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# *In Situ* XAS of the Solvothermal Decomposition of Dithiocarbamate Complexes

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**Abstract.** An *in situ* XAS study of the solvothermal decomposition of iron and nickel dithiocarbamate complexes was performed in order to gain understanding of the decomposition mechanisms. This work has given insight into the steps involved in the decomposition, showing variation in reaction pathways between the iron and nickel dithiocarbamates, and the non-innocent role of oleylamine as the solvent and capping agent in the reaction.

## 1. Introduction

Solvothermal synthesis of nanoparticles from single source precursors (SSPs) is a widely researched area.<sup>1,2</sup> There is a long standing interest in metal dithiocarbamate complexes as SSPs for the synthesis of sulfides due to their versatility in stabilizing transition metals in a range of oxidation states.<sup>3,4,5</sup> Our group is interested in the synthesis of iron and nickel sulfide nanoparticles which are important materials in several fields, including the naturally occurring conversion of CO<sub>2</sub> to small organic molecules which led to the suggestion that they played a role in pre-biotic catalysis.<sup>6</sup>

The solvothermal synthesis method generally involves heating a molecular complex in a solvent which may also act as a capping agent. It has been noted that the solvent has an effect on the size and morphology of the resulting nanoparticles,<sup>2,7</sup> however, it is generally believed that the solvent is innocent, acting as a heat sink and coordinating to the nanoparticles as they are forming thereby directing and capping their growth.

This paper reports an *in situ* XAS investigation that has enabled the proposition of possible mechanisms of sulfide particle formation in the solvothermal decomposition of nickel(II) bis-, and iron(III) tris-isobutyl dithiocarbamates. *In situ* characterization is a valuable tool for understanding fundamental mechanistic detail of the structural changes that occur during a reaction. Through this study, it has been found that the decomposition pathways vary significantly between the two dithiocarbamate complexes, and the solvent oleylamine plays a non-innocent role in both mechanisms.

## 2. Experimental

XAS data was acquired on beamline BM26A at the ESRF, Grenoble<sup>8</sup>. The beamline is equipped with a double crystal Si(111) monochromator and a 9 element Germanium solid state detector for fluorescence measurements. The *in situ* solvothermal cell, developed by the catalysis group at UCL, was used to conduct *in situ* measurements. The reaction chamber at the centre of the cell has a capacity of about 400 $\mu$ L and is sealed between two 127 $\mu$ m Kapton windows. The cell can reach 200 $^{\circ}$  C. A calibration of the temperature inside the reaction chamber was performed prior to on-line experiments to account for heat loss during *in situ* measurements. In a typical on-line experiment, 400 $\mu$ L of a stock organic solution containing 0.1mmol dithiocarbamate complex and 20mL oleylamine, was loaded into the solvothermal cell and sealed. The temperature was set to 240 $^{\circ}$  C at a ramp rate of 1 $^{\circ}$  C/min: on account of heat loss, the maximum temperature within the cell reached 170 $^{\circ}$

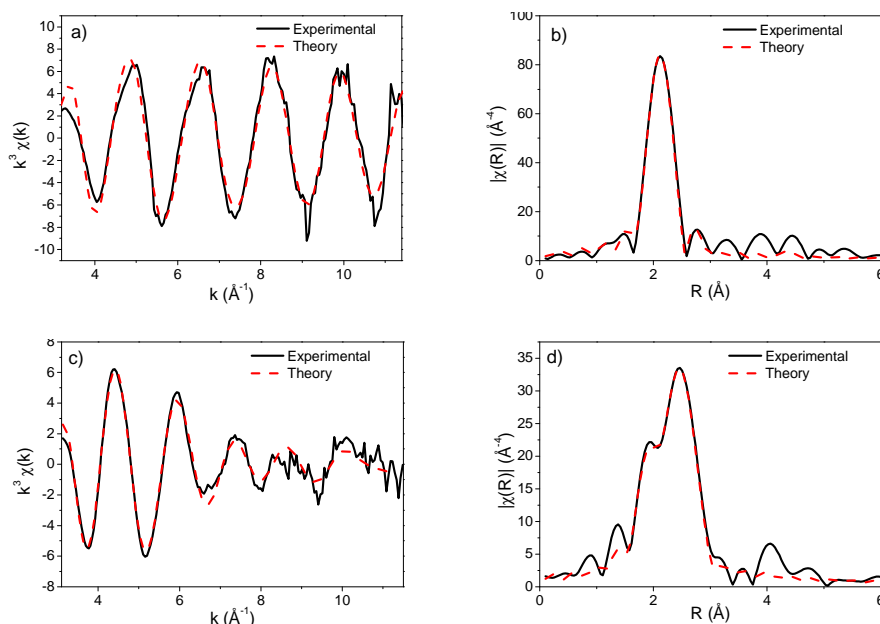
C. XAS measurements lasted approximately 12 minutes and were acquired up to  $10\text{\AA}^{-1}$  in fluorescence on iron and nickel K-edges. Temperature was recorded at the beginning of each scan. After careful analysis of the XANES data, further measurements were performed to acquire XAFS data at temperatures of interest. Data was acquired typically up to  $14\text{\AA}^{-1}$  using the set up above. Solid metal dithiocarbamate data was also acquired in transmission for comparison. Data was processed using the Horae Athena software, and XAFS data was analyzed using Excurv version 9.273.

### 3. Results and Discussion

#### 3.1. Dithiocarbamate Complexes in Oleylamine Environment

A direct comparison between the metal dithiocarbamate complexes in the solid state and when dissolved in oleylamine reveals unexpected results. For both the nickel and the iron dithiocarbamate species, a significant variation in the XAFS data is observed which strongly indicates the presence of metal-oleylamine interactions.

**3.1.1. Nickel(II) bis-isobutyl dithiocarbamate.** Modelling of XAFS data for nickel(II) bis-dithiocarbamate produces four Ni-S bond distances at  $2.20\text{\AA}$  as expected according to XRD data indicating that the ligand bidentate geometry remains intact in the solid state. As a complex dissolved in oleylamine, the Ni-S bond distances increase to between  $2.37$  and  $2.51\text{\AA}$  and an additional two Ni-N distances are observed at  $2.05\text{\AA}$ . A summary of the parameters are listed in Table 1 and XAFS fits are shown in Figure 1. The latter result reveals that oleylamine forms chemical bonds with the nickel centre of the dithiocarbamate complex— most likely at axial positions of the square planar molecule. The new bonding causes an increase in bond length of the Ni-S distances.



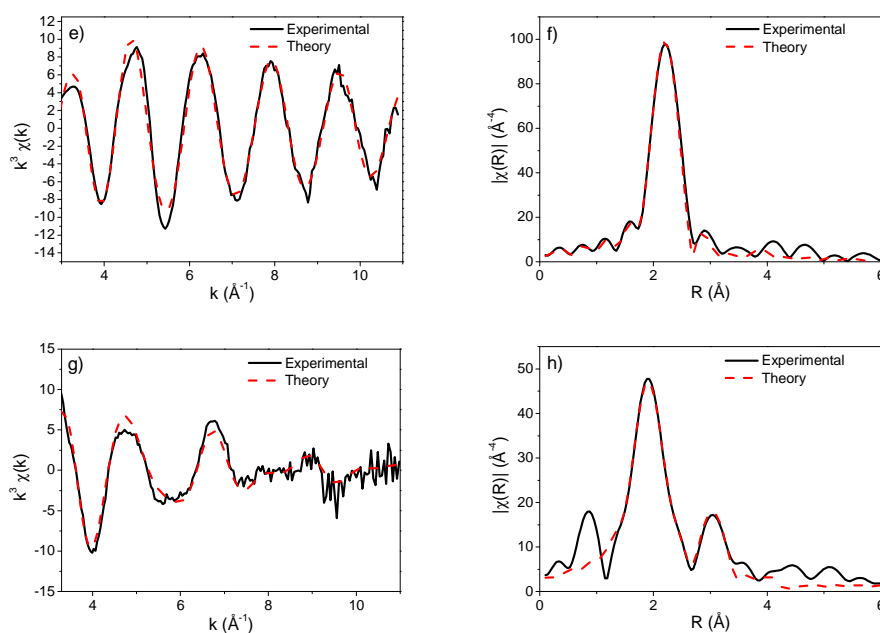
**Figure 1:** Experimental and theoretical a) XAFS and b) Fourier transform of solid nickel(II) bis dithiocarbamate, and c), and d) Fourier transform of oleylamine dissolved nickel(II) bis dithiocarbamate.

**3.1.2. Iron(III) tris-isobutyl dithiocarbamate.** The extensive changes seen in the XAFS of iron(III) tris-dithiocarbamate upon dissolution in oleylamine is initially an unexpected result as this complex is

a fully coordinated species and therefore oleylamine interaction would require the breakdown of existing Fe-S bonding. Data of the solid species is in agreement with XRD data, indicating a six coordinated iron centre of 2.30Å Fe-S distances. XAFS modeling of the iron dithiocarbamate in oleylamine indicates three Fe-S distances at 2.21Å, and a further three sulfur atoms at a longer distance of 3.08Å thus indicating that the bidentate ligand becomes monodentate, with weak interactions of the furthest sulfurs with the iron(III) centre. In addition, modeling reveals the presence of two Fe-N distances at 1.90Å arising from direct coordination of oleylamine to the iron centre. The parameters are listed in Table 1 and XAFS fits are shown in Figure 2.

**Table 1:** List of fitting parameters derived from XAFS analysis of nickel(II) bis- and iron(III) tris- isobutyl dithiocarbamate complexes as solids and as dissolved in oleylamine.

Sample	Scatter	N	R (Å)	$\sigma^2$ (Å <sup>2</sup> )	F
$\text{Ni}(\text{Bu}_2\text{NCS}_2)_2$	S	4	2.20	0.007	24
	C	2	2.70	0.006	
	N	2	4.33	0.010	
$\text{Ni}(\text{Bu}_2\text{NCS}_2)_2$ in oleylamine	N	2	2.05	0.006	22
	S	2	2.37	0.008	
	S	2	2.51	0.009	
	C	2	2.76	0.007	
$\text{Fe}(\text{Bu}_2\text{NCS}_2)_3$	S	6	2.30	0.011	16
	C	3	2.79	0.011	
	N	3	4.09	0.012	
	N	2	1.90	0.006	
	S	3	2.21	0.009	
$\text{Fe}(\text{Bu}_2\text{NCS}_2)_3$ in oleylamine	S	3	3.08	0.012	36
	S	3	3.08	0.012	
	C	3	2.69	0.006	



**Figure 2:** Experimental and theoretical a) XAFS and b) Fourier transform of solid iron dithiocarbamate, and c) and d) Fourier transform of oleylamine dissolved nickel dithiocarbamate.

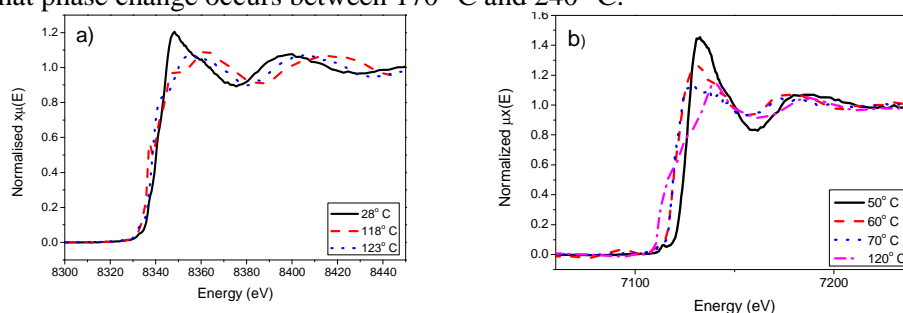
### 3.2. Nickel(II) bis-isobutyl dithiocarbamate decomposition

*In situ* XANES data of the nickel(II) bis dithiocarbamate decomposition, shown in Figure 3a, reveals that between room temperature and 118° C, a continuous transformation occurs to the nickel environment. At 118° C, XAFS can be fit to the original square planar conformation of nickel(II) bis-dithiocarbamate. This confirms that oleylamine dissociates from the nickel centre between the two temperatures, reforming the square planar complex. At 123° C, an abrupt change in the XANES and XAFS indicates the formation of the NiS structure. In summary, *in situ* data shows that a slow

dissociation of oleylamine from the nickel centers occurs. When this has reached completion, a facile process converts the dithiocarbamate complex into a sulfide. It is unclear at this stage whether the mechanism leading to the formation of NiS is initiated by temperature, vacant coordination, or both.

### 3.3. Iron(III) tri- isobutyl dithiocarbamate decomposition

*In situ* XAS data of iron(III) tris dithiocarbamate decomposition is significantly different from that of the nickel(II) complex (Figure 3b). The iron(III) dithiocarbamate-oleylamine structure is stable up to 60° C according to XANES. At 60° C, an edge shift indicates reduction from iron(III) to iron(II). XAFS analysis reveals that the modified complex consists of two bidentate dithiocarbamate ligands and two chemically bound oleylamine molecules, the XAFS is fit equally within statistical error to both cis and trans conformations. By 70° C, oleylamine no longer forms chemical bonds to the iron(II) centre. It is possible that the oleylamine ligands migrate to the carbon backbone, similar to a mechanism reported by Jung *et al.*<sup>9</sup> The dithiocarbamate ligands bind with two long and two short distances at 2.23 and 2.46Å. Between 70° C and 120° C a four coordinated sulfide structure is formed which remains up to the 170° C temperature limit. The structure is not the same as the six coordinated pyrrhotite formed under laboratory conditions at higher temperatures of up to 240° C leading to the conclusion that phase change occurs between 170° C and 240° C.



**Figure 3:** a) *In situ* XAS of nickel(II) bis isobutyl dithiocarbamate decomposition, and b) *in situ* XAS of iron(III) tris isobutyl dithiocarbamate decomposition.

## 4. Conclusions

XAFS data reveals significant differences between the well-studied solid state structures of the dithiocarbamate complexes, and the structures dissolved in oleylamine prior to decomposition. These severe changes to the metal dithiocarbamate coordination environment influence the decomposition pathway. The mechanistic pathway is unique to each system with the nickel complex decomposing in a two-step process and the iron complex in a three-step process including a bulk change in oxidation state.

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