

## Synthesis and Characterization of some Uranium(IV) Pseudohalides

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### Abstract

Nine coordinate complexes of the type  $[\text{Et}_4\text{N}][\text{U}(\text{NCX})_5(\text{AA})_2]$  [ $\text{X} = \text{Se}, \text{S}$  and  $\text{AA} = 2,2'$ -bipyridyl (bipy); 1,10-phenanthroline (phen); 4,4'-dimethyl-2,2'-bipyridyl (dmb)] have been synthesized and characterized by X-ray powder diffraction, magnetic susceptibility, and infrared spectra. X-ray powder diffraction data indicates the compounds  $[\text{Et}_4\text{N}][\text{U}(\text{NCS})_5(\text{bipy})_2]$  and  $[\text{Et}_4\text{N}][\text{U}(\text{NCSe})_5(\text{bipy})_2]$  to be isostructural. In addition, the tetraphenylarsonium salts of  $\text{U}(\text{NCS})_8^{4-}$  and  $\text{U}(\text{NCSe})_8^{4-}$  have been prepared and characterized. A brief study of the solution infrared spectra of the  $\text{U}(\text{NCS})_8^{4-}$  ion in acetone has been made and compared to previous studies. In this instance, solution infrared spectra in the CN stretching region was not useful as a diagnostic tool for determining the structure of this ion in solution, but indicated dissociation of the  $\text{U}(\text{NCS})_8^{4-}$  complex in acetone.

### Introduction

The nine coordinate compound  $[\text{Et}_4\text{N}][\text{U}(\text{NCS})_5(2,2'\text{-bipyridine})_2]$  has been prepared and structurally characterized by single crystal X-ray diffraction [1]. This was the first nine coordinate complex of the type  $\text{ML}_5(\text{AA})_2$  and is one of a small number of nine coordinate uranium complexes known [2, 3]. In an effort to determine the uniqueness, or lack thereof, of this type of structure it was undertaken to prepare a series of similar compounds.

In the course of this work some eight coordinate octaisothiocyanato and octaisoselenocyanato complexes of uranium(IV) were also prepared and some interesting observations on the solution infrared spectra of these complexes were made. It has been proposed that the symmetry nature of eight coordinate complexes of the type  $\text{ML}_8$  may be deduced by analysis of specific symmetry dependent features of the absorption spectra [4–7]. As applied to complexes of the type  $\text{M}(\text{NCS})_8^{4-}$ , group theoretical analysis of the common eight coordinate polyhedra

predicts one infrared active CN stretching band for cubic symmetry ( $\text{O}_h$ ), two infrared active bands for the square antiprismatic ( $\text{D}_{4d}$ ) and four infrared active bands for dodecahedral symmetry ( $\text{D}_{2d}$ ). The solid state and solution infrared spectra of a number of uranium and thorium compounds containing a variety of counter ions has been analyzed in the light of this prediction [4]. The conclusions reached in this study were that the solid state structure of the  $\text{M}(\text{NCS})_8^{4-}$  ion could be either dodecahedral or square antiprismatic depending on the counter ion present, while in solution all of the ions adopted a square antiprismatic structure. It has been suggested [8] that the square antiprismatic structure should be energetically most favorable in the absence of distorting crystal lattice effects.

Attempts to observe the solution infrared spectra of  $\text{U}(\text{NCS})_8^{4-}$  ions under stringent anaerobic conditions resulted in the conclusion that this ion dissociates in acetone. Spectra resulting from this dissociation are very similar to the spectra observed in earlier work [4].

### Experimental

#### Physical Measurements

Solid state infrared spectra were obtained from 200 to  $4000\text{ cm}^{-1}$  using a Nicolet MX-1 FT infrared spectrometer. Spectra in the region from 200 to  $650\text{ cm}^{-1}$  were obtained using nujol mulls placed between polyethylene sheets. Spectra in the region from 500 to  $4000\text{ cm}^{-1}$  were obtained by the use of KBr disks. Solution spectra of some of the complexes in the region  $2200\text{--}1900\text{ cm}^{-1}$  were obtained in dry acetone in a KBr sample cell of 0.1 mm fixed path length. X-ray powder diffraction patterns were recorded using a Norelco X-ray source with a copper element X-ray tube operating at 40 kV and 18 mA. Samples were sealed in glass capillary tubes and mounted in a Debye-Scherrer powder camera. Magnetic susceptibility measurements from 80 to 300 K were made with an Alpha Scientific electromagnet Model 1900 powered by a 200 ampere Alpha Scientific power supply. Measurements were made employing the standard Faraday technique. Temperature was measured and controlled

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TABLE I. Elemental Analysis.

Compound <sup>a</sup>	Carbon		Nitrogen		Hydrogen	
	calc.	anal.	calc.	anal.	calc.	anal.
[Et <sub>4</sub> N][U(NCS) <sub>5</sub> (bipy) <sub>2</sub> ]	40.82	40.46	14.42	14.18	3.74	3.78
[Et <sub>4</sub> N][U(NCSe) <sub>5</sub> (bipy) <sub>2</sub> ]	32.88	32.81	11.62	11.48	3.01	3.08
[Et <sub>4</sub> N][U(NCS) <sub>5</sub> (phen) <sub>2</sub> ]	43.61	43.40	13.74	13.99	3.56	3.55
[Et <sub>4</sub> N][U(NCSe) <sub>5</sub> (phen) <sub>2</sub> ]	35.45	35.33	11.17	10.76	2.89	2.91
[Et <sub>4</sub> N][U(NCS) <sub>5</sub> (dmb) <sub>2</sub> ]	43.27	43.25	13.64	13.69	4.32	4.40
[Et <sub>4</sub> N][U(NCSe) <sub>5</sub> (dmb) <sub>2</sub> ]	35.22	35.25	11.10	11.07	3.52	3.58
[(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> As] <sub>4</sub> [U(NCS) <sub>8</sub> ]	55.86	55.72	5.01	4.98	3.61	5.59
[(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> As] <sub>4</sub> [U(NCSe) <sub>8</sub> ]	47.84	49.37	4.29	4.30	3.09	3.29

<sup>a</sup>All compounds were green in color.

using a Lake Shore Cryotronics Model DTC-500 automatic temperature control unit. Carbon, hydrogen and nitrogen analyses were performed either by Guelph Chemical Laboratories, Ltd. in Guelph, Canada or by Galbraith Laboratories, Inc. in Knoxville, Tennessee.

### Syntheses

Starting materials and solvents were obtained commercially and purified and dried by standard techniques and stored under vacuum or nitrogen until used. Non-commercially available starting materials tetraethylammonium octaisothiocyanatouranate(IV) [9], tetraethylammonium octaisoselenocyanatouranate(IV) [9], tetraethylammonium octaisoselenocyanatouranate(IV) [10] and uranium tetrachloride [11] were prepared by published methods.

Due to the susceptibility of both starting materials and products to hydrolysis, particularly in solution, all manipulations were carried out using standard inert atmosphere and vacuum techniques. Selenocyanate complexes were extremely sensitive to water and were rapidly decomposed yielding red elemental selenium in its presence.

The eight coordinate tetraphenylarsonium octaisothiocyanato and octaisoselenocyanato complexes of uranium(IV) were prepared by the stoichiometric reaction of UCl<sub>4</sub>, (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>AsCl and KSCN or KSeCN in dry acetonitrile. Insoluble KCl was removed by filtration and the product isolated by vacuum distilling away the solvent. Slow vacuum distillation of the solvent from the solution yielded macroscopic crystals of the products.

Syntheses of nine coordinate complexes of the type M<sup>1</sup>UX<sub>5</sub>(AA)<sub>2</sub> was achieved in essentially quantitative yields by the stoichiometric reaction of UCl<sub>4</sub> with Et<sub>4</sub>NCl, KXCN and the appropriate bidentate ligand in acetonitrile. Following stirring for four hours, the reaction was filtered removing the insoluble KCl and yielding a solution containing

the product. The product was isolated by removal of the solvent. Slow vacuum distillation of the solvent away from the solution resulted in the formation of macroscopic crystals of the product.

The compounds [Et<sub>4</sub>N][U(NCS)<sub>5</sub>(bipy)<sub>2</sub>] and [Et<sub>4</sub>N][U(NCSe)<sub>5</sub>(bipy)<sub>2</sub>] could also be prepared by reaction of a twofold excess of 2,2'-bipyridyl with [Et<sub>4</sub>N]<sub>4</sub>U(NCS)<sub>8</sub> or [Et<sub>4</sub>N]<sub>4</sub>U(NCSe)<sub>8</sub> in acetonitrile. Products were isolated from the resulting solutions as macroscopic crystals by the slow vacuum distillation of the solvent away from the solution.

## Results and Discussion

### Analytical Data and Infrared Spectra

Elemental analysis of compounds prepared in this work are presented in Table I. Significant solid state infrared absorption bands of the compounds prepared in this work are presented in Table II. CN stretching absorption bands assigned for the thiocyanate and selenocyanate ligands are in each case consistent with nitrogen bound ligands. The CX stretching absorption and the NCX bending absorption, along with its first overtone, are typically weak absorptions and in the presence of organic counter ions can be extremely difficult to identify. In all cases assigned bands are consistent with nitrogen bonding [12–14]. Vibrational bands observed arising from neutral organic ligands indicate coordination at the metal site. No evidence for any free ligand was observed.

Examination of the number of bands observed as CN stretches has been used as an indication of the coordination geometry of M(NCS)<sub>8</sub><sup>4-</sup> ions. Group theoretical analysis of the common eight coordinate polyhedra predicts one IR active CN stretching band for cubic symmetry (O<sub>h</sub>), two IR active bands for square antiprismatic symmetry (D<sub>4d</sub>) and four IR active bands for dodecahedral symmetry (D<sub>2d</sub>). Smith and Grey [4] examined the solid state and solution

TABLE II. Infrared Absorptions for Thiocyanate and Selenocyanate Complexes.

Complex	$\nu$ CN	$\delta$ NCS $\delta$ NCSe	$\nu$ CS $\nu$ CSe	$\delta$ NCS $\delta$ NCSe
[Et <sub>4</sub> N][U(NCS) <sub>5</sub> (bipy) <sub>2</sub> ]	2037s		922m	496m 482w 464m
[Et <sub>4</sub> N][U(NCS) <sub>5</sub> (dmb) <sub>2</sub> ]	2069sh 2037s	977w		504w 496w 487w
[Et <sub>4</sub> N][U(NCS) <sub>5</sub> (phen) <sub>2</sub> ]	2029s		922m	506w 490w 463w
[(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> As] <sub>4</sub> [U(NCS) <sub>8</sub> ]	2056s 2029s			
[Et <sub>4</sub> N][U(NCSe) <sub>5</sub> (bipy) <sub>2</sub> ]	2028s	889w 875w		449w 440w 433w
[Et <sub>4</sub> N][U(NCSe) <sub>5</sub> (dmb) <sub>2</sub> ]	2060sh 2032s 2016sh		645w	448m 440w 435w
[Et <sub>4</sub> N][U(NCSe) <sub>5</sub> (phen) <sub>2</sub> ]	2024s			
[(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> As] <sub>4</sub> [U(NCSe) <sub>8</sub> ]	2093sh 2064s 2050sh 2022sh		637w	430w

infrared spectra of M<sub>4</sub>[Th(NCS)<sub>8</sub>]·2H<sub>2</sub>O (M = Rb<sup>+</sup> or Cs<sup>+</sup>), M<sub>4</sub>[U(NCS)<sub>8</sub>]·H<sub>2</sub>O (M = Rb<sup>+</sup> or Cs<sup>+</sup>) and [NH<sub>4</sub>]<sub>4</sub>[U(NCS)<sub>8</sub>] in the region 2200–1900 cm<sup>-1</sup>. Solid state spectra of all of the compounds in Nujol mulls, with the exception of [NH<sub>4</sub>]<sub>4</sub>[U(NCS)<sub>8</sub>], displayed four bands in this region, consistent with the dodecahedral structure in the solid state. [NH<sub>4</sub>]<sub>4</sub>[U(NCS)<sub>8</sub>] displays only two absorption bands in this region, consistent with a square-antiprismatic structure.

Solution spectra, in acetone, of all the compounds were virtually identical displaying a medium intensity peak at ca. 2088 cm<sup>-1</sup> and a very strong band at ca. 2050 cm<sup>-1</sup>. The authors conclude that this data indicates a square-antiprismatic structure for the M(NCS)<sub>8</sub><sup>4-</sup> ions in solution. It is noted that an interesting concentration effect was observed in that as the solutions were diluted, the intensity of the stronger band decreased with respect to the weaker band until in sufficiently dilute solutions the two bands were of equal intensity. Solution spectra of M<sub>4</sub>[U(NCS)<sub>8</sub>] (M = Et<sub>4</sub>N<sup>+</sup> and Cs<sup>+</sup>) reported by Al-Kazzaz *et al.* [10] in nitromethane display only one band at 2060 cm<sup>-1</sup> for [Et<sub>4</sub>N]<sub>4</sub>[U(NCS)<sub>8</sub>] and 2045 cm<sup>-1</sup> for Cs<sub>4</sub>[U(NCS)<sub>8</sub>]. Figure 1 shows the solution IR spectra of acetone, KNCS and [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As]<sub>4</sub>[U(NCS)<sub>8</sub>]. Figure 2 shows the IR spectra of [Et<sub>4</sub>N]<sub>4</sub>[U(NCS)<sub>8</sub>] at three different concentrations. The observed infrared absorptions are listed in Table III.

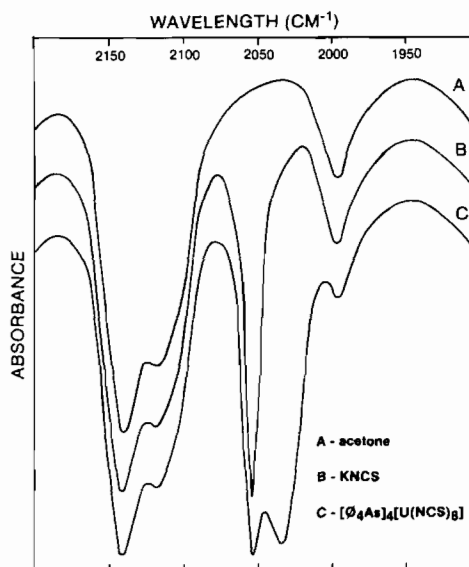


Fig. 1. Solution infrared spectra (2200–1900 cm<sup>-1</sup>) of acetone, KNCS, and [(φ<sub>4</sub>As)<sub>4</sub>[U(NCS)<sub>8</sub>].

Conclusions based on the solution spectra of M<sub>4</sub>[U(NCS)<sub>8</sub>] (M = (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As<sup>+</sup> or Et<sub>4</sub>N<sup>+</sup>), in acetone, made in this study are in marked contrast to earlier conclusions on the solution spectra of the U(NCS)<sub>8</sub><sup>4-</sup> ion. The solution spectrum of a saturated solution of [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As]<sub>4</sub>[U(NCS)<sub>8</sub>] in acetone displays two bands of approximately equal intensity at 2056 and 2037 cm<sup>-1</sup>. The bandwidth of the

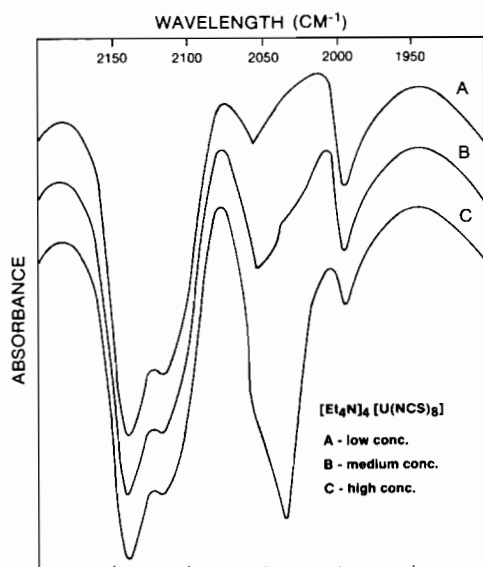


Fig. 2. Solution infrared spectra (2200–1900  $\text{cm}^{-1}$ ) of  $[\text{Et}_4\text{N}]_4[\text{U}(\text{NCS})_8]$  at three different concentrations.

2037  $\text{cm}^{-1}$  absorption appears to be significantly greater than that for the 2056  $\text{cm}^{-1}$  band. The solution spectrum of  $[\text{Et}_4\text{N}]_4[\text{U}(\text{NCS})_8]$  was examined at three different concentrations. The spectrum of the most concentrated solution showed a very strong band at 2037  $\text{cm}^{-1}$  with a shoulder arising from a medium intensity band at approximately 2056  $\text{cm}^{-1}$ . Upon dilution it was observed that the 2037  $\text{cm}^{-1}$  band decreased with respect to the 2056  $\text{cm}^{-1}$  band until at the lowest concentration the 2056  $\text{cm}^{-1}$  band was the only easily observable

TABLE III. Solution Infrared Absorptions of Acetone, KNCS,  $[(\text{C}_6\text{H}_5)_4\text{As}]_4[\text{U}(\text{NCS})_8]$  and  $[\text{Et}_4\text{N}]_4[\text{U}(\text{NCS})_8]$  from 2200–1900  $\text{cm}^{-1}$ .

Compound	Observed Absorptions $\nu(\text{CN})$		
Acetone	2144s		1999m
	2122sh		
KNCS	2144s	2057s	1999m
	2122sh		
$[(\text{C}_6\text{H}_5)_4\text{As}]_4[\text{U}(\text{NCS})_8]$	2144s	2056s	1999m
	2122sh	2037s	
$[\text{Et}_4\text{N}]_4[\text{U}(\text{NCS})_8]$			
High concentration	2144s	2055sh	1999m
	2122sh	2037s	
Medium concentration	2144s	2056m	1999m
	2122sh	2047sh	
		2036sh	
Low concentration	2144s	2057w	1999m
	2122sh		

absorption. At the intermediate concentration it was apparent that the observed absorption consisted of at least three bands at ca. 2056, 2046 and 2037  $\text{cm}^{-1}$ .

In all of the spectra, a band was observed at ca. 2057  $\text{cm}^{-1}$ , due to the dissociation of the  $\text{U}(\text{NCS})_8^{4-}$  ion and subsequent liberation of free  $\text{NCS}^-$  ions. In addition one or more bands due to the CN stretch in the metal complex or some metal complex of the form  $\text{U}(\text{NCS})_{8-n}(\text{C}_3\text{H}_6\text{O})_n^{4-}$  were observed. The concentration effect noted by Grey and Smith is remarkably similar to that observed here and, yet, the band positions reported were shifted approximately 12  $\text{cm}^{-1}$ . It is unfortunate that the position of the free  $\text{NCS}^-$  absorption in acetone was not reported in their study since this would clearly resolve the question of instrument calibration. It is difficult to understand the concentration effect they observed unless dissociation is invoked.

The solubility of  $[(\text{C}_6\text{H}_5)_4\text{As}]_4[\text{U}(\text{NCS})_8]$  and  $[\text{Et}_4\text{N}]_4[\text{U}(\text{NCS})_8]$  is not particularly high in acetone and herein may lie one possible explanation for the tremendous differences observed. If the solubilities of the salts examined by Grey and Smith were significantly greater than that of the salts examined in this study, it is possible that they would have observed no dissociation and thus no absorption due to free  $\text{NCS}^-$ . This explanation still leaves the questions raised by the observed concentration effect unresolved. Dissociation of the  $\text{U}(\text{NCS})_8^{4-}$  ion is known to occur in water [15, 16].

#### Magnetic Susceptibility

The results of magnetic susceptibility measurements from 80 to 300 K on the compounds prepared in this work are given in Table IV. All compounds exhibit very nearly Curie-Weiss behavior and show no dependence on field strength. Data given in Table IV is in terms of the Curie-Weiss expression;

$$1/X'_m = \text{Slope}(T - \theta)$$

Examination of the residuals generated in the least squares fit calculations for the  $\text{U}(\text{NCS})_8^{4-}$  compounds clearly show a slight curvature in the data. A similar curvature in the  $1/X'_m$  vs.  $T$  plot was previously noted in the compound  $[\text{Et}_4\text{N}]_4[\text{U}(\text{NCS})_8]$  [9] and was attributed to second order Zeeman effects.

Since calculated  $\theta$  temperatures are significantly large, effective magnetic moments, calculated as;

$$\mu_{\text{eff}} = 2.83 (X'_m T)^{1/2}$$

vary considerably with temperature. Effective magnetic moments are given only for 300 K. The data observed for the compounds examined in this work is in accord with that reported for other uranium(IV) complexes [2, 17–19].

TABLE IV. Magnetic Susceptibility of Uranium(IV) Compounds.

Compound	Slope	$\theta$ (K)	$\mu_{\text{eff}}^{300}$ (B.M.)
[Et <sub>4</sub> N] [U(NCSe) <sub>5</sub> (bipy) <sub>2</sub> ]	0.5880(0.3) <sup>a</sup>	-149(0)	3.02
[Et <sub>4</sub> N] [U(NCS) <sub>5</sub> (bipy) <sub>2</sub> ]	0.6043(5)	-125(1)	3.05
[Et <sub>4</sub> N] [U(NCSe) <sub>5</sub> (dmb) <sub>2</sub> ]	0.6065(1)	-95(0)	3.18
[Et <sub>4</sub> N] [U(NCS) <sub>5</sub> (dmb) <sub>2</sub> ]	0.7394(2)	-46(0)	3.07
[Et <sub>4</sub> N] [U(NCSe) <sub>5</sub> (phen) <sub>2</sub> ]	0.6361(3)	-104(1)	3.06
[Et <sub>4</sub> N] [U(NCS) <sub>5</sub> (phen) <sub>2</sub> ]	0.7280(2)	-82(0)	2.93
[(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> As] <sub>4</sub> [U(NCSe) <sub>8</sub> ]	0.7837(101)	-253(6)	2.37
[(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> As] <sub>4</sub> [U(NCS) <sub>8</sub> ]	0.4606(22)	-330(3)	2.86
[Et <sub>4</sub> N] [U(NCSe) <sub>8</sub> ]	0.9399(26)	-58(1)	2.69

<sup>a</sup>Values given in parenthesis are standard deviations, as calculated from least squares data, of the last digit given.

### X-Ray Powder Diffraction

X-ray powder diffraction data collected on [Et<sub>4</sub>N]-[U(NCS)<sub>5</sub>(bipy)<sub>2</sub>] and [Et<sub>4</sub>N][U(NCSe)<sub>5</sub>(bipy)<sub>2</sub>] indicates these two compounds are probably isomorphous. Slightly larger d spacings observed for the isoselenocyanate complex are expected due to the larger size of selenium as compared to sulfur. Structural isomorphism between analogous thiocyanate and selenocyanate complexes has been observed elsewhere [20]. None of the other analogous pairs of compounds prepared in this work appear to be isomorphous.

### Additional Data

More complete data on the infrared spectra and X-ray powder diffraction data of the compounds prepared in this work is available upon request from the authors. Electronic spectra in the 400–800 nm region of the complexes in acetonitrile solution is also available.

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