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# Main Group Metal Halide Complexes with Sterically Hindered Thioureas. VIII*. Complexes of Lead(II) Halides with 1,3-Dimethyl-2(3H)-imidazolethione

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## Abstract

Two new complexes of 1,3-dimethyl-2(3H)-imidazolethione (dmit) and lead(II) halides have been synthesized and characterized. Addition of dmit in molar excess to $PbX_2$ (X = Cl, Br, I, SCN) solutions in hot water yielded $PbCl_2$dmit and $Pb(NCS)_2(dmit)_2$. No adducts were isolated for $PbBr_2$ or $PbI_2$. Complexes were characterized via standard methods including both solid state and solution state information. Both complexes were high melting solids and appeared to be polymeric in the solid state, and IR data indicated polymerization occurred through halogen (or pseudohalogen) bridges only. Thiocyanate was N-bonded to the metal. Solution studies concluded that both were dissociated in DMF with $PbCl_2$dmit being a non-electrolyte and $Pb(NCS)_2(dmit)_2$ acting like a 1:1 electrolyte.

## Introduction

Several new complexes of lead(II) halides and pseudohalides have appeared in the literature over the past ten to fifteen years where prior to that time very little work had been done with regard to synthesis and structural characterization. Wharf *et al.* [2] reported several new lead(II) halide complexes with O-, N-, and S-donor ligands, and in the same year Baranyi *et al.* [3] reported the crystal and molecular structure of bis-(dimethylsulfoxide)di(*N*-thiocyanato)lead(II). Prior to this time, Nardelli and Fava [4] had reported the crystal structure of $PbCl_2(tu)_2$ (tu = thiourea), and a few other complexes of Pb(II) halides had been reported but not to the extent, as Wharf pointed out, as those reported for tin(II) halides [2]. More recently, Herbstein and Reisner [5] published a report of several complexes of $PbBr_2$ and tu including a crystal structure of $PbBr_2(tu)_2$.

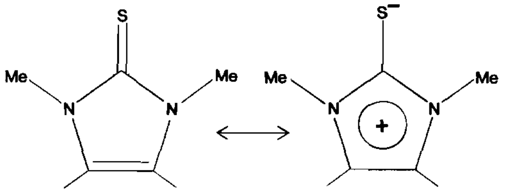

Fig. 1. dmit.

Our interest with respect to lead(II) halide and pseudohalide complexes arose from previous work done with main group halide complexes and sterically hindered thioureas such as 1,1,3,3-tetramethyl-2-thiourea (tmtu) and 1,3-dimethyl-2(3H)-imidazolethione (dmit, Fig. 1) [6–10]. Many novel structural differences were noted using these ligands in complexation with pnicogen halides, and of particular interest to us was the role of lone pairs in addition to the steric bulk of the donor ligands in determining the stereochemistry. Lead(II) halide complexes tend to be highly polymerized with six to seven coordination sites around the lead atom, not including the lone pair [3, 5], when combined with compact donors such as dmso or tu. We were particularly interested in seeing how a bulky ligand would affect this tendency toward polymerization and ultimately what the stereochemistry about the lead atom would be.

This paper reports the synthesis, characterization, and solid state infrared data for two new Pb(II) complexes of dmit—$PbCl_2$dmit and $Pb(NCS)_2(dmit)_2$— which represent the only two complexes we were able to isolate and characterize after treating $PbX_2$ (X = Cl, Br, I, SCN) with a stoichiometric excess of dmit. Below is a report of our results.

## Experimental

### *Chemicals*

Lead(II) chloride (Baker) and spectroscopic grade dimethylformamide (DMF, Fisher) were used as

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*Part I is ref. 1; Part II, ref. 6; Part III, ref. 8; Part IV, ref. 7; Part V, ref. 15; Part VI, ref. 9; Part VII, ref. 10.

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obtained without further purification. The DMF was, however, stored over Linde 4 Å molecular sieves prior to use in NMR and conductivity studies. Dmit was prepared according to methods outlined in the literature [11], and the remaining lead salts (Br, I, SCN) were derived by precipitation from aqueous solutions with the respective sodium halide and lead(II) acetate or nitrate.

*Solution Studies*

Specific conductivity was measured in DMF using a dip-type cell on a YSI Model 31 conductivity bridge. Proton NMR data were collected on a Brucker Model WM300 FT-NMR (300 MHz) using DMF as the solvent. Chemical shifts in ppm ($\delta$) are reported relative to an external tetramethylsilane standard.

*Infrared Spectra*

Solid state infrared data from 4000–400 $cm^{-1}$ were collected as Nujol mulls between AgBr plates on a Perkin-Elmer Model 735 infrared spectrophotometer. Peak values are reported in $cm^{-1}$ (±5). Key: vs, very strong; s, strong; m, medium; w, weak.

*Analytical*

Carbon, hydrogen, nitrogen, and halogen analyses were determined by Atlantic Microlabs, Inc., Atlanta, Ga., and molecular weights by Galbraith Laboratories, Inc., in Knoxville, Tenn.

*[1,3-Dimethyl-2(3H)-imidazolethione]dichlorolead(II)*

To a solution of 2.56 g dmit (20.0 mmol) dissolved in 100 ml boiling water was added 2.78 g $PbCl_2$ (10.0 mmol). A yellow color was noted immediately, and the solution was concentrated to half the original volume. Upon cooling, long white rods formed along with smaller white needles. Yield: 3.45 g (85%). Anal. calc. for $C_5H_8Cl_2N_2PbS$: C, 17.45; H, 1.98; N, 6.90; Cl, 17.45. Found: C, 17.21; H, 2.03; N, 7.00; Cl, 17.21%. Molecular weight: calc. 406; found 195. Melting point (m.p.) >300 °C. $^1H$ NMR (DMF): $\delta$ 3.53 (s, 3H, methyl), $\delta$ 7.13 (s, 1H, ethylenic). $\Lambda_M$ ($10^{-3}$ M in DMF) = 7.0 $cm^2$ $mol^{-1}$ $ohm^{-1}$. IR(mull): 1570m, 1240s, 1180s, 1090w, 720s ($cm^{-1}$).

*Bis-[1,3-dimethyl-2(3H)-imidazolethione]di[N-thiocyanato]lead(II)*

$Pb(SCN)_2$ was precipitated *in situ* by mixing 1.62 g NaSCN (20 mmol) and 3.30 g $Pb(NO_3)_2$ (10 mmol) in 100 ml water. The supernatant liquid was decanted and the precipitate was washed with a few small portions of distilled water. Approximately 300 ml of distilled water were added to the precipitated $Pb(SCN)_2$ and brought to a boil. 5.00 g dmit (40 mmol) were added to the above suspension with stirring, and a bright yellow color appeared immediately. The solution cleared, and the volume was reduced to half the original. Bright lemon yellow needles appeared on cooling and were filtered. The solid was stirred with 100 ml acetone and refiltered. Excess dmit was recovered from filtrates. Yield: 3.52 g (61%). Anal. Calc. for $C_7H_8N_4PbS_3$: C, 24.86; H, 2.78; N, 14.50. Found: C, 24.94; H, 2.86; N, 14.62. Molecular weight: calc. 580; found 185. m.p. 166–168 °C. $^1H$ NMR (DMF): $\delta$ 3.61 (s, 3H, methyl), $\delta$ 7.19 (s, 1H, ethylenic). $\Lambda_M$ ($10^{-3}$ M in DMF) = 104 $cm^2$ $mol^{-1}$ $ohm^{-1}$. IR(mull): 2050vs, 1565s, 1230m, 1170m, 1080w, 718w ($cm^{-1}$).

*Other IR Spectra*

$Pb(SCN)_2$: 2040vs ($cm^{-1}$). Dmit: 1570m, 1230s, 1170s, 1070w, 710s ($cm^{-1}$).

Attempts to generate the adducts of $PbBr_2$ and $PbI_2$ and dmit followed the same procedure as that described for $Pb(SCN)_2$ as described above. Both reactions yielded recovery of starting material.

## Results and Discussion

Reactions in water of at least two-fold or more molar excess dmit and $PbX_2$ (X = Cl, Br, I, SCN) yielded a 1:1 adduct for $PbCl_2$ and a 1:2 adduct for $Pb(SCN)_2$. Both substances were high melting solids which dissolved only to a very limited extent in very highly polar solvents such as DMF and water. Non-polar to slightly polar solvents did not dissolve these substances, and the thiocyanate adduct appeared to decompose in hot acetonitrile. No adducts could be isolated from reactions of excess dmit and $PbBr_2$ or $PbI_2$.

Both solution state data and solid state vibrational data were collected and examined for these two adducts. Structural implications of these data are discussed below.

*Solution State*

The solution state data suggest two different modes of behavior for these complexes. Molecular weight and conductivity data for $PbCl_2$dmit suggest that the complex is fully dissociated and the mode of dissociation is molecular and not ionic. Molecular weight data yields a van't Hoff factor, $i = 2$, and the conductivity data implies a non-conductor in DMF. The degree of dissociation, $\alpha$, as defined by $\alpha = (i - 1/\nu - 1)$ is 1.00 with regard to molecular dissociation ($\nu = 2$) and 0.50 with regard to all possible modes of dissociation ($\nu = 4$).

The complete molecular dissociation of $PbCl_2$dmit is further supported by proton NMR. Previous studies have shown the methyl protons of dmit to be sensitive to coordination [6]. Uncoordinated dmit shows the methyl proton resonance at $\delta$ 3.50 in DMF, and the spectrum for $PbCl_2dmit$ shows the resonance for the methyl group at $\delta$ 3.53—essentially an insignificant difference.

Solution data for $Pb(NCS)_2(dmit)_2$ suggest that this complex is also dissociated, but the conductivity data implies a 1:1 electrolyte since the observed value of 104 $cm^2$ $mol^{-1}$ $ohm^{-1}$ falls slightly above the range for a two ion conductor (65–90 $cm^2$ $mol^{-1}$ $ohm^{-1}$) [12]. Based on molecular weight data, the van't Hoff factor is in slight excess of 3 (3.13) and taken in conjunction with the conductivity data suggests a mode of dissociation as seen in eqn. (1).

$$Pb(NCS)_2(dmit_2) \rightleftharpoons [Pb(NCS)(dmit)]^+ + SCN^- + dmit \qquad (1)$$

The proton NMR also supports this mode of dissociation which shows one of the dmit molecules still coordinated to Pb since there is a significant difference in shifts between the methyl resonance of uncoordinated dmit ($\delta$ 3.50) and that of the complex ($\delta$ 3.62). The fact that only a single resonance is observed is due probably to rapid exchange between the coordinated and uncoordinated dmit molecules thus showing the time-averaged single resonance. A similar phenomenon is observed for the partially dissociated $AsX_3tmtu$ ($X = Cl$, Br) where solution state IR shows the presence of both coordinated and uncoordinated tmtu, but the NMR spectrum shows a single resonance for the methyl protons [6].

The slight excess in van't Hoff factor (3.13) and the fact that the conductivity data is above the range of a 1:1 electrolyte could be explained by a secondary, less-significant equilibrium as seen in eqn. (2) below.

$$Pb(NCS)_2(dmit)_2 \rightleftharpoons [Pb(dmit)]^{2+} + 2SCN^- + dmit \qquad (2)$$

The principle mode of dissociation, however, is more than likely the one demonstrated by eqn. (1), and the degree of dissociation relative to all modes of dissociation ($\nu = 5$) is computed to be 0.50.

### *Solid State*

Based on crystal morphology, high melting points, low solubility in all but a few very polar solvents, and literature precedence it may be concluded that these substances are polymeric in the solid state. Nardelli and Fava [3] reported the crystal and molecular structure of $PbCl_2(tu)_2$ which consisted of polymeric polyhedra linked together by bridging sulfur and chlorine atoms, and they observed an unusual coordination number of seven (not including the lone pair) around the lead atom. Wharf *et al.* [2] reported the vibrational spectra for this complex and noted a split in the C=S stretch as well as in the NCN asymmetric stretch of thiourea which are due to the presence of both bridging and terminal thioureas in the solid state structure. They also noted high melting points for the $PbX_2$ ($X = Cl$, Br, I) adducts of thiourea and rationalized this on the basis of polymeric structures already demonstrated for $PbCl_2(tu)_2$ noted above. Herbstein and Reisner [5] further substantiated this with the crystal structure of $PbBr_2(tu)_2$ which consisted of six- and seven-coordinated polyhedra linked by bridging thiourea and halide atoms, and the vibrational data reported by Wharf *et al.* again showed splits in C=S and NCN vibrational modes [2].

For dmit, the peak at 1570 $cm^{-1}$ is assigned as the NCN asymmetric stretch while the peak at 1170 $cm^{-1}$ is the C=S stretch. Both complexes show single peaks as opposed to split peaks at frequencies very near the above modes (1565 and 1170 $cm^{-1}$ for the thiocyanate complex and 1570 and 1180 $cm^{-1}$ for the chloride) thus suggesting terminal bonding only. However, it can also be seen that these modes do not shift greatly upon complexation. Complexes with other metal halides show similar results [13, 14], and can be in part explained on the basis of little structural difference in the aromatic ring structure of this ligand in the non-complexes *versus* the complexed states [6, 13]. Thus the IR data is not totally conclusive with regard to the mode of polymerization, but one would expect either splitting or at least line broadening of the observed modes if both bridging and terminal ligands were present, and these modes tended to give relatively sharp peaks in the IR spectra. Furthermore, based on other known main group structures incorporating this ligand, it may be concluded that polymerization is accomplished exclusively through halogen (or pseudohalogen) bridges [3, 8, 9] although in the case of $SbCl_3dmit$, very long Sb–S bridges are observed very near the sum of the van der Waal's radii [15].

Another structural conclusion that may be derived from the solid state IR spectra is the fact that the thiocyanate ligand is N-bonded to the metal and polymerization is accomplished through bridging Pb–S contacts. The CN stretching frequency of thiocyanate is a diagnostic indicator in most instances for the bonding mode of this ligand where frequencies near to or below 2050 $cm^{-1}$ are observed for N-bonded species [16]. We observe this mode for $Pb(SCN)_2$ at 2040 $cm^{-1}$, and the known solid state structure of this compound demonstrates N-bonding [17]. For $Pb(NCS)_2(dmit)_2$, we observe this peak at 2050 $cm^{-1}$ and thus conclude that the mode of bonding is as described above. A similar bonding mode is observed by Baranyi *et al.* [3] in bis-(dimethylsulfoxide)di-(*N*-thiocyanato)lead(II) as mentioned before, and bis-thiourea complexes of Zn(II) and Cd(II), thought also to be N-bonded to the metal [18], show similar CN stretching frequencies.

On the basis of the observed characteristics for these two complexes, we speculate that the steric bulk of the dmit ligand largely influences the types of complexes and bonding modes observed. The only compound isolated for a lead(II) halide was the 1:1 complex of $PbCl_2$ despite the presence of molar excess dmit, and none for the other halides. Since these halide complexes tend toward a high degree of polymerization, it is possible that the size of dmit in combination with the steric bulk of the heavier halogen atoms diminishes the Lewis acid properties of $PbX_2$ such that only a 1:1 dmit complex with the chloride is favorable. The thiocyanate ligand tends to be linear in the solid state [3, 17] and polymerizes through long Pb—S bridges thus leading to less steric repulsion in the coordination sphere of lead. Hence a 2:1 dmit complex is observed for $Pb(SCN)_2$.

As in other main group halide complexes of dmit and tmtu, far-IR and Raman spectra were not helpful in delineating the nature of polymerization or coordination sphere geometry in the solid state and hence were not pursued in this study [6, 7, 15]. A single crystal X-ray crystallographic study would be most useful in determining a more detailed view of the stereochemistry about the lead atom and will be the focus of future studies with these complexes.

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