

## Solid State NMR Studies of Lead(II) Thiourea Materials

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### ABSTRACT

Solid-state <sup>13</sup>C and <sup>207</sup>Pb NMR have been used to characterize a series of lead(II) ion complexes containing thiourea – widely used in materials science – as the organic complexing molecule. NMR data for the complexes have been measured and discussed with respect to the reported structures for the complexes.

### INTRODUCTION

Thiourea is extensively used in materials science. It can be the basis of the materials themselves, or it may play a role in the syntheses of materials. For example, thiourea-based materials containing zinc and cadmium are used as electro-optic modulators,<sup>1</sup> while transition-metal-ion-doped urea materials have been used as ferroelectric materials.<sup>2</sup> Thiourea has also been used in inclusion complexes of organometallics as nonlinear optical materials,<sup>3</sup> a synthetic template for the synthesis of copper(I)-doped ZnS nanoparticles,<sup>4</sup> and for the synthesis of metal sulfide semiconductor nanocrystallites.<sup>5</sup>

The present work describes <sup>13</sup>C and <sup>207</sup>Pb NMR investigations of a series of lead(II) halides that are complexed with thiourea. The spectral parameters for the compounds are given, with a discussion of their dependence on the state of co-ordination. The changes in NMR parameters from the complexed state to the uncomplexed state are indicators of structural and electronic changes in the materials.

### EXPERIMENTAL

**Chemicals.** Lead(II) halides were purchased as reagent-grade chemical (Alfa Chemicals), while reagent-grade thiourea was purchased from Aldrich Chemical. All were used as received without further purification.

**Synthesis.** The synthesis of thiourea complexes followed a procedure due to Wharf.<sup>6</sup> PbCl<sub>2</sub> was dissolved in a boiling solution of thiourea and water. Filtration of the hot solution followed by slow cooling of the filtrate gave the bis-adduct, PbCl<sub>2</sub>(thiourea)<sub>2</sub>. Using the same procedure with PbBr<sub>2</sub> also gave the bis-adduct, PbBr<sub>2</sub>(thiourea)<sub>2</sub>. Carrying the PbBr<sub>2</sub>/thiourea solution through similar procedures, but with fast cooling, yielded the mono-adduct, PbBr<sub>2</sub>(thiourea). PbI<sub>2</sub> was reacted with

thiourea while stirring for two hours and filtered hot to produce the mono-adduct,  $\text{PbI}_2(\text{thiourea})$ . The purity of these complexes has been checked by melting points as reported in the literature.<sup>7</sup>

**<sup>207</sup>Pb NMR Analyses of Thiourea Complexes.** Lead spectra were obtained with a Bruker MSL 300 NMR spectrometer at a nominal frequency of 62.601 MHz, using a spin-echo technique on a standard Bruker CP-MAS probe. All <sup>207</sup>Pb spectra reported are of static powders. All shifts are reported relative to  $\text{Pb}(\text{CH}_3)_4$  (TML). Solid  $\text{Pb}(\text{NO}_3)_2$  was used as a secondary reference, defined as -3491.6 ppm relative to TML at 295 K.<sup>8</sup> The shifts were determined by fitting the experimental data to a broadened theoretical powder pattern. Recycle delays of 40 seconds were used, with nominal  $\pi/2$  pulse of 2.7 microseconds.

**<sup>13</sup>C NMR Analyses of Thiourea Complexes.** Carbon spectra were obtained at room temperature ( $295 \pm 1$  K) with dipolar decoupled cross-polarized magic-angle spinning on the Bruker MSL 300 NMR spectrometer at a nominal frequency of 75.456 MHz using a standard Bruker CP-MAS probe. The optimal contact time was 500 microseconds. Recycle delays varied from ten to thirty seconds, as appropriate for each compound. The proton  $90^\circ$  pulse was 6 microseconds long. The chemical-shift scale was referenced through the methyl peak of hexamethylbenzene, HMB, at 17.6 ppm to  $\text{Si}(\text{CH}_3)_4$  (TMS). Spectra were the co-addition of several thousand scans. Isotropic shifts were identified from comparison of spectra at two or more spinning frequencies between 200 Hz and 4000 Hz. Chemical-shift parameters were obtained through Herzfeld-Berger analysis of the spinning sidebands.<sup>9</sup> We used the program HBA1.2 to find the shift parameters.<sup>10</sup> As a check on the graphical procedure, we analyzed the data for the  $\text{PbCl}_2$ -thiourea complex by the Herzfeld-Berger graphical procedure, and the two techniques gave results that were the same, within experimental error. Carbon and lead NMR data are reported in terms of the isotropic position  $\delta_{\text{iso}}$ , the span  $\Omega$ , and the skew  $\kappa$ .<sup>11</sup>

## RESULTS AND DISCUSSION

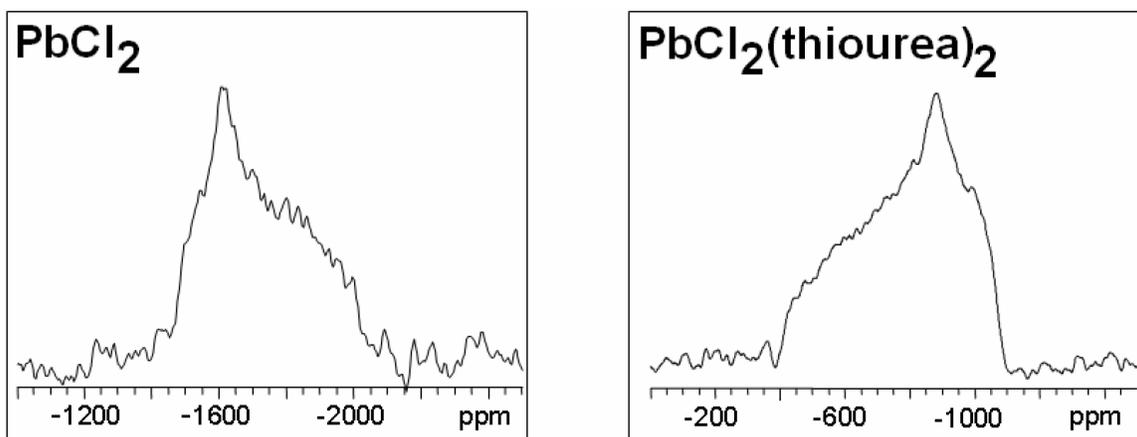
The structures of the lead(II) thiourea complexes have been previously published.<sup>12,7,13</sup> Lead(II) halide complexes with thiourea exist in polymeric structures. Crystals of  $\text{PbCl}_2(\text{thiourea})_2$  are orthorhombic, in space group  $\text{Pna}2_1$ .<sup>12</sup> The site of the lead atom in this structure has  $\text{C}_{2v}$  symmetry. The bridges between lead atoms are formed by sulfur atoms of thiourea and by some chlorine atoms. The bonds to the bridging chlorine atoms are significantly longer than the bonds to the non-bridging chlorine atoms. Each lead atom coordinates four sulfur atoms, all of which are bridging, and three chlorine atoms, two of which are bridging, for a coordination number of seven. The geometry is a distorted trigonal prism, with the non-bridging chlorine extending from a lateral face.  $\text{PbBr}_2(\text{thiourea})$  is monoclinic, in space group  $\text{P}2_1/\text{a}$ .<sup>7</sup> The lead atom is at a site of  $\text{C}_{2h}$  symmetry.  $\text{PbI}_2(\text{thiourea})$ ,<sup>13</sup> while monoclinic, is in space group  $\text{P}2_1/\text{a}$ , and the lead atom is at a site of  $\text{C}_{2h}$  symmetry, possessing an additional mirror plane compared to the chloride complex. In these two complexes, only the halide atoms form bridges between lead atoms. The primary coordination around the lead atom is fivefold in both complexes, with four bridging halide ions and one non-bridging sulfur atom. It can be

described as a distorted square pyramid, with the overall coordination number of lead in both complexes being seven as a result of weaker intermolecular bonds to two other halides.

Examples of the  $^{207}\text{Pb}$  NMR spectra of pure lead dichloride and a complex of lead dichloride with thiourea are shown in Figure 1. The NMR parameters of these two materials are obviously different from each other. The resonance of the complex is substantially isotropically deshielded from the halide by almost 100 ppm, as can be seen from the parameters in Table 1. A principal change in all cases is the change of the skew, as can easily be seen in spectra such as those of Figure 1.

	$\delta_{\text{iso}}$ (ppm)	$\Omega$ (ppm)	$\kappa$
$\text{PbCl}_2$	-1715	533	0.52
$\text{PbCl}_2(\text{thiourea})_2$	-799	660	-0.43
$\text{PbBr}_2$	-981	669	0.58
$\text{PbBr}_2(\text{thiourea})$	-1076	546	-0.56
$\text{PbI}_2$	-29	$\geq 250$	1
$\text{PbI}_2(\text{thiourea})$	643	998	0.17

Isotropic shifts have an uncertainty of  $\pm 5$  ppm.  
 Spans have an uncertainty of  $\pm 8$  ppm.  
 Skews have a rather large uncertainty of approximately 30%.



**Figure 1.  $^{207}\text{Pb}$  spectra of  $\text{PbCl}_2$  and  $\text{PbCl}_2(\text{thiourea})_2$ .**

$^{13}\text{C}$  NMR spectral analysis is straightforward, since there is only one unique carbon per compound. A spin rate of 200 Hz provides a sufficient number of well-resolved sidebands to enable Herzfeld-Berger analysis of the spectra of thiourea and the lead(II) thiourea complexes. [Figure 2] The chemical-shift tensor parameters obtained from Herzfeld-Berger analysis of the spectra of the complexes of thiourea with the lead(II) halides are given in Table 2.

Upon complexation to lead, the isotropic position of the thiourea carbon is significantly shielded, by 5 ppm relative to uncomplexed thiourea, indicating an increase in electron density at the carbon nucleus. Changing the counterion to the lead ion does not significantly affect the  $^{13}\text{C}$  NMR spectrum of the ligand, a not-too-surprising feature, considering that there are four bonds between the halide ion and the carbon. The span of the carbon resonance decrease slightly upon complexation in all cases, and seems to be determined by the number of thioureas co-ordinated to the lead. All values of the skew are positive, and the skew is larger in magnitude by the complexes than for uncomplexed thiourea. The skews of the complexes are closer to 1 (the axially symmetric case) than that of the uncomplexed thiourea, which implies that the electronic structure becomes more closely axial than in the uncomplexed thiourea. Interestingly, for the isostructural complexes  $\text{PbBr}_2(\text{thiourea})$  and  $\text{PbI}_2(\text{thiourea})$ , the  $^{13}\text{C}$  chemical-shift parameters for the ligand are identical, within experimental error.

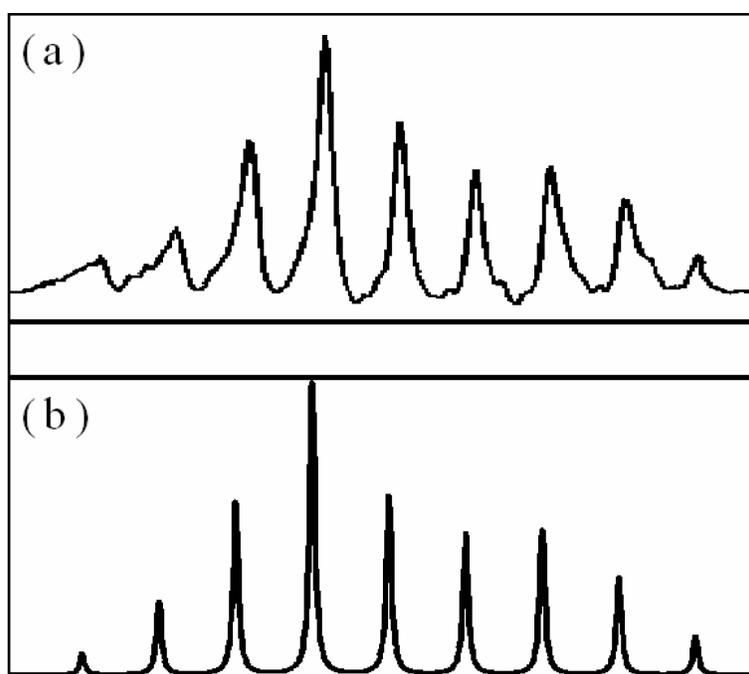


Figure 2. (a)  $^{13}\text{C}$  MAS spectrum of  $\text{PbCl}_2(\text{thiourea})_2$ ; (b) theoretical spectrum, showing the relative intensities of sidebands for the data given in the text.

<b>Table 2. <math>^{13}\text{C}</math> chemical-shift-tensor parameters for thiourea and its complexes.</b>			
	$\delta_{\text{iso}}$ (ppm)	$\Omega$ (ppm)	$\kappa$
Thiourea	182	204	0.29
$\text{PbCl}_2(\text{thiourea})_2$	176	184	0.46
$\text{PbBr}_2(\text{thiourea})$	176	199	0.39
$\text{PbI}_2(\text{thiourea})$	176	199	0.39

Isotropic shifts have an uncertainty of  $\pm 1$  ppm.  
Spans have an uncertainty of  $\pm 4$  ppm.  
Skews have an uncertainty of approximately 30%.

## CONCLUSIONS

The lead and carbon NMR spectra of complexes of thiourea with lead halides show that complexation produces significant changes in the electronic structure at both the lead center and at the ligand. Changes in isotropic shifts indicate an average change in the electronic environment. Change in span and skew indicate more subtle changes in the geometry of the electronic structure. The NMR shifts indicate changes at the ligand are consistent from complex to complex and are relatively small, whereas changes at the lead site are substantial and vary with counterion.

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