oxidation of the amide ligand to CO_2 and HCl. Some free armide is also released in the thermal decomposition in air. However, when heated under nitrogen, clean release of DMA or DMF is observed. In both cases, the amide is released two steps. From 30 to 40% of the amide is initially released with little or no associated enthalpy as measured by DTA. As the temperature is increased, the remaining 60 to 70% of the amide is released *via* an endothermic process. The enthalpy for this release is 53.1 ± 3.8 kJ/mole for DMF and 40.9 ± 1.1 kJ/mole for DMA, suggesting that DMF binds more strongly to Nd(III) than does DMA. Steric effects caused by the additional methyl group in DMA might be responsible for the weaker binding of this amide compared to DMF.

Keywords: Neodymium; Thermal analysis; Dimethylformamide; Dimethylacetamide

INTRODUCTION

A number of research groups have been investigating the extraction of lanthanide and actinide ions by amide ligands. These extractants are of potential use in separating long-lived radionuclides from high-level radioactive wastes. Monoamides are known to extract tetravalent and hexavalent actinides [1–7], whereas diamides extract trivalent actinides and lanthanides along with the tetravalent and hexavalent actinides [8–14]. Although studies have been performed to determine the relative binding affinities of amides to lanthanide and actinide ions, as reflected in the relative distribution coefficients, obtaining quantitative measurements of the metal–amide binding thermodynamics has proved difficult.

We have been investigating the use of thermochemical methods to measure the binding affinity of amides to lanthanide and actinide ions. In particular, we have

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applied differential thermal analysis (DTA) to determine the enthalpy of the following type of reaction:

$$MX_nL(s) \rightarrow MX_n(s) + L(g) \tag{1}$$

where M is a lanthanide or actinide ion, X is the counter anion, and L is a neutral ligand. The DTA and thermogravimetric analysis (TGA) methods have been described by Boerio-Goates and Callanan [15]. We report here the thermal decomposition of complexes of the type $NdCl_3L$, where $L =$ N,N-dimethylformamide (DMF) or *N*,*N*-dimethyacetamide (DMA). Similar TGA results have been reported for uranyl amide complexes [16] and for thorium(IV) pyridine N-oxide complexes [17], although these earlier studies did not report reaction enthalpies. In our studies, the complexes were subjected to DTA as well as TGA to determine the reaction enthalpies. Determination of reaction enthalpies by DTA assumes that the heat capacities are constant over the temperature range in which the reaction occurs. The decomposition was followed by monitoring the off-gas with Fourier transform infrared (FTIR) spectroscopy. In addition, the FTIR spectra of the residues were obtained after heating to specific temperatures. Similar methodology has recently been applied to the study of erbium oxalate hexahydrate [18], chromium(III) formate [19], and magnesium pyridine complexes [20].

EXPERIMENTAL

DMF was obtained from Aldrich Chemical Company (Milwaukee, Wisconsin), DMA was obtained from Mallinckrodt Specialty Chemicals Co. (Paris, Kentucky), and $NdCl_3 \cdot 6H_2O$ was obtained from Alfa Aesar (Ward Hill, Massachusetts). These were used as received.

The $NdCl_3L$ complexes formed as sticky semi-solids when methanolic solutions of $NdCl_3 \cdot 6H_2O$ and one molar equivalent of amide (L) were evaporated under vacuum. The FTIR spectra of these complexes were obtained as thin films on KBr plates after the methanolic solutions were evaporated. Shifting of the amide carbonyl stretching vibrations to lower energy confirmed the formation of the Nd amide complexes (Table I). Attempts to crystallize these materials failed. For the TGA and FTIR spectroscopic experiments, stock solutions were prepared by mixing equimolar quantities of $NdCl_3 \cdot 6H_2O$ and L in MeOH.

A Seiko 320 series thermogravimetric calorimeter was used in this study to monitor mass losses and the associated enthalpy changes. The TGA/DTA was operated at

TABLE I Summary of amide carbonyl stretching frequencies for $NdCl_3L$ compounds

	$\nu(C{=}O)$, cm^{-1}		$\Delta\nu(C{=}O)$, cm^{-1}
	Complex	*Free Amide*	
$NdCl_3{\cdot}DMF$	1653	1673	20
$NdCl_3{\cdot}DMA$	1610	1643	33

DMF = *N*,*N*-dimethylformamide.
DMA = *N*,*N*-dimethylacetamide.

TABLE II Ending temperatures (°C) for the TGA experiments

Run#	*DMF*	*DMA*
1	260	260
2	350	300
3	–	350

a scan rate of 1°C/min using either dry air or nitrogen as the carrier gas. The off-gas from the decomposition of the $NdCl_3L$ complexes was routed through a Nicolet 750 FTIR spectrometer. Each TGA run was initiated by placing an aliquot of the $NdCl_3L$ stock solution in an Al TGA pan. Dry air was passed over the sample to evaporate the MeOH until the rate of mass change was less than 10 µg/min. For the enthalpy determination runs, the system was purged with nitrogen for 10 min before beginning the TGA/DTA run. In one series of tests, the TGA scans were run to specified temperatures (Table II) under nitrogen and then the residues were collected for analysis by FTIR. The FTIR spectra for the residues were measured as KBr pellets. The DTA was calibrated using the heat of fusion for indium (28.6 J/g), tin (60.6 J/g), and lead (23.2 J/g) standards.

RESULTS AND DISCUSSION

When heated in air, the $NdCl_3 \cdot L$ (L = DMF or DMA) compounds decompose by a mechanism involving the oxidation of the amide ligand. Figure 1 presents the TGA data for the thermal decomposition of $NdCl_3 \cdot$DMF in air and the species identified

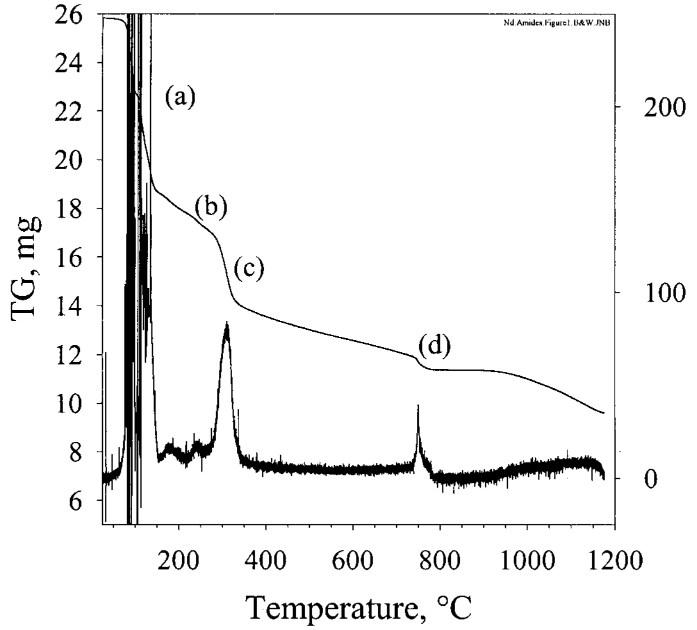

FIGURE 1 Thermogravimetric analysis of $NdCl_3 \cdot$DMF in air. The chemical species identified in the off-gas by FTIR spectroscopy were: (a) H_2O + MeOH; (b) DMF; (c) DMF + HCl + CO_2; (d) HCl.

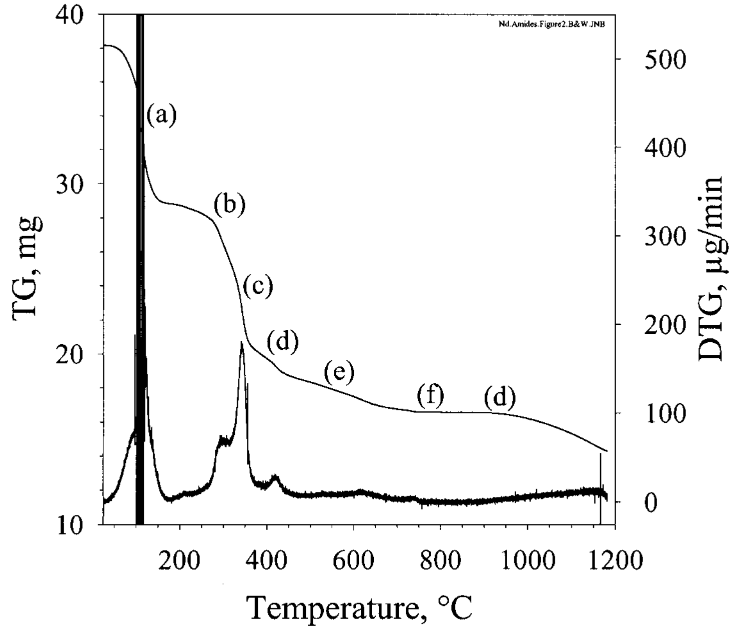

FIGURE 2 Theromogravimetric analysis of $NdCl_3 \cdot DMA$ in air. Chemical species indicated are those identified in the off-gas by FTIR spectroscopy. The chemical species identified in the off-gas by FTIR spectroscopy were: (a) $H_2O + MeOH$; (b) $DMF + CO_2$(minor) + H_2O(minor); (c) $DMF + CO_2 + H_2O$; (d) $H_2O + HCl + CO_2$; (e) $HCl + CO_2$; (f) $H_2O + CO_2$.

by FTIR in the off-gas. When $NdCl_3 \cdot DMF$ is heated from 80 to 150°C, TGA indicates a complex series of weight losses. FTIR analysis of the off-gas indicates these mass losses are from release of water and methanol. Release of DMF becomes evident at ~ 155°C although the DMF release is gradual from 155 to 270°C. From 270 to 340°C, a more rapid mass loss occurs. All of the DMF is released by the time the sample is heated to 340°C. Gas evolution becomes more complex during the accelerated mass loss between 270 and 340°C. In addition to DMF, HCl and CO_2 are evident in the off-gas, indicating combustion of DMF.

Similar to $NdCl_3 \cdot DMF$, water and methanol are released in a complicated series of steps when $NdCl_3 \cdot DMA$ is heated to 165°C in air. DMA is first evident in the off-gas at about 200°C (Fig. 2). The DMA loss occurs primarily in two regimes. The first occurs from 270 to 310°C. In this regime, free DMA and a small amount of CO_2 and H_2O are evident in the off-gas. However, as the temperature is increased above 310°C, CO_2 and H_2O become more dominant. Between 340 and 370°C, little free DMA is present in the off-gas; HCl, CO_2 and H_2O are the dominant species evolved. Unlike for $NdCl_3 \cdot DMF$, CO_2 continues to evolve as the DMA complex is heated to ~ 700°C. HCl is also released as the sample is heated to ~ 700°C. Above 700°C, the CO_2 and HCl release become diminished, and water becomes a dominant feature in the off-gas. HCl becomes evident again at 900°C.

Because of the concurrent combustion of the amides during the decomposition of the $NdCl_3L$ complexes in air, the enthalpy of the amide release cannot be obtained by DTA when air is used as the purge gas. However, when nitrogen is used as the purge gas, the

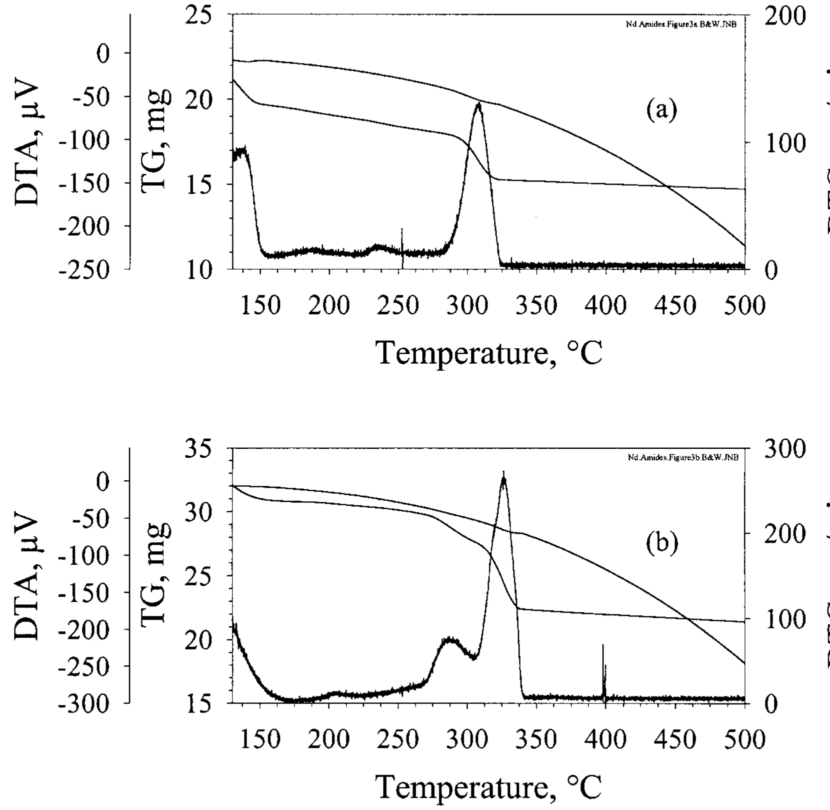

FIGURE 3 Thermogravimetric analysis of $NdCl_3 \cdot DMF$ (a) and $NdCl_3 \cdot DMA$ (b) under nitrogen.

amide is cleanly released from $NdCl_3 \cdot DMF$. The DMF release can be divided into two regimes (Fig. 3a). First, there is a gradual release of 0.4 mole DMF/mol Nd between 160 and 280°C. The DTA indicates little enthalpy associated with this initial loss. Second, there is a sharp loss of 0.6 mol DMF/mol Nd between 280 and 320°C. The enthalpy for the latter endothermic DMF release can be determined by DTA. Similarly, DMA is released from $NdCl_3 \cdot DMA$ in two events when heated under nitrogen (Fig. 3b). As was the case with $NdCl_3 \cdot DMF$, little enthalpy is associated with the first DMA release (from 260 to 305°C). This release corresponds to 0.3 mol DMA/mol Nd, and this event is accompanied by evolution of a small amount of CO_2. The second amide release between 305 and 340°C (0.7 mol DMA/mol Nd) resembles that seen with $NdCl_3 \cdot DMF$; that is, the off-gas indicates predominantly DMA during this endothermic event. Analyzing these endothermic amide releases, the enthalpy of binding can be obtained by DTA. It is not entirely clear why the initial amide release has little associated enthalpy. The FTIR spectra of the materials before and after the initial amide release are virtually identical (*vide infra*) indicating no major structural changes.

Fig. 4 presents the FTIR spectra of the residues left after heating $NdCl_3 \cdot DMF$ to 260°C and 350°C under nitrogen. For comparison, the spectrum of $NdCl_3 \cdot 6H_2O$ after heating to 400°C is also presented, as is the spectrum of a thin film of $NdCl_3 \cdot DMF$ formed by evaporating a portion of the methanolic solution on a KBr

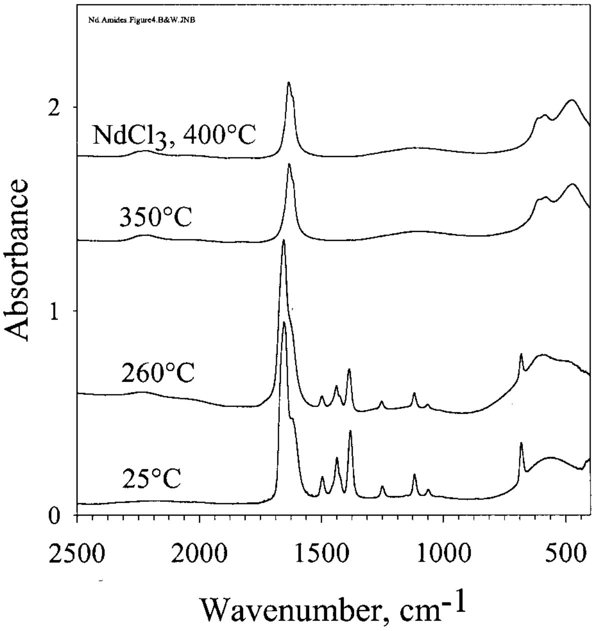

FIGURE 4 FTIR spectra of $NdCl_3$·DMF after evaporating the stock solution at ambient temperature (25°C) and after heating to 260°C and 350°C under nitrogen. The spectrum of $NdCl_3$, after heating to 400°C under nitrogen, is also presented.

plate at room temperature. The spectrum of $NdCl_3 \cdot$ DMF after heating to 260°C is virtually identical to that obtained after evaporating the $NdCl_3 \cdot$ DMF stock solution at ambient temperature, indicating that desolvation does not significantly perturb the DMF–Nd binding. The spectrum dramatically changes after heating to 350°C, and all the bands associated with DMF are lost. The spectrum is nearly identical to that of $NdCl_3 \cdot 6H_2O$ after heating to 400°C. This confirms the complete loss of DMF from $NdCl_3 \cdot$ DMF after heating to 350°C. The band at 1628 cm^{-1} in the $NdCl_3$ spectrum is attributed to the bending vibration of H_2O. No precautions were taken to keep the specimens dry so the $NdCl_3$ residues rehydrated before the FTIR spectra were recorded.

Similar observations can be made by examining the residues remaining after heating $NdCl_3 \cdot$ DMA to specified temperatures under nitrogen. The FTIR spectrum of $NdCl_3 \cdot$ DMA after heating to 260°C is virtually identical to that obtained after evaporating the $NdCl_3 \cdot$ DMA stock solution at ambient temperature. Again, this suggests that desolvation does not significantly perturb the amide–Nd binding. Further heating to 300°C (corresponding to the initial release of DMA) results in no significant change to the DMA vibrational bands. However, after heating to 350°C the bands associated with DMA are no longer present, and the FTIR spectrum of the residue is essentially identical to that of $NdCl_3$, confirming the complete loss of DMA.

Table III presents the enthalpy binding data for the $NdCl_3 \cdot L$ compounds. The data are presented in terms of the enthalpy per mole of amide released during the second amide release regime; i.e., the amide released with no associated enthalpy is not included. The values presented are the mean values from triplicate measurements,

TABLE III Binding enthalpies for $NdCl_3L$ compounds

L	*Reaction Temperature,* °C			ΔH, kJ/mol[a]
	Start	*Center*	*End*	
DMF	280	307	320	53.1 ± 3.8
DMA	305	325	340	40.9 ± 1.1

[a] Per mole of amide released during the second amide release region (see text).

and the uncertainties are the standard deviation from the mean. The results suggest that DMF binds more strongly to Nd(III) than does DMA. This result is opposite to that expected based on the basicity of the ligands. The gas-phase proton affinities for DMF and DMA are 887.5 kJ/mol and 908.0 kJ/mol, respectively [21]. Thus, DMA is more basic than DMF, yet the latter amide binds Nd(III) more strongly. The reason for the stronger DMF binding compared to DMA might be the steric congestion caused by the additional methyl group in DMA. Steric effects have been observed in the solid-state structures of trivalent lanthanide amide complexes by the increase in the average M–O–C bond angles from 134° for DMF complexes to 152° for DMA complexes [22]. Investigations of solvation effect on lanthanide complexation have also provided evidence for steric effects in DMA solutions *vs.* DMF solutions [23,24].

CONCLUSION

The complexes $NdCl_3 \cdot L$ ($L =$ DMF or DMA) were examined by TGA/DTA techniques and by FTIR spectroscopy. The FTIR spectra suggest that dehydration of the complexes yields no significant change in the amide–Nd binding. When heated, a portion (from 30 to 40%) of the amide is initially released with little or no associated enthalpy as measured by DTA. As the temperature is increased further, the remaining 60–70% of the amide is released *via* an endothermic process. The results suggest that DMF binds more strongly to Nd(III) than does DMA.

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