



Rare earth thiocyanate complexes with 18-crown-6 co-ligands

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ARTICLE INFO

Article history:

Available online 24 August 2012

Dedicated to Alfred Werner on the 100th Anniversary of his Nobel prize in Chemistry in 1913.

Keywords:

Lanthanoids
Rare earths
Thiocyanates
Crown ethers

ABSTRACT

Reaction of $[\text{Ln}(\text{NCS})_3(\text{THF})_4]_2$ or $[\text{Yb}(\text{NCS})_3(\text{THF})_4]$ with 18-crown-6 yields the moisture-stable $[\text{Ln}(\text{NCS})_3(18\text{-crown-6})]$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Dy}, \text{Yb}$) complexes. Although the Ln contraction does not affect the coordination number, the crown ether is decreasingly folded with decreasing ion size.

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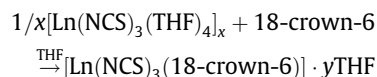
1. Introduction

Building on earlier interest in complexes of lanthanoid(II/III) thiocyanates with tetrahydrofuran (THF) and 1,2-dimethoxyethane (dme) [1–6], we have recently published a comprehensive study of their syntheses from the commercially available $\text{Hg}(\text{SCN})_2$ by redox transmetallation, and the structures of a wide range of $[\text{Ln}(\text{NCS})_3(\text{L})_n]$ and $[\text{Ln}(\text{NCS})_2(\text{L})_n]$ ($\text{L} = \text{THF}$ or dme) complexes [7]. All were highly moisture sensitive. However, it is apparent that multidentate ligands can give water-stable complexes. For example, $[\text{Ln}(\text{NCS})_3(\text{tetg})(\text{H}_2\text{O})]$ ($\text{Ln} = \text{Sm}$ or Ce ; $\text{tetg} = \text{tetramethylene glycol}$) species are isolated as aqua complexes, which are nine coordinate [8a,b]. 2,2'-6',2''-Terpyridine complexes are also moisture stable [8c]. With the same intention, a miscellaneous range of $\text{Ln}(\text{NCS})_3$ complexes with an *N-p*-chlorophenyl-aza-15-crown-5 ligand [9], with diaza-18-crown-6 ligands [10,11], hexa-aza-18-crown-6 [12], dibenzo-30-crown-10 [13], and dibenzo-18-crown-6 [14] have been structurally characterised. However, only one X-ray crystal structure of a $\text{Ln}(\text{NCS})_3$ complex with 18-crown-6 has been reported, namely 10-coordinate $[\text{La}(\text{NCS})_3(18\text{-crown-6})(\text{Me}_2\text{NCHO})]$ [15]. Other complexes have been prepared but their structures have not been determined [16]. We now report the synthesis and structures of $[\text{Ln}(\text{NCS})_3(18\text{-crown-6})]$ complexes with a wide variation in Ln^{3+} ionic radius. Previous $\text{Ln}^{\text{II/III}}(\text{NCS})_n$ ($n = 2, 3$) complexes with THF and dme show several different structural responses to the lanthanoid contraction [7]. Complexes between LnCl_3 and 18-crown-6 show considerable variety [17]. There is a change from $[\text{LnCl}_2(\text{H}_2\text{O})]$

(18-crown-6)Cl for $\text{Ln} = \text{La}, \text{Ce}$ to $[\text{LnCl}(\text{H}_2\text{O})_2(18\text{-crown-6})]\text{Cl}_2$ for $\text{Ln} = \text{Pr-Tb}$, though all are nine-coordinate [17a] and there are variations in associated water of crystallisation for $\text{Ln} = \text{La}, \text{Ce}$. Variation in crystallisation conditions lead to anhydrous $[\text{LaCl}_3(18\text{-crown-6})]$ [17a], $[\text{Ln}(\text{H}_2\text{O})_7(\text{MeOH})][\text{LnCl}(\text{OH})_2(18\text{-crown-6})]_2\text{Cl}_7$ ($\text{Ln} = \text{Tb}, \text{Dy}$) with eight coordination for the complex cations without the crown ether [17b], or even expulsion of the crown from the coordination sphere in $[\text{Dy}(\text{H}_2\text{O})_8]\text{Cl}_3 \cdot 18\text{-crown-6} \cdot 4\text{H}_2\text{O}$ [17c].

2. Results and discussion

Treatment of $[\text{Ln}(\text{NCS})_3(\text{THF})_4]_2$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Dy}$) and $[\text{Yb}(\text{NCS})_3(\text{THF})_4]$ [7] with dried 18-crown-6 in THF gave complexes **1a–1d**.



($\text{Ln} = \text{La}$ (**1a**), $x = 2, y = 0$; $\text{Ln} = \text{Nd}$ (**1b**), Dy (**1c**), $x = 2, y = 1$; $\text{Ln} = \text{Yb}$ (**1d**), $x = 1, y = 1$).

Single crystals were obtained of **1b–1d**, and microanalyses or metal analyses on the crystals were in agreement with the single crystal composition. On the other hand, **1a** deposited as a powder under the same conditions that gave single crystals of **1b–1d**, and was isolated without THF of crystallisation, as indicated by microanalysis. The X-ray powder diffractogram of **1a** was in agreement with that of powdered **1b** and both differed from the X-ray powder diffractogram generated from single crystal data for **1b**. In addition, the IR spectra of all four compounds after grinding to powders for Nujol mulls were similar and showed no clear evidence for the presence of tetrahydrofuran. Thus, it appears from both X-ray

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powder and IR data that the THF of crystallisation of **1b–1d** is lost on grinding the crystals into a powder. The complexes were all air (moisture)-stable in contrast to the THF complexes used as reagents. Thus, a Nujol mull of **1a** was exposed to the atmosphere for three days without significant change in the IR spectrum. From **1a** to **1d**, $\nu(\text{CN})$ [18] increases progressively from 2038 to 2057 cm^{-1} attributable to increased Lewis acidity of Ln^{3+} as the ionic radius contracts, whilst $\nu(\text{CS})$ is observed near 835 cm^{-1} as expected for an isothiocyanato complex [18].

2.1. Structures of complexes **1b–1d**

X-ray structure determinations showed that they were isostructural and isomorphous, with the composition $[\text{Ln}(\text{NCS})_3(18\text{-crown-6})]\cdot\text{THF}$. The lanthanoid metal atoms are nine-coordinate (commonly observed for Ln halide crown ether complexes [17,19]), bonding to three isothiocyanate ligands and six oxygen donor atoms from the 18-crown-6 which is bonded in an in cavity fashion (Fig. 1a). The THF molecule resides in the lattice. The 18-crown-6 molecule was disordered in (**1d**) and successfully modelled over two positions.

The stereochemistry of the metal centres for compounds (**1b–1d**) is distorted monocapped square antiprismatic, where the capping atom is O(4) (Fig. 1b) [20,21]. From the bond length data (Table 1), $\langle\text{Ln}-\text{N}\rangle$ decreases by more than expected from ionic radius differences [22], whereas $\langle\text{Ln}-\text{O}\rangle$ decreases by less than expected, indicating that the steric strain imposed by the lanthanoid contraction is borne by the 18-crown-6 O–Ln binding. However, unlike THF and dme complexes of $\text{Ln}(\text{NCS})_3$, there is no change in coordination number/stereochemistry from Nd to Yb, nor is there any displacement of NCS from the coordination sphere by the donor solvent (THF) as observed in $\text{LnCl}_3/18\text{-crown-6}$ complexes [17].

Reported nine-coordinate Nd complexes, $[\text{Nd}(\text{NCS})_3(\text{DD18C6})]$ (DD18C6 = dibenzylidiazia-18-crown-6, [11b]) $[\text{Nd}(\text{terpy})_2(\text{NCS})_3]\cdot x\text{EtOH}$ (terpy = 2,2':6',2''-terpyridine; $x = 0$ or 2) [8c] and $[\text{Nd}(\text{phen})_3(\text{NCS})_3]\cdot\text{EtOH}$ (phen = 1,10-phenanthroline) [8c] display Nd–N_(NCS) bond lengths ranging between 2.466(1)–2.522(2), 2.498(2)–2.580(2) and 2.488(4)–2.498(4) Å respectively. These are somewhat larger, and the first two cover a larger range than those of (**1b**) (Table 1), indicating that the steric demands of 18-crown-6 are less than for DD18C6, 2 × terpy or 3 × phen ligands because of greater flexibility of 18-crown-6. $[\text{Dy}(\text{NCS})_3(\text{dibenzo-30-crown-10})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}\cdot\text{MeCN}$ displays Dy–N bond lengths ranging between 2.26(1) and 2.402(9) Å encompassing the much narrower range for (**1c**) [13a]. The average length of Dy–N bonds in eight coordinate $[\text{Dy}(\text{NCS})_3(\text{dme})_2(\mu\text{-dme})_{0.5}]$ is 2.35 Å [7], which is relatively

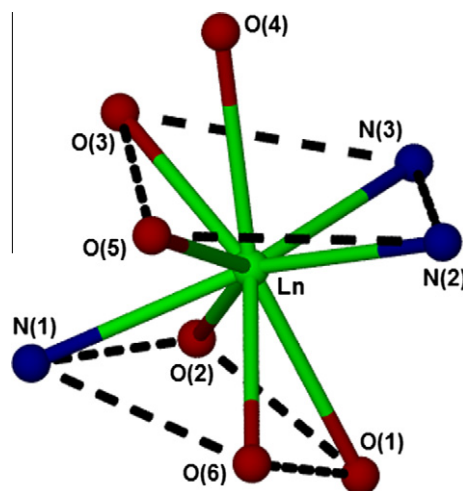


Fig. 1b. The donor atom geometry about the metal centres in (**1b–1d**).

Table 1
Selected bond lengths (Å) and angles (°) for complexes (**1b–1d**).

	(1b)	(1c)	(1d)
<i>Bond lengths</i>			
Ln(1)–N(1)	2.460(5)	2.367(3)	2.320(5)
Ln(1)–N(2)	2.469(5)	2.351(3)	2.312(5)
Ln(1)–N(3)	2.471(5)	2.381(3)	2.335(5)
Ln–N(av)	2.47	2.37	2.32
Ln(1)–O(1)	2.579(4)	2.512(2)	2.476(5)
Ln(1)–O(2)	2.564(4)	2.517(2)	2.466(5)
Ln(1)–O(3)	2.579(4)	2.527(2)	2.499(4)
Ln(1)–O(4)	2.585(4)	2.519(2)	2.487(5)
Ln(1)–O(5)	2.550(4)	2.487(2)	2.477(5)
Ln(1)–O(6)	2.593(4)	2.539(2)	2.507(5)
Ln–O(av)	2.58	2.52	2.49
N(1)–C(1)	1.171(7)	1.158(4)	1.154(7)
N(2)–C(2)	1.177(7)	1.162(4)	1.148(8)
N(3)–C(3)	1.151(7)	1.158(4)	1.171(7)
S(1)–C(1)	1.619(6)	1.615(3)	1.617(6)
S(2)–C(2)	1.625(6)	1.617(3)	1.626(7)
S(3)–C(3)	1.636(6)	1.629(3)	1.631(6)
<i>Bond angles</i>			
N(1)–Ln(1)–N(2)	142.0(2)	141.69(9)	143.2(2)
N(2)–Ln(1)–N(3)	75.8(2)	76.59(9)	76.1(2)
N(1)–Ln(1)–N(3)	142.0(2)	140.66(9)	140.6(2)
Ln(1)–N(1)–C(1)	136.2(4)	174.3(2)	165.7(5)
Ln(1)–N(2)–C(2)	165.7(5)	170.0(2)	172.8(5)
Ln(1)–N(3)–C(3)	173.4(4)	174.9(2)	170.2(5)

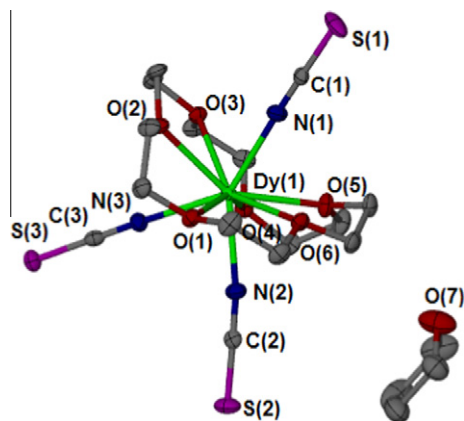


Fig. 1a. The structure of (**1c**), isostructural with (**1b**) and (**1d**). Ellipsoids shown at 50% probability, hydrogen atoms omitted for clarity.

slightly longer compared with the average Dy–N bond length in (**1c**) after consideration of the effects of the different coordination numbers [22]. The nine-coordinate Yb complex $[\text{Yb}(\text{NCS})_3(\text{TDCO})]$ (TDCO = 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane) displays Yb–N_(NCS) bond lengths (2.351(9)–2.385(9) Å) [10] which are longer than in (**1d**) perhaps indicating extra steric crowding in the former complex because of reduced flexibility from inclusion of two N-donor atoms in the crown host.

By contrast with Nd–N bond lengths of (**1b**), the Nd–O bond lengths are somewhat longer than those of $[\text{Nd}(\text{NCS})_3(\text{DD18C6})]$ (2.546(1)–2.571(3) Å) [11b] but within the range for $[\text{Nd}(\text{NCS})_3(\text{dme})_3]$ (2.518(2)–2.642(2) Å) [7], though the difference in Nd–N values is much more than in Nd–O data. Comparable Dy–O_(ether) bond lengths are found between (**1c**) and $[\text{Dy}(\text{Hoda})_3]\cdot\text{H}_2\text{O}\cdot\text{H}_2\text{O}$ (oda = oxydiacetate) [23]. Nine-coordinate $[\text{Yb}(\text{NCS})_3(\text{TDCO})]$ exhibits an average Yb–O bond length of 2.52 Å [10] which is slightly longer than in (**1d**) (2.49 Å), but again the effect is much less marked than differences in Yb–N bond lengths.

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