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Synthesis of complexes of 2,2′:6′,2″-terpyridine and 1,10-phenanthroline with lanthanide thiocyanates; the molecular structures of $[Ln(terpy)_2(NCS)_3]$ (Ln = Pr, Nd), $[Nd(terpy)_2(NCS)_3]\cdot 2EtOH$ and $[Ln(phen)_3(NCS)_3]\cdot EtOH$ (Ln = Pr, Nd)

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Abstract

The complexes $[Ln(terpy)_2(NCS)_3]$ (Ln = Pr (**1**), Nd (**2**); terpy = 2,2′:6′,2″-terpyridine), $[Nd(terpy)_2(NCS)_3]\cdot 2EtOH$ (**3**) and $[Ln(phen)_3(NCS)_3]\cdot EtOH$ (Ln = Pr(**4**), Nd (**5**); phen = 1,10-phenanthroline) have been synthesised in high yield by the reaction of $[Ln(NO_3)_3]\cdot 6H_2O$ (Ln = Pr, Nd) with KNCS and subsequently with terpy or phen, respectively. The five complexes have been characterised crystallographically, and it is found that the pairs of complexes, **1** and **2**, and **4** and **5** are isomorphous with each other. In all the complexes the lanthanoid ions are nine co-ordinate, and all contain meridionally disposed thiocyanate groups. The molecular geometry of **3** is very similar to that of **2**, and the crystal structure differs only in the presence of the two ethanol solvent molecules. In the whole series of complexes the Ln–N(thiocyanate) distances are shorter than the Ln–N(terpy/phen) distances and there is a shortening of all the lanthanoid–ligand bonds in the neodymium complexes compared with the praseodymium, consistent with the expected ‘lanthanide contraction’ that occurs as additional electrons enter the 4f orbitals. In all the complexes the thiocyanate groups are linear, but there is a significant variation in the angle at the thiocyanate at nitrogen and Ln–N–C angles lie in the range 147–177°.

Keywords: Praseodymium; Neodymium; 2,2′:6′,2″-Terpyridine; 1,10-Phenanthroline; X-ray crystal structures

1. Introduction

Whilst anionic thiocyanate complexes of the lanthanoids have been studied in considerable detail [1] and exhibit a striking variety of structures including $[M(NCS)_6]^{3-}$, $[M(NCS)_7]^{4-}$, $[M(NCS)_7(H_2O)]^{4-}$, $[M(NCS)_6(H_2O)(MeOH)]^{3-}$ and $[M(NCS)_8]^{5-}$, less is known about neutral complexes.

Two series of the hydrated salts have been characterised by X-ray diffraction; $[Ln(NCS)_3(H_2O)_6]\cdot H_2O$ (Ln = La, Ce, Pr, Nd) and $[Ln(NCS)_3(H_2O)_5]\cdot H_2O$ (Ln = Sm, Eu, Gd, Y) [2]. In a family $[Ln(NCS)_3(thf)_4]$, dimeric structures involving eight co-ordination have been confirmed for earlier lanthanoids (La–Er), whilst the ytterbium compound has a monomeric seven co-ordinate structure [3]. A synthetic route to Yb(III) thiocyanate complexes such as $[Yb(NCS)_3(thf)_4]$ and $[YbCl_2(thf)_5]^+[Yb(NCS)_4(thf)_3]^-$ by oxidation of $[Yb(NCS)_2(thf)_2]$ has recently been described [4].

In addition to our studies [5–7] of terpy complexes of lanthanoid nitrates, a number of other groups have examined the structures of chloride [8]9a, nitrate 9b10, perchlorate 9c and bromide 9d complexes. We were

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interested to see whether stable thiocyanate complexes could be obtained. In contrast to the nitrates where some or all of the nitrates act as bidentate ligands [5–7] and afford nine or ten co-ordinate complexes with monodentate thiocyanate ligand complexes, having a 1:1 stoichiometry would be co-ordinatively unsaturated, being formally six co-ordinate. Hence with the thiocyanates possibilities exist for either a higher ligand:metal ratio, as with the perchlorates, or the co-ordination of additional solvent or water molecules, as observed with the chlorides and bromides.

Since the first reports 11 of $[LnL_3(NCS)_3]$ (L = bipy, phen), there have been suggestions that $[Ln(phen)_3(NCS)_3]$(La–Eu) also co-ordinate water for heavier lanthanides (Dy–Yb) 12a, whilst a series $[Ln(phen)_3(NCS)_3(H_2O)]$ was reported 12b and assigned structures $[Ln(phen)_3(NCS)(H_2O)](NCS)_2$. However, $[Pr(bipy)_3(NCS)_3]$ has a monomeric structure [13]. We, therefore, wished to clarify the structure of comparable $[Ln(phen)_3(NCS)_3]$ complexes and use them to compare with the new series of terpy complexes prepared as part of this study.

2. Experimental

Hydrated lanthanoid nitrates, 2,2′:6′,2″-terpyridine, 1,10-phenanthroline and solvents were obtained as commercial products (Aldrich) and were used without purification. IR spectra (4000–750 cm^{-1}) were recorded on powdered samples using an Avatar 320 FT-IR spectrometer.

2.1. Synthesis

2.1.1. $[Ln(terpy)_2(NCS)_3]$ (Ln = Pr (**1**), Nd (**2**))

Solutions of $Ln(NO_3)_3\cdot 6H_2O$ (0.10 g, 0.23 mmol) in ethanol (2 ml) and KNCS (0.07 g, 0.72 mmol) in ethanol (3 ml) were mixed and the white precipitate of KNO_3 filtered off. The solution was warmed and a hot solution of 2,2′:6′,2″-terpyridine (0.10 g, 0.43 mmol) in ethanol (40 ml) added. On cooling small, block-shaped crystals were formed. $[Pr(terpy)_2(NCS)_3]$ (**1**) 2067 (sh), 2041 (thiocyanate), 1595, 1578, 1479, 1456, 1447, 1431, 1305, 1231, 1172, 1160, 1008, 797, 767 cm^{-1}. Calc. for $C_{33}H_{22}N_9PrS_3$ (**1**) C, 50.70; H, 2.84; N, 16.13%. Observed for $Pr(terpy)_2(NCS)_3$ C, 49.69; H, 2.79; N, 15.80%. $[Nd(terpy)_2(NCS)_3]$ (**2**) 2069 (sh), 2062 (sh), 2043 (thiocyanate), 1596, 1575, 1479, 1456, 1447, 1433, 1307, 1232, 1172, 1160, 1007, 792, 768 cm^{-1}. Calc. for $C_{33}H_{22}N_9NdS_3$ (**2**) C, 50.48; H, 2.82; N, 16.06%. Observed for $Nd(terpy)_2(NCS)_3$ C, 49.87; H, 2.83; N, 16.05%.

2.1.2. $[Nd(terpy)_2(NCS)_3]\cdot 2EtOH$ (**3**)

The complex **3** was prepared as described as for **2** above, and the isolated crystals were found to contain unco-ordinated molecules of ethanol solvent.

2.1.3. $[Ln(phen)_3(NCS)_3]\cdot EtOH$ (Ln = Pr (**4**), Nd (**5**))

Solutions of $Pr(NO_3)_3\cdot 6H_2O$ (0.17 g, 0.39 mmol) in ethanol (2 ml) and KNCS (0.13 g, 1.34 mmol) in ethanol (5 ml) were mixed and the white precipitate of KNO_3 filtered off. The solution was warmed and a hot solution of phenanthroline (0.20 g, 1.11 mmol) in ethanol (35 ml) added. On cooling fine needles were formed. $[Pr(phen)_3(NCS)_3]$ (**4**) 2057 (sh), 2037 (thiocyanate), 1516, 1420, 1140, 1099, 862, 846, 768, 728, 718 cm^{-1}. Calc. for $C_{39}H_{24}N_9PrS_3$ (**4**) C, 54.74; H, 2.83; N, 14.73%. Observed for $Pr(phen)_3(NCS)_3$ C, 53.38; H, 2.71; N, 14.49%. $[Nd(phen)_3(NCS)_3]$ (**5**) 2057 (sh), 2038 (thiocyanate), 1625, 1589, 1516, 1420, 1140, 1099, 862, 843, 770, 728, 717 cm^{-1}. Calc. for $C_{39}H_{24}N_9NdS_3$ (**5**) C, 54.52; H, 2.82; N, 14.67%. Observed for $Nd(phen)_3(NCS)_3$ C, 53.74; H, 2.75; N, 14.47%.

FAB or electrospray mass spectra were obtained for all the complexes, but the results were not informative as no identifiable peaks due to lanthanide-containing species were observed.

2.2. X-ray crystallography

The crystal data, data collection parameters, and structure solution and refinement details for the five structures determined are presented in Table 1. Data collections for **1**, **3** and **4** were carried out on a Bruker–Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα radiation, and that for **2** and **5** on a Bruker AXS SMART diffractometer, at Station 9.8, at the Daresbury CCLRC synchrotron. Both instruments were equipped with an Oxford Cryostream cooling apparatus. In each case the data was corrected for Lorentz and polarization effects and for absorption using SORTAV [14] for **1**, **3** and **4** and SADABS [15] for **2** and **5**. Structure solution was achieved by Patterson methods (SHELXS-86 [16]) and refined by full-matrix least-squares on F^2 (SHELXL-97 [17]) with all non-hydrogen atoms assigned anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were placed in idealised positions and allowed to ride on the relevant carbon atom. In structures **3**, **4** and **5** the ethanol solvent molecules were disordered, and individual atomic sites were refined with partial occupancies, but with the sites tied together that the total occupancy for each atom summed to unity. In the structure of **1** one of the thiocyanates was also partially disordered and S(8′) was refined over two sites with the occupancy summing to unity. In the final cycles of refinement a weighting scheme that gave a relatively flat analysis of

Table 1
Crystallographic data for compounds **1**, **2**, **3**, **4** and **5**

Compound	**1**	**2**	**3**	**4**	**5**
Molecular formula	$C_{33}H_{22}N_9PrS_3$	$C_{33}H_{22}N_9NdS_3$	$C_{37}H_{34}N_9NdO_2S_3$	$C_{41}H_{30}N_9OPrS_3$	$C_{41}H_{30}N_9ONdS_3$
M	781.69	785.02	877.15	901.83	905.16
Crystal system	triclinic	triclinic	monoclinic	triclinic	triclinic
a (Å)	12.524(1)	12.5114(4)	9.822(1)	10.9360(12)	10.9237(6)
b (Å)	15.472(1)	15.3681(5)	13.534(1)	12.2270(12)	12.1738(6)
c (Å)	16.848(1)	16.7776(5)	28.859(1)	15.6370(15)	15.6575(8)
α (°)	81.88(1)	81.827(2)	90	97.768(4)	97.722(1)
β (°)	89.28(1)	89.147(2)	99.62(1)	102.052(6)	101.872(1)
γ (°)	89.20(1)	89.338(2)	90	101.286(6)	101.393(1)
U (Å^3)	3231.4(4)	3192.67(17)	3782.3(5)	1971.2(3)	1952.68(18)
T (K)	230(2)	150(2)	180(2)	180(2)	150(2)
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Z	4	4	4	2	2
D_{calc} (Mg m^{-3})	1.607	1.633	1.540	1.519	1.539
μ (mm^{-1})	1.741	1.862	1.585	1.440	1.536
Wavelength λ (Å)	0.71069	0.6867	0.71069	0.71069	0.6893
Data collection range (°)	$3.63 < \theta < 25.08$	$1.94 < \theta < 30.47$	$3.58 < \theta < 27.50$	$2.93 < \theta < 25.00$	$3.42 < \theta < 29.50$
Reflections measured	16 224	33 113	13 648	42 106	18 580
Independent reflections	11 295 ($R_{int} = 0.032$)	17 421 ($R_{int} = 0.033$)	8639 ($R_{int} = 0.032$)	6878 ($R_{int} = 0.076$)	10 229 ($R_{int} = 0.041$)
Parameters	838	829	490	520	490
wR_2 (all data) [a]	0.0723	0.0787	0.0957	0.0871	0.1120
R_1 $[I > 2\sigma(I)]$ [a]	0.0427	0.0312	0.0377	0.0411	0.0480

[a] $R_1 = \Sigma ||F_o|| - ||F_c||/\Sigma ||F_o||$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^2$.

variance was introduced and refinement continued until convergence was reached.

3. Results and discussion

The complexes [Ln(terpy)$_2$(NCS)$_3$] (Ln = Pr (**1**), Nd (**2**)) were prepared from the reaction of Ln(NO$_3$)$_3$·6H$_2$O with 3 equiv. of KNCS, in ethanol at room temperature. The solution was warmed and an excess of 2,2′:6′,2″-terpyridine added, in hot ethanol, with stirring. Upon cooling suitable crystals for X-ray diffraction studies were obtained. In the case of the reaction with Nd(NO$_3$)$_3$·6H$_2$O, a second batch of crystals with a formulation [Nd(terpy)$_2$(NCS)$_3$]·2EtOH (**3**), confirmed by X-ray diffraction were obtained. Once formed the crystals of **1**, **2** and **3** were sparingly soluble in ethanol, methanol or water, and completely insoluble in less polar organic solvents. Limited spectroscopic characterisation was, therefore, possible.

Infrared spectra are listed in the Section 2. None of the spectra showed bands due to ethanol, which was presumably lost during the sampling process. All exhibited bands due to ν(CN) (thiocyanate) just above 2000 cm^{-1}; in each case, splitting of the band was observed, as expected because of the molecular symmetry. The spectra of each pair of complexes [Ln(terpy)$_2$(NCS)$_3$] and [Ln(phen)$_3$(NCS)$_3$] were very similar. The spectra of the terpy complexes exhibited strong bands at 1596–1575 and 1432–1479 cm^{-1} due to ν(CN) and ν(CC) [18]. Microanalyses were obtained for the compounds, but the carbon analyses in particular tended to be misleading. With the facilities available, limited precautions could be taken in handling the compounds prior to microanalysis and it is believed that loss of ethanol occurred and that some carbide formation may have taken place on combustion. Our crystallographic results give us confidence in the composition of these compounds. Mass spectra were uninformative, as no lanthanoid-containing species could be identified.

Therefore, in order to establish the stoichiometry and structure of the three complexes single crystal X-ray diffraction studies were undertaken.

The complexes [Ln(terpy)$_2$(NCS)$_3$] (Ln = Pr (**1**), Nd (**2**)) are isomorphous, crystallising in the triclinic space group $P\bar{1}$, with no solvent molecules trapped in the crystal lattice. In each case there are two independent but structurally similar molecules in the asymmetric unit. The structure of one of the independent molecules of **1** is illustrated in Fig. 1, that includes the atom numbering scheme used for both the Pr and Nd derivatives, while selected bond parameters for the complexes are presented in Table 2. The complexes **1** and **2** are monomeric, and the metal ions are nine coordinate being bound to three monodentate thiocyanate groups, bonded through nitrogen, and the six nitrogen atoms from two tridentate terpy ligands. Because of the geometric requirements of the chelating terpy groups the co-ordination geometry deviates considerably from the 'idealised' tricapped trigonal prismatic geometry [19] that gives the lowest energy configuration for nine

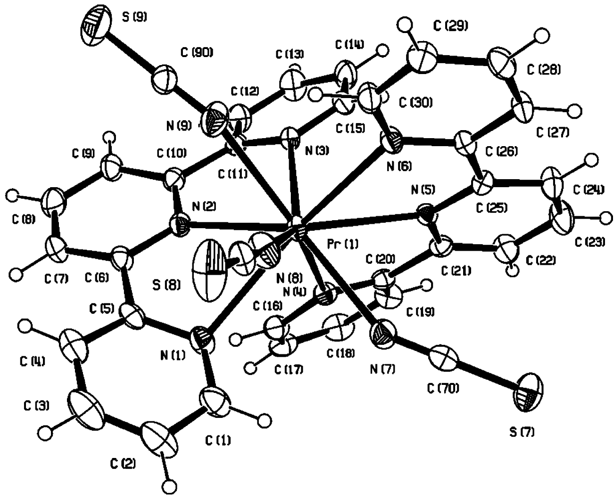

Fig. 1. The molecular structure of one of the two independent molecules of [Pr(terpy)$_2$(NCS)$_3$] (**1**) showing the atom numbering scheme used for this complex and the analogous Nd derivative **2**. Anisotropic displacement ellipsoids are drawn at the 30% probability level.

monodentate ligands surrounding a metal centre. However, within the observed geometry, if the two terpy ligands are viewed as occupying only one co-ordination site each, then the co-ordination sphere approximates to a trigonal bipyramid with two of the thiocyanates occupying pseudo axial sites and one a pseudo equatorial site, to give a meridional arrangement for these three groups. The molecular structures of **1** and **2** confirm that the thiocyanate is a ligand of fairly strong co-ordinating power but small steric demand, allowing two terpy groups to bind to the lanthanoid ion. This has not been observed hitherto in any neutral lanthanoid complex, the cationic species in [La(terpy)$_2$(NO$_3$)$_2$]$^+$[La(terpy)(NO$_3$)$_4$]$^-$ being the only previous example 10a.

An analysis of the bond parameters within the structures of **1** and **2** reveals a number of interesting features. The Ln–N(thiocyanate) distances {average 2.533 Å for **1** and 2.527 Å for **2**} are shorter than the Ln–N(terpy) distances {average 2.655 Å for **1** and 2.638 Å for **2**}, and there is a slight decrease of approximately 0.01 Å in the average distances for both the metal–thiocyanate and the metal–terpy bonds in going from the Pr^{3+} ion (**1**) to the Nd^{3+} ion (**2**), consistent with the 'lanthanide contraction'. However, as can be seen from individual bond lengths in Table 2 there is a considerable spread of values from 2.599(3) to 2.712(3) Å for the Pr–N(terpy) distances in **1** and from 2.498(2) to 2.580(2) Å for the Nd–N(thiocyanate) distances in **2**, for example, and, as a result, too great a reliance should not be placed on a detailed analysis of the bond parameters. It does appear, however, that, on average, the Ln–N distance to the central nitrogen of the terpy ligands is shorter than the distances to the two other nitrogen atoms on these ligands {for **1** the Pr–N distance to the central terpy N atom averages 2.646 Å while the distance to the two other nitrogen atoms averages 2.659 Å, and for **2** the Nd–N distance to the

Table 2
Selected bond lengths (Å) and angles (°) for compounds **1**, **2**, **3**, **4** and **5**

	1 [a] (Pr)	**2** [a] (Nd)	**3** (Nd)	**4** (Pr)	**5** (Nd)
Bond lengths					
Ln(1)–N(1)	2.683(4), 2.634(4)	2.613(2), 2.674(2)	2.622(3)	2.698(3)	2.679(3)
Ln(1)–N(2)	2.631(3), 2.656(3)	2.6111(19), 2.645(2)	2.652(3)	2.723(3)	2.705(3)
Ln(1)–N(3)	2.712(3), 2.666(3)	2.5807(19), 2.639(2)	2.669(3)	2.679(3)	2.655(3)
Ln(1)–N(4)	2.634(3), 2.688(4)	2.672(2), 2.628(2)	2.643(3)	2.691(3)	2.661(4)
Ln(1)–N(5)	2.634(3), 2.663(3)	2.6068(19), 2.637(2)	2.635(3)	2.716(3)	2.694(3)
Ln(1)–N(6)	2.599(3), 2.655(4)	2.696(2), 2.651(2)	2.623(3)	2.718(3)	2.701(3)
Ln(1)–N(7)	2.558(4), 2.524(4)	2.580(2), 2.518(2)	2.535(3)	2.513(4)	2.493(4)
Ln(1)–N(8)	2.510(4), 2.530(4)	2.498(2), 2.523(2)	2.530(3)	2.507(4)	2.498(4)
Ln(1)–N(9)	2.536(4), 2.538(4)	2.516(2), 2.526(2)	2.523(3)	2.504(4)	2.488(4)
N(7)–C(70)	1.158(5), 1.166(5)	1.130(3), 1.165(3)	1.162(5)	1.163(5)	1.159(5)
C(70)–S(7)	1.633(5), 1.616(5)	1.640(3), 1.627(3)	1.625(4)	1.621(5)	1.620(4)
N(8)–C(80)	1.147(5), 1.156(5)	1.152(3), 1.156(4)	1.154(5)	1.153(5)	1.151(6)
C(80)–S(8)	1.618(5), 1.606(13)	1.632(3), 1.633(3)	1.640(4)	1.624(5)	1.628(4)
N(9)–C(90)	1.163(5), 1.167(5)	1.155(4), 1.159(3)	1.165(5)	1.175(5)	1.166(6)
C(90)–S(9)	1.598(5), 1.609(5)	1.634(3), 1.630(3)	1.629(4)	1.615(5)	1.617(4)
Bond angles					
Ln(1)–N(7)–C(70)	147.0(4), 138.5(4)	147.5(2), 138.1(2)	154.9(3)	157.3(3)	158.4(4)
Ln(1)–N(8)–C(80)	174.7(4), 175.3(4)	173.9(2), 174.3(3)	177.2(3)	167.2(4)	167.0(4)
Ln(1)–N(9)–C(90)	155.4(3), 154.9(3)	156.4(2), 153.7(2)	159.1(3)	157.9(3)	158.3(4)
N(7)–C(70)–S(7)	178.7(4), 178.2(5)	179.1(2), 179.0(3)	179.4(4)	179.2(4)	178.0(4)
N(8)–C(80)–S(8)	179.2(4), 169.5(7)	179.2(3), 179.5(3)	178.4(4)	179.3(5)	179.4(4)
N(9)–C(90)–S(9)	178.5(4), 178.0(4)	178.4(3), 178.5(2)	178.7(3)	178.4(4)	178.2(4)

[a] Complexes **1** and **2** have two independent molecules in the asymmetric unit and the two values recorded here refer to the two molecules.

Table 3
Hydrogen bonding interactions in **1** and **2**

Donor–H···acceptor	H···S′ (Å) for **1**	C–H···S′ (°) for **1**	H···S′ (Å) for **2**	C–H···S′ (°) for **2**	Acceptor related by symmetry operation
C(3)–H(3)···S(7)′	2.876	160.03	2.847	164.22	$1-x$, $1-y$, $-z$
C(8)–H(8)···S(8′)′	2.822	172.90	2.749	169.55	$x-1$, y, $z-1$
C(24)–H(24)···S(8′)′	2.779	156.97	2.778	153.66	$x-1$, y, z
C(9′)–H(9′)···S(7)′	2.832	160.39	2.821	159.42	x, y, z

central terpy N atom averages 2.625 Å while the distance to the two other nitrogen atoms averages 2.644 Å}. The Pr–N(terpy) distances in **1** are comparable with those in $[Pr(terpy)Cl(OH_2)_5]Cl_2\cdot 3H_2O$, where the Pr atom is also nine co-ordinate, in which the Pr–N distances [8] average 2.630(3) Å. There is also a close comparison with nine co-ordinate $[Pr(bipy)_3(NCS)_3]$ [13] where the Pr–N(bipy) average is 2.702 Å. There is a close similarity between the Pr–N(thiocyanate) distances in **1** and those in $[Pr(bipy)_3(NCS)_3]$ [13] where the average is 2.508 Å. In $[Pr(terpy)_3(NCS)_3]$ (**1**) the N–Pr–N angles involving the thiocyanate groups average 74.5° for the *cis* ligands and 147.6° for the *trans* ligands. The corresponding values for $[Pr(bipy)_3(NCS)_3]$ [13] are 78.6° for the *cis*-N–Pr–N and 152.3° for the *trans*-N–Pr–N angles. The comparable *cis*-N–Nd–N and *trans*-N–Nd–N angles involving the thiocyanates in **2** are 74.6° and 147.5°, respectively. For the thiocyanate ligands the N–C and C–S distances average 1.16 and 1.61 Å for **1**, and 1.15 and 1.63 Å for **2**, respectively, consistent with the 'idealised' values. While for both complexes the N–C–S angles of the thiocyanate ligands approximate very closely to linearity, there is a significant difference in the Ln–N–C angles. For both **1** and **2** two of the thiocyanates show a significant bending at the nitrogen {average Ln–N–C 149° for both **1** and **2**} the other thiocyanate is close to linear at the nitrogen {average Ln–N–C 175° for **1** and 174° for **2**}. For both complexes it is the thiocyanate that takes up the pseudo-equatorial co-ordination site in the meridional arrangement that is close to linear. The bond parameters within the terpy ligands in both complexes are within the range observed in 2,2′:6′,2″-terpyridine itself [20], in substituted organic molecules [21], and in related lanthanoid complexes [5–7]. Although the six-membered rings within the terpy groups are planar, the ligands show significant twisting between the adjacent rings. For complex **1** the dihedral angle between the ring containing N(1) and that containing N(2) is 23.55° (4.39° in the second molecule), that between N(2)/N(3) is 22.25° (25.06°), that between N(4)/N(5) is 18.37° (15.01°), and that between N(5)/N(6) 5.93° (16.00°). The dihedral angles between the terminal rings on each ligand are 44.18° (29.40°) for N(1)/N(3) and 24.26° (28.03°) for N(4)/N(6). For complex **2** the dihedral angles follow the same general pattern with N(1)/N(2) 16.50° (5.50°), N(2)/N(3) 16.50° (18.54°), N(4)/N(5) 24.96° (24.34°), and N(4)/N(6) 23.40° (5.18°), and the dihedral angles between the terminal rings on each ligand being N(1)/N(3) 27.44° (24.04°) and N(4)/N(6) 30.13° (46.34°).

In the crystal structures of **1** and **2** there are no solvent molecules present in the lattice. However, there are hydrogen bonds involving sulfur atoms of two of the thiocyanate groups (acting as the acceptors) and aromatic protons from the terpy rings acting as hydrogen bond donors. Each independent molecule in each of the two structures is involved, and the key interactions are listed in Table 3. There is also evidence for graphitic packing between the aromatic rings of the terpy ligands on adjacent symmetry related molecules whereby the rings are necessarily parallel. The rings in the π-stacks are offset and the ring-centroid–ring-centroid distances lie in the range 3.4–3.9 Å as is observed in many organic π-stacked systems [22]. The centroid–centroid distances are presented in Table 4.

The structure of the neodymium complex in $[Nd(terpy)_3(NCS)_3]\cdot 2EtOH$ (**3**) that is illustrated in Fig. 2 closely resembles that of **2** and **1**. Selected bond parameters are listed in Table 2. The metal is again nine co-ordinate, bonding to the six nitrogen atoms of the two tridentate, chelating terpy ligands, and the three nitrogen atoms of the three thiocyanate groups. The three thiocyanates adopt a meridional arrangement. The average Nd–N(thiocyanate) distance of 2.529 Å is approximately 0.11 Å shorter than the average Nd–N(terpy) distance of 2.641 Å, and the average distances are comparable with the equivalent distances observed in **2**. The average N–C and C–S distances for the three thiocyanate groups are 1.16 and 1.63 Å, respectively, and the N–C–S angles average 178.8°. As with **2**, the equatorial thiocyanate has an approximately linear arrangement at N(8) {Nd(1)–N(8)–C(80) 177.2(3)°}, while the other two thiocyanates show a much greater deviation from linearity at the nitrogen {average Nd–N–C 157.0°}. The dihedral angles between the planes of the pyridine rings of the two terpy ligands are N(1)/N(2) 12.18°, N(2)/N(3) 21.79°, N(1)/N(3) 18.68°, and N(4)/N(5) 21.71°, N(5)/N(6) 19.42° and N(4)/N(6) 21.45°, where the rings are referred to by the nitrogen atom that they contain.

On a molecular level the differences between the structures of **2** and **3** are hardly significant, the main

Table 4
π–π Stacking interactions in **1** and **2**

Ring 1	Ring 2	Centroid···centroid distance in **1** (Å)	Centroid···centroid distance in **2** (Å)	Symmetry operation relating the two rings
N(4)C(16)C(17)C(18)C(19)C(20)	N(4)C(16)C(17)C(18)C(19)C(20)	3.462	3.430	$-x, 1-y, -z$
N(3)C(11)C(12)C(13)C(14)C(15)	N(3)C(11)C(12)C(13)C(14)C(15)	3.871	3.847	$-x, -y, -z$
N(3′)C(11′)C(12′)C(13′)C(14′)C(15′)	N(3′)C(11′)C(12′)C(13′)C(14′)C(15′)	3.637	3.588	$1-x, 1-y, 1-z$

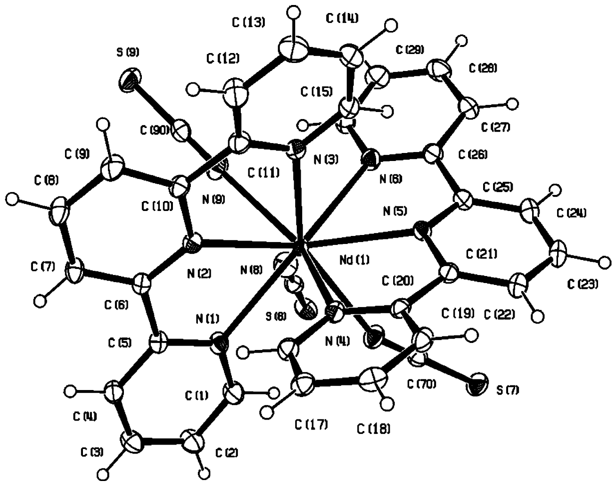

Fig. 2. The molecular structure of the complex $[Nd(terpy)_2(NCS)_3]$ (**3**) showing the atom numbering scheme. Two ethanol molecules of crystallisation are not shown. Anisotropic displacement ellipsoids are drawn at the 30% probability level.

difference is the presence of two disordered ethanol solvent molecules in the crystal lattice of **3**, that results in a different crystal packing arrangement. However, the two ethanol molecules are not heavily involved in hydrogen bonding to the complex. The ethanolic oxygen atoms do act as hydrogen bond acceptors for aromatic C–H hydrogens. There is a C(14)–H(14)···O(100) interaction with a H(14)···O(100) distance of 2.625 Å and a C(14)–H(14)···O(100) angle of 143.22°, and a H(24)···O(101) distance of 2.884 Å and C(24)–H(24)···O(101) 105.04° where the oxygen atom is related by the symmetry operation $1-x, -y, -z$, may perhaps be representative of a hydrogen bond. A more significant interaction is a C–H···S hydrogen bond involving one of the sulfur centres on a thiocyanate group. The H(7)···S(8) distance is 2.842 Å and the C(7)–H(7)···S(8) angle is 171.16°, where the sulfur atom is related by the symmetry operator $-0.5-x, 0.5+y, 0.5-z$. As in **2** there is an indication of graphitic stacking between one ring of one of the terpyridyl ligands and another terpyridyl group on an adjacent molecule. In this case the N(6)C(26)C(27)C(28)C(29)C(30) ring is parallel to its symmetry equivalent ring (related by the operator $-x, -y, -z$) and the centroid–centroid distance is 3.657 Å.

The two 1,10-phenthroline complexes $[Ln(phen)_3(NCS)_3]\cdot EtOH$ (Ln = Pr (**4**), Nd (**5**)) were prepared in an analogous method to that described for the terpy complexes. Crystals of each of the complexes that contained a molecule of crystallisation of ethanol were obtained by slow evaporation of the solution. The crystals were found to be suitable for single crystal X-ray studies and the structures were determined for comparison with the terpy complexes **1**–**3**.

The two complexes $[Ln(phen)_3(NCS)_3]\cdot EtOH$ (Ln = Pr (**4**), Nd (**5**)) are isomorphous and isostructural, crystallising in the triclinic space group $P\bar{1}$ (No. 2) with a disordered ethanol molecule in the asymmetric unit. Fig. 3 shows the molecular structure of the Nd complex and includes the atom numbering scheme applied to both **4** and **5**. Selected bond parameters for the two structures are listed in Table 2.

As with complexes **1**–**3** the lanthanoid ions in **4** and **5** are both nine co-ordinate, and are bound to the six nitrogen atoms of the three bidentate 1,10-phenanthroline ligands, and to the three nitrogen atoms of the three monodentate thiocyanate groups. As with the terpy complexes the three thiocyanate groups adopt a meridional arrangement in a pseudo-octahedral arrangement if each phen ligands is considered as occupying only one co-ordination site. This metal co-ordination geometry has already been observed for the analogous bipy complex $[Pr(bipy)_3(NCS)_3]$ [13]. In neither **4** or **5** are there either co-ordinated water molecules (despite the presence of small amounts of water in the reaction mixture) or ionic thiocyanate groups present.

As observed in the terpy complexes **1**–**3** the Ln–N(thiocyanate) bond lengths are shorter (2.508 Å for **4** and 2.493 Å for **5**) than the Ln–N(phen) bond lengths (2.704 Å for **4** and 2.684 Å for **5**), although there is a significant spread of individual distances, e.g. 2.679(3)–2.723(3) Å for the Pr–N(phen) in **4**. There is the expected decrease of approximately 0.02 Å in the comparable distances between **4** and **5**, consistent with the expected ‘lanthanide contraction’ in going from praseodymium to neodymium. A comparison of the Pr–N distances in **1** with those in **4** and the Nd–N distances in **2** and **3** with those **5**, shows that the Pr–

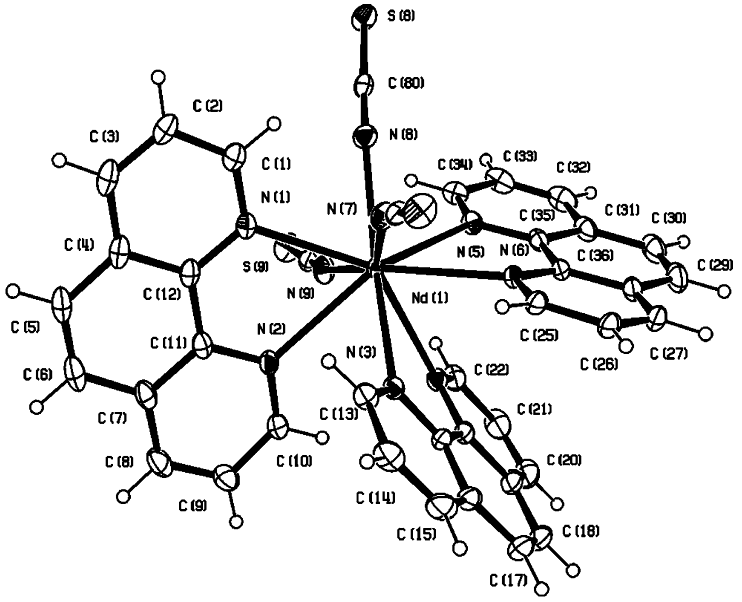

Fig. 3. The molecular structure of $[Nd(phen)_3(NCS)_3]\cdot EtOH$ (**5**) showing the atom numbering scheme used for this complex and for the Pr analogue. The ethanol molecule that is hydrogen bonded to the complex is not shown. Anisotropic displacement ellipsoids are drawn at the 30% probability level.

N(NCS) average distance in the phen complex are approximately 0.02 Å shorter than that in the terpy complex while the average Pr–N(phen) distance is approximately 0.04 Å longer than the average Pr–N(terpy) distance. Similarly, the average Nd–N(NCS) distance in **5** is approximately 0.04 Å shorter than the equivalent average in either **2** or **3**, and the average Nd–N(phen) distance in **5** is approximately 0.04 Å is longer than the average Nd–N(terpy) distance in **2** or **3**. The increase in the metal–ligand distance in the phen complexes compared with the terpy complexes can be explained in terms of greater ligand–ligand repulsion in the former systems because the steric crowding between three two-ring ligands will be greater than between two three-ring ligands. The average angles involving the thiocyanate groups at the metal centres are *cis*-N–Pr–N of 79.8° and *trans*-N–Pr–N of 151.42(13)° for **4** and *cis*-N–Nd–N of 79.5° and *trans*-N–Nd–N of 151.03(14)° for **5**. This is a small but significant increase in angle compared with the terpy that may relieve some inter-thiocyanate steric crowding that might occur with the shorter Ln–N(NCS) distances. Within the thiocyanate groups in **4** and **5** the average N–C and C–S distances are 1.29 and 1.62 Å for **4** and 1.16 and 1.62 Å, respectively. These distances are not significantly different from those found in the terpy complexes. Again the thiocyanate groups are linear in both complexes with average N–C–S angles of 179.0° for **4** and 178.5° for **5**. The three thiocyanate ligands in each complex show a significant deviation from linearity at the nitrogen atoms, but as with the terpy complexes the two pseudo-axial thiocyanates show greater deviations than the pseudo-equatorial ligand {average of 157.6° vs. 167.2(4)° for **4** and 158.4° vs. 167.0(4)° for **5**}. What is of significance is that the pseudo-equatorial Ln–N–C angles in **4** and **5** show a approximately 9° greater deviation from linearity than those in **1**–**3**. This may reflect the slightly increase in steric crowding around the lanthanoid centre in the phen complexes compared with the terpy complexes. The bond lengths and angles of the 1,10-phenanthroline ligands in each of the two complexes **4** and **5** are close to those found in 1,10-phenanthroline itself [23]. Within each structure the three phen rings are essentially planar with a maximum deviation from the plane of 0.09 Å for both **4** and **5**. The three ligand planes make angles of 76.13° for **4** (75.99° for **5**) for the ring containing N(1) and N(2) with the ring containing N(3) and N(4), 84.04° (84.34°) for N(1)/N(2) with N(5)/N(6), and 35.32° (36.37°) for N(3)/N(4) with N(5)/N(6).

Within the crystal lattices of **4** and **5** the hydrogen bonding interactions involve the ethanol solvent molecule, where the O–H group acts as a hydrogen bond donor and the same oxygen atom as a hydrogen bond acceptor. The O–H group donates the hydrogen to the sulfur atom of one of the axial thiocyanate groups; O(1)–H(51B)···S(2), H(51B)···S(2) 2.66 Å for **4** (2.43 Å for **5**), O(1)–H(51B)···S(2) 139.3° for **4** (149.3° for **5**). The oxygen atom, O(1), also accepts a hydrogen from an aromatic ring C(8)–H(8); H(8)···O(1) 2.58 Å for **4** (2.56 Å for **5**) and C(8)–H(8)···O(1) 156.8° for **4** (156.5° for **5**). Perhaps the dominant intermolecular interaction in these crystal structures is the extensive graphitic π–π stacking between phenanthroline ligands on adjacent molecules. For each of the complexes two of the three phen groups form the classical "offset" stacking ar-

Table 5
π–π Stacking interactions in **4** and **5**

Ring 1	Ring 2	Centroid···centroid distance in **4** (Å)	Centroid···centroid distance in **5** (Å)	Symmetry operation relating the two rings
N(1)C(1)C(2)C(3)C(4)C(12)	C(4)C(5)C(6)C(7)C(11)C(12)	3.707	3.696	$1-x,\ 1-y,\ -z$
C(4)C(5)C(6)C(7)C(11)C(12)	N(1)C(1)C(2)C(3)C(4)C(12)	3.707	3.696	$1-x,\ 1-y,\ -z$
N(5)C(31)C(32)C(33)C(34)C(35)	N(6)C(25)C(26)C(27)C(28)C(36)	3.718	3.709	$1-x,\ 2-y,\ 1-z$
C(28)C(29)C(30)C(31)C(35)C(36)	C(28)C(29)C(30)C(31)C(35)C(36)	3.843	3.816	$1-x,\ 2-y,\ 1-z$
N(6)C(25)C(26)C(27)C(28)C(36)	N(5)C(31)C(32)C(33)C(34)C(35)	3.718	3.709	$1-x,\ 2-y,\ 1-z$

rangement of the aromatic rings [23] with ring-centroid–ring-centroid distances in the range 3.69–3.82 Å. The details of these interactions are presented in Table 5.

4. Conclusions

The crystal structures of the five complexes [Ln(terpy)$_2$(NCS)$_3$] (Ln = Pr (**1**), Nd (**2**); terpy = 2,2′:6′,2″-terpyridine), [Nd(terpy)$_2$(NCS)$_3$]·2EtOH (**3**) and [Ln(phen)$_3$(NCS)$_3$]·EtOH (Ln = Pr (**4**), Nd (**5**); phen = 1,10-phenanthroline) confirm that 2:1 terpy:Ln and 3:1 phen:Ln complexes form with three co-ordinated thiocyanate ligands for Pr and Nd. The metals in the complexes are all nine co-ordinate and the Ln–N(thiocyanate) distances are shorter than the Ln–N(terpy/phen) distances. There is also a shortening of all the lanthanoid–ligand bonds in the neodymium complexes compared with the praseodymium, consistent with the expected ‘lanthanide contraction’ that occurs. In all the complexes the three thiocyanate ligands take up a meridonal configuration around the lanthanoid centre, with two pseudo-axial groups and an equatorial groups. While the NCS groups are all linear, the pseudo-axial ligands show a significant bending at the nitrogens while the equatorial thiocyanates are closer to linear at nitrogen. This effect is more marked in the terpy complexes than in the phen as, in the latter, the equatorial thiocyanates show a greater deviation from linearity at nitrogen. A search of the Cambridge Structural Database [24] shows that the bending of thiocyanate ligands in lanthanoid complexes is a common feature, whereas in transition metal thiocyanates they remain close to linear. This structural difference can be attributed to steric interactions around the metal centres. In the lanthanides the bonding is essentially ionic and non-directional, so that a bending of the ligand that will reduce steric crowding will not weaken the bonding significantly. In contrast, in transition metal thiocyanates there is a greater component of directional covalent bonding, and the linear co-ordination of the thiocyanates is retained in order to maximise the metal–ligand bonding interaction. The thiocyanates in all the complexes are involved in intermolecular C–H···S hydrogen bonding, the sulfur atoms acting as hydrogen bond acceptors from aromatic protons. The terpy and phen ligands in the complexes also show π–π stacking interactions to a greater or lesser extent.

5. Supplementary material

Crystallographic supplementary data are available from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) quoting the deposition numbers CCDC 193618–193622.

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