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Thiocyanate complexes of the lanthanides, Am and Cm

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The synthesis and single crystal structures of Am(III) and Cm(III) thiocyanate complexes are reported along with an isostructural series of lanthanide thiocyanate complexes. Because the complexes are isostructural, a comparative study of the metal-thiocyanate bonds was conducted using Raman spectroscopy indicating very similar and electrostatic metal-ligand interactions.

The participation of the 5f orbitals and electrons in the formation of metal-ligand bonds along with the hybridization of the 5f and 6d orbitals in the actinides was first proposed by Seaborg in a study of the behaviour of the trivalent lanthanides and actinides on ion-exchange columns in chloride media.[1] These early observations have evolved into what is currently known as the soft-donor hypothesis in f-element chemistry. Generally, soft-donors are considered any ligand softer than oxygen.[2] The soft-donor hypothesis posits that the actinides, because of their more radially extended f-orbitals will preferentially coordinate to soft-donor ligands, forming bonds that are more covalent than those formed with the lanthanides.[3-6] This change in bonding behaviour is thought to drive selectivity in trivalent actinide-lanthanide separations, a technologically significant and difficult separation, where soft-donor containing amphiphilic extractants or ligands are employed.[1, 4, 7]

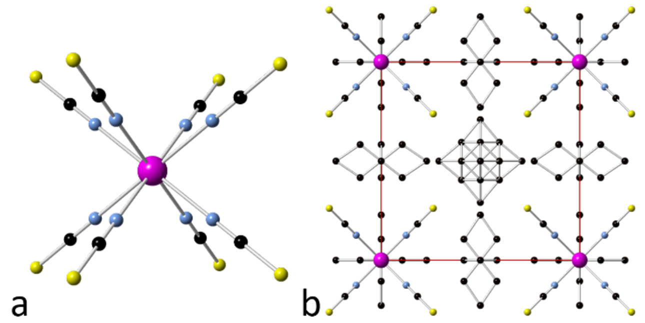

Figure 1 a. The coordination environment of the trivalent lanthanide and actinide thiocyanate complexes, the metal is shown in magenta, nitrogen in blue, carbon in black and sulfur in yellow. The thiocyanates are 7/8th occupied making the metals seven coordinate, $An(NCS)_7^{4-}$ b. Packing diagram for the *Pm*3*m* phases with the tetraethylammonium groups shown.

Chloride and the pseudo-halide thiocyanate (NCS), both considered soft on Pearson's hard-soft acid-base scale, are among the simplest of the myriad ligands that demonstrate trivalent actinide-lanthanide selectivity in separations systems.[6, 8] Within the framework of the soft-donor hypothesis the selectivity arises from differences in the coordination chemistry of the trivalent actinides versus the lanthanides. To study this hypothesis we investigated the coordination chemistry of trivalent actinide and lanthanide NCS complexes in a comparative study of their structure and spectroscopic properties. Early studies by Choppin investigated the thermodynamics of complex formation of the trivalent lanthanides and actinides demonstrating that the metal-NCS interaction was very weak, likely forming an outer-sphere complex, and that the marginally more stable interaction between the actinides and NCS was due to a nephelauxetic effect arising from the greater radial extent of the 5f orbitals.[9, 10] More recent studies have demonstrated largely ionic interactions between actinides and NCS.[11-13] To our knowledge this is the first report of the single crystal-structure and synthesis of a trivalent actinide thiocyanate complex.

Single crystals of the Am(III) and Cm(III) thiocyanate complexes were synthesized using their aquated triflate salts[14, 15], $[An(H_2O)_9](CF_3SO_3)_3$, in a methanol solution containing an excess of $[Et_4N]NCS$. Similar procedures were used to synthesize the corresponding lanthanide salts and the previously reported $(Et_4N)_4U(NCS)_8$ and $(Et_4N)_4Pu(NCS)_8$ complexes.[12, 13] Detailed synthetic protocols are available in the ESI. The Am(III) and Cm(III) thiocyanate complexes crystallize in the cubic space group P*m*3*m* similarly to the $(Et_4N)_4Pu(NCS)_8$

Table 1 Relevant bond distances and Raman vibrational frequencies for the lanthanide and actinide thiocyanate complexes.

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	Nd (*Pm*3*m*)	Sm (*Pm*3*m*)	Eu (*I*4/*mmm*)	Gd (*I* 4/*mmm*)
M-NCS *d*-Å	2.475(10)	2.452(8)	2.417(7)	2.412(8)
υ (M-NCS) cm^{-1}	181(2)	183(2)	196(2)	201(2)
υ (N≡CS) cm^{-1}	2046(2), 2089(2)	2048(2), 2088(2)	2053(2), 2094(2)	2056(2), 2096(2)
Δυ	43 cm^{-1}	40 cm^{-1}	39 cm^{-1}	40 cm^{-1}
			Am (*Pm*3*m*)	Cm (*Pm*3*m*)
M-NCS *d*-Å			2.484(12)	2.475(19)
υ (M-NCS) cm^{-1}			186(2)	190(2)
υ (N≡CS) cm^{-1}			2048(2), 2088(2)	2056(2), 2096(2)
Δυ			40 cm^{-1}	40 cm^{-1}

complex, Figure 1. Across the early lanthanide series, a change in phase occurs whereby the lighter lanthanides La to Sm crystallize in the cubic P*m*3*m* space group, while those from Eu to Lu crystallize in the tetragonal space group I4/*mmm*; lattice parameters and crystallographic details are available in the ESI. Determination of their molecular structure using single crystal X-ray diffraction reveals that the Am, Cm, and lanthanides are seven coordinate thiocyanate complexes with the formula $(Et_4N)_4(An(NCS)_7)\cdot xH_2O$ (x=1 Gd, Cm), bonded to the nitrogen of the thiocyanate anion, not the eight coordinate homoleptic square prismatic complex identified previously for the tetravalent actinides, Figure 1.‡

While the site symmetries of the metal cations and the NCS^- dictate an eight-fold square prismatic coordination environment, refinement of the site occupancies for the atomic positions associated with the NCS^- groups resulted in 7/8ths occupancy. This is in agreement with the charge balancing constraints of the trivalent oxidation state and the four cations of tetraethylammonium in the crystals.

Inspection of the difference maps did not reveal any excess electron density that supported the inclusion of a water molecule in the lanthanides or the Am and Cm coordination spheres as has been included in earlier refinements of the lanthanide salts.[16] FT-IR spectra taken of the lanthanide series of complexes, available in the ESI, show the characteristic vibration of bound water at ~1650 cm^{-1}, indicating that while not identified in the crystallographic data, there is a water molecule bound to the metal cation. This is in agreement with our earlier study of the Ce(III) complex.[12] Because there was no electron density to assign to the bound water molecule, we chose not to include it in the model as the metal-water bond distance would have been arbitrarily assigned. In the cases of, Gd and Cm, the inclusion of an interstitial water molecule was supported by the data and included in the refinement. The refined Am-NCS and Cm-NCS bond distances were 2.484(12) and 2.475(19) Å respectively, as compared to the 2.452(8), 2.417(7), and 2.410(8) Å bond distances observed in the Nd, Sm, Eu, and Gd complexes, Table 1, and the ESI. The An-NCS bond distances are systematically longer than the lanthanide bond distances when accounting for the differences in ionic radii between the actinides and the lanthanides.[17] Similar results were obtained by Jensen and others where it was demonstrated that there was little to no bond-length contraction between lanthanide and actinide sulphur bonds in a series of studies with dithiophosphinate ligands.[3, 18] This observation is counter to trends observed in other metal ligand complexes where soft metal-ligand interactions are observed, such as the contracted metal ligand bonds in $[(CH_3)_4N]_2PtCl_6$ and $[(CH_3)_4N]_2TeCl_6$ as compared to $[(CH_3)_4N]_2ZrCl_6$.[19]

As in previous studies, the structural data provide limited insight into the origin of the increased selectivity in separations systems as a result of differences in the metal-ligand interactions. To further investigate if there is a difference in the coordination chemistry between the trivalent lanthanides and the trivalent actinides we measured the Raman spectra of the as synthesized single crystals of these complexes. The full series of lanthanide thiocyanates and the isostructural Am(III) and Cm(III) complexes afford a valuable opportunity to compare the spectroscopic properties of the metal-ligand bond. The vibrational spectra of thiocyanate are sensitive to the metal-NCS interaction[20], and it is our hypothesis that a change in the nature of the lanthanide or actinide thiocyanate bonding interaction should manifest itself in these measurements. This is particularly so if there is a change from an electrostatic to a more covalent type of bonding that would perturb the electronic structure of the thiocyanate ligand, in particular the M-NCS and N≡CS vibrations.

There are three diagnostic vibrations for metal thiocyanate complexes, the M-NCS vibration which occurs near 200 cm^{-1}, and the NC-S and N≡CS vibrations at 746 cm^{-1} and 2053 cm^{-1},

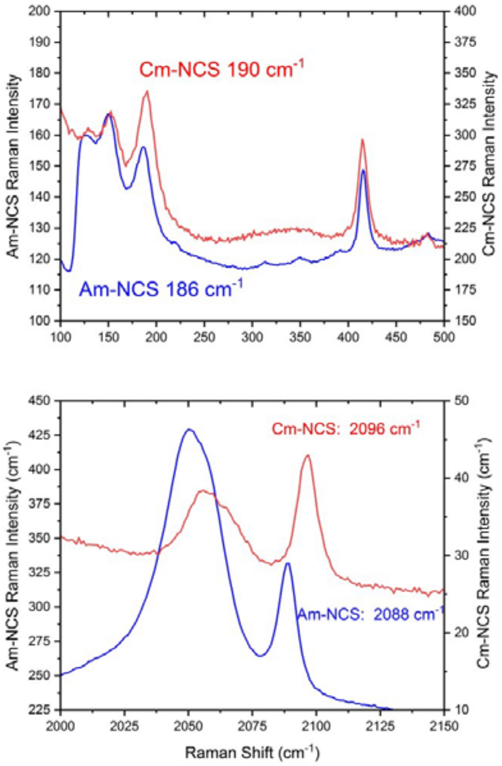

Figure 3 Raman spectra of the americium and curium thiocyanate complexes in the regions of the metal-nitrogen stretch as well as the N≡CS stretch at higher frequency.

respectively for the free NCS anion.[20] An assignment of the NC-S based vibrations cannot be made because of interference from the Et_4N^+ vibrations near 800 cm^{-1}. With respect to the M-NCS vibrational frequency, this frequency increases as Z is increased across the lanthanide series and also shows a modest increase from Am (186 cm^{-1}) to Cm (190 cm^{-1}), Table 1 and Figures 2 and 3. A similar, albeit smaller trend, is observed in the behaviour of the N≡CS vibration near 2000 cm^{-1}, where the vibration of the free thiocyanate is split into two main peaks with an average splitting of about 40 cm^{-1}. There is a shoulder on the lower frequency peak that does not appear in the homoleptic eight coordinate thiocyanate complexes Th(IV) and Pu(IV), indicating a lower symmetry coordination environment about the trivalent ions.[12] This splitting is consistent across the lanthanide and actinide series of spectra. Included in the plot are the vibrational frequencies observed for the tetravalent ions Th, and Pu highlighting the higher frequencies observed for these complexes, an effect we attribute to a stronger electrostatic attraction between the actinide and thiocyanate.[12, 21] Taken together, there are no significant differences between the trivalent lanthanide or actinide thiocyanate spectra. The trends shown in the data track with the decreasing ionic radii across the lanthanide and actinide series suggesting a stronger metal-thiocyanate interaction as the ions become smaller and more acidic. . This is supported by the higher frequency M-NCS vibrations observed in the case of the tetravalent actinides.

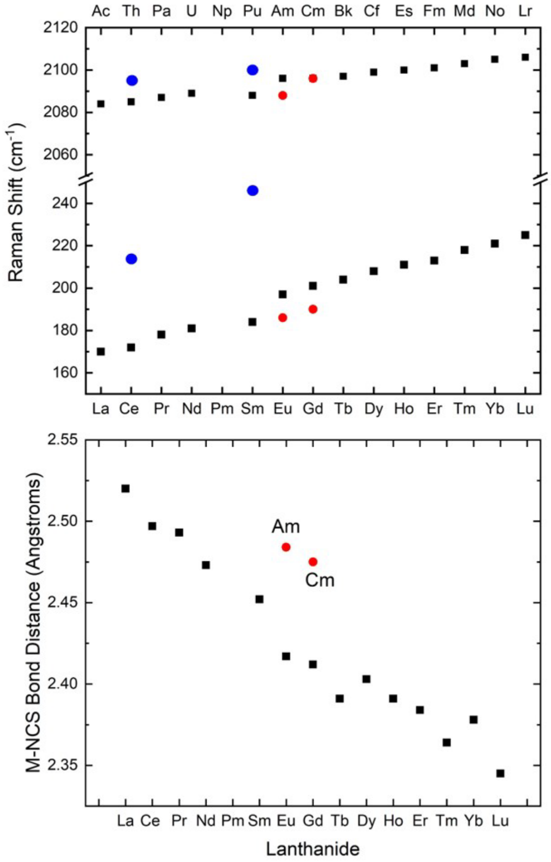

Figure 2 The observed Raman frequencies for the actinide and lanthanide thiocyanate complexes, top panel. The lanthanide frequencies are represented by the black squares, the Am(III) and Cm(III) frequencies are the red dots, Th(IV) and Pu(IV) in the blue dots[12]. The higher frequency vibrations (2080-2100 cm^{-1}) are associated with the N≡C vibrations of NCS, while the lower frequencies (160-250 cm^{-1}) arise from the M-N vibrations. The lower panel highlights the trend in bond distances in the data.

Computational studies of actinide and lanthanide thiocyanate complexes have demonstrated that the metal-ligand interaction is principally ionic.[11, 13, 22] Within the actinides, a marginally larger covalent interaction is observed for the tetravalent ions than the trivalent ions as defined within the quantum theory of atoms in molecules rubric.[11, 22] These trends have been recently confirmed in a study by Neese, wherein the computed covalent interactions between metal and ligand were small, and decreased as Z increased across both series.[23] Our data are consistent with these computed trends demonstrating an increasingly electrostatic interaction between metal and ligand and not an increased covalent interaction.This interpretation is in contrast to that from recent experiments measuring the core shell X-ray spectra of lanthanide and actinide halide complexes and ions, where it is suggested that there is an increasingly covalent metal-ligand interaction as the actinide and lanthanide series are crossed.[24-26] However, this increasingly covalent interaction is not due to increasing f-orbital overlap with the ligands, but is hypothesized to arise from the periodic energetic stabilization of the f-orbitals in the actinides in what is referred to as a degeneracy driven covalent interaction.[5] Recent computational and theoretical treatments show that this interpretation may be incorrect and that the spectra from the X-ray spectroscopy experiments are not representative of the ground state metal-ligand interactions.[27]

Our data do not provide for any evidence for an increasingly covalent interaction in the actinides versus the lanthanides, degeneracy driven or otherwise; the trends in both the structural data and Raman spectra can be interpreted as, and support an increasing electrostatic interaction between the metal ions and the thiocyanate ligands. In the prior work by Jensen[3] that investigated increases in covalency in f-element soft donor systems, and recent work by Knight et. al.[28], it is suggested that chemical effects beyond the coordination chemistry, may be driving the enhancements in selectivity in the trivalent lanthanide-actinide systems and not enhanced covalent interactions between the metal and ligand.[29-31]

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Conflicts of interest

There are no conflicts to declare

Notes and references

‡ Further details of the refinements are available in the supplemental information and in the deposited CIFs with the CCDC under reference codes Am (1956287), Cm(1956300), La(1956291), Ce(1956286), Pr(1956293), Nd(1956292), Sm(1956301), Eu(1956289), Gd(1956288), Tb(1956294), Dy(1956297), Ho(1956295), Er(1956299), Tm(1956296), Yb(1956298), Lu(1956290).

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