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Praseodymium complexes of 2,2′-bipyridine; the crystal and molecular structures of $Pr(bipy)_3(NCS)_3$, $Pr(bipy)_2(NO_3)_3$, $Pr(bipy)_2Cl_3(OH_2)\cdot EtOH$ and $Pr(bipy)(S_2CNEt_2)_3$

John F. Bower [a], Simon A. Cotton [a,*], John Fawcett [b], Robert S. Hughes [b], David R. Russell [b]

[a] *Uppingham School, Uppingham, Rutland, LE15 9QE, UK*
[b] *Chemistry Department, University of Leicester, Leicester, LE1 7RH, UK*

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Abstract

The structures of $Pr(bipy)_3(NCS)_3$, $Pr(bipy)_2(NO_3)_3$, $Pr(bipy)_2Cl_3(OH_2)\cdot EtOH$ and $Pr(bipy)(S_2CNEt_2)_3$ are reported. $Pr(bipy)_3(NCS)_3$ has a monomeric structure with three N-bonded thiocyanates and three bidentate bipyridyl ligands, giving nine-coordinate praseodymium. Praseodymium is eight-coordinate in $Pr(bipy)_2Cl_3(OH_2)\cdot EtOH$ and in $Pr(bipy)(S_2CNEt_2)_3$ whilst $Pr(bipy)_2(NO_3)_3$ is isostructural with the La, Nd and Lu analogues, having three bidentate nitrates and two bipyridyl ligands, affording 10-coordinate praseodymium. Factors affecting bond lengths in the compounds are discussed.

Keywords: Praseodymium complexes; Lanthanide; 2,2′-Bipyridine; Thiocyanate; Chloride; Nitrate; Dithiocarbamate; Crystal structures

1. Introduction

2,2′-Bipyridine (bipy) forms a range of complexes with lanthanide salts having typical stoichiometries $Ln(bipy)(OAc)_3$, $Ln(bipy)_2Cl_3(OH_2)$, $Ln(bipy)_2(NO_3)_3$, $Ln(bipy)_3(NCS)_3$ [1] and $Ln(bipy)(S_2CNEt_2)_3$ [2] (typically La = Y, La–Lu except Pm). Interest, however, has been almost wholly concentrated [3] upon the 10-coordinate nitrate complexes $Ln(bipy)_2(NO_3)_3$. Complexes with more than two molecules of bipy coordinated have not been confirmed structurally, since a compound analysing [4] as $Nd(bipy)_3(NO_3)_3$ has been shown to have the structure $Nd(bipy)_2(NO_3)_3\cdot bipy$, with the third bipyridyl molecule held in the lattice [5]. Since the report [1] of $Ln(bipy)_2Cl_3(OH_2)$ (Ln = La–Lu) and $Ln(bipy)_3(NCS)_3$ (Ln = La, Ce, Dy) in 1965, little attention has been paid to these compounds, though Hart and Laming synthesised [6] 1,10-phenanthroline analogues $Ln(phen)_2Cl_3(OH_2)$ and $Ln(phen)_3(NCS)_3$; subsequent to our experimental work, Khan and Iftikhar reported a number of thiocyanates of varying stoichiometry, $Ln(bipy)_x(NCS)_3(H_2O)_y$ (e.g. Ln = La, $x = 3$, $y = 1$; Ln = Pr, $x = 0$, $y = 0$; Ln = Nd, $x = 3$, $y = 1$; Ln = Sm, $x = 2$, $y = 1$; Ln = Er, $x = 2$, $y = 1$), though no structural data were presented [7]. Recently, the entire series $Ln(bipy)(S_2CNEt_2)_3$ (Ln = Y, La–Lu except Pm) has been synthesised [2] and the structure of $Er(bipy)(S_2CNEt_2)_3$ determined.

Most recent studies of complexes of this type have focussed on studying the effect of varying the lanthanide upon the structure and stoichiometry of compounds with the same ligands [8]. By way of contrast, here we report the structures of four bipyridyl complexes of the same metal, praseodymium.

2. Experimental

2.1. Synthesis

Although most of these compounds have been reported before, we report the synthetic methods used,

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* Corresponding author. Tel.: +44-1572-822-216; fax: +44-1572-821-872

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since small differences in solvent and other conditions can have a significant effect upon the stoichiometry of simple lanthanide complexes of this type.

The complexes were prepared by methods similar to those in the literature [1,2,4] as follows.

2.1.1. Pr(bipy)$_3$(NCS)$_3$ (**1**)

This was synthesised from an ethanolic solution of Pr(NCS)$_3$ prepared metathetically, by mixing warm solutions of $Pr(NO_3)_3 \cdot 6H_2O$ (0.35 g, 0.8 mmol) in EtOH (2.5 ml) and KNCS (0.235 g, 2.74 mmol) in EtOH (10 ml). After standing, white crystals of KNO_3 were removed by filtration, the solution warmed, and a warm solution of bipy (0.375 g, 2.4 mmol) in EtOH (10 ml) added. Green crystals formed on standing overnight.

2.1.2. Pr(bipy)$_2$(NO$_3$)$_3$ (**2**)

Hot solutions of $Pr(NO_3)_3 \cdot 6H_2O$ (0.218 g, 0.5 mmol) in EtOH (15 ml) and bipy (0.156 g, 1 mmol) in EtOH (10 ml) were mixed. Green crystals formed on standing overnight.

2.1.3. Pr(bipy)$_2$Cl$_3$(OH$_2$) (**3**)

Hot solutions of $PrCl_3 \cdot 6H_2O$ (0.47 g, 1.32 mmol) in EtOH (15 ml) and bipy (0.43 g, 2.75 mmol) in EtOH (15 ml) were mixed. An initial faint cloudiness was removed by filtration and the solution left to stand overnight, when small green crystals formed.

2.1.4. Pr(bipy)(S$_2$CNEt$_2$)$_3$ (**4**)

The reported synthesis [2] of this compound requires the use of $Pr(ClO_4)_3$, therefore two alternative routes were employed, the products being shown to be identical by X-ray diffraction:

a) $Pr(NO_3)_3 \cdot 6H_2O$ (0.08 g, 0.18 mmol), $(Et_2NH_2)S_2CNEt_2$ (0.12 g, 0.54 mmol) and bipy (0.03 g, 0.19 mmol) were dissolved together in hot MeCN (20 ml). Well formed emerald green crystals were deposited on cooling.

b) Solutions of $Pr(NO_3)_3 \cdot 6H_2O$ (0.08 g, 0.18 mmol) in cold MeCN (3 ml) and NaS_2CNEt_2 (0.10 g, 0.58 mmol) in cold MeCN (5 ml) were mixed and the immediate precipitate of $NaNO_3$ removed by filtration. A solution of bipy (0.03 g, 0.19 mmol) in MeCN (3 ml) was added; green crystals formed within 30 min and were filtered off.

2.2. Crystallography

Data for **1**, **2**, **3** and **4** were measured at 190 K on a Bruker P4 diffractometer using omega scans and graphite monochromated Mo Kα radiation ($\lambda = 0.7197$ Å). Three standard reflections monitored periodically showed no significant variations in intensity, the data were corrected for Lp effects and an absorption correction based on psi scan data was applied. The structures were solved and refined (on F^2) using the program SHELXTL/PC [9]. For compound **2**, the Pr atom and N2 and O5 of one of the nitrate groups lie on a twofold axis. All hydrogen atoms were included in calculated positions (C–H 0.96 Å) using a riding model with isotropic displacement parameters set to 1.2 U_{eq}(C), the water H atoms in **3** were not located. All nonhydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data and refinement parameters are listed in Table 1; selected geometric parameters are given in Table 2.

3. Results and discussion

3.1. The structure of Pr(bipy)$_3$(NCS)$_3$

Crystals of **1** contain isolated nine-coordinate Pr(*N*,*N′*-bipy)$_3$(NCS)$_3$ molecules (Fig. 1). The geometry adopted evidently minimises interactions between the bipy molecules. If each bipy molecule is considered to occupy one co-ordination site, then the geometry could be thought of as *mer*-octahedral, though the greater bulk of the bipy ligand means that the SCN–Pr–NCS bond angles are less than 90°, 77.4° (N3–Pr–N1) and 79.8° (N2–Pr–N1). The average Pr–N(bipy) distance of 2.702 Å in **1** compares closely with a distance of 2.693 Å in the structure of $[Pr(bipy)(O_2CCMe_3)_3]_2$ which also has nine-coordinate praseodymium [10] but is rather longer than that in $Pr(bipy)_2(NO_3)_3$ (**2**), $Pr(bipy)_2Cl_3(OH_2)$ (**3**) and $Pr(bipy)(S_2CNEt_2)_3$ (**4**) (vide infra). The range of values (2.632–2.743, S.D. 0.038 Å) spans a larger range than expected and there is an interesting inverse correlation between the Pr–N distances and the twist angle about the bond connecting the two pyridyl rings in the bipy ligand. A survey of 373 bipy metal complexes in the Cambridge Crystallographic Data Base [11] reveals that this dihedral twist angle in 418 bipy moieties has a range of 0°–18.4°, mean 0.69°, S.D. 4.6°. In compound **1**, the dihedral angle about C5–C6 for planes containing atoms N1, C1–C5 and N2, C6–C10 is 9.5(2)°, for the corresponding bipy containing N1A. For N2A it is 21.8(3)° and for N1B, N2B, 26.9(4)°. The corresponding average Pr–N distances for the three bipy moieties are 2.728(6), 2.720(6), 2.658(6) Å, respectively, a trend which suggests that due to steric crowding, a shorter (stronger) Pr–N bond is being achieved at the expense of a twist away from the favoured coplanarity of the two pyridyl rings. The average Pr–N(NCS) distance of 2.508 Å can be compared with values for Pr–N obtained for anionic thiocyanate complexes studied by Japanese workers [12]; thus in $(Me_4N)_5[Pr((NCS)_8] \cdot 2C_6H_6$ Pr–N distances fall in the range 2.50(1)–2.57 (1) Å. In the nine-coordinate $[Pr((NCS)_3(OH_2)_6]$, the Pr–N distances [13] are

Table 1
Crystallographic information for **1**, **2**, **3**, **4**

	1	**2**	**3**	**4**
Empirical formula	$C_{33}H_{24}N_9PrS_3$	$C_{20}H_{16}N_7O_9Pr$	$C_{22}H_{24}Cl_3N_4O_2Pr$	$C_{25}H_{38}N_5PrS_6$
Formula weight	783.7	639.3	623.71	741.87
Crystal system	triclinic	orthorhombic	triclinic	monoclinic
Space group	$P\text{-}\bar{1}$	*Pbcn*	$P\text{-}\bar{1}$	$P2_1/c$
Unit cell dimensions				
a (Å)	11.101(1)	16.973(2)	10.463(1)	17.505(1)
b (Å)	11.387(2)	9.097(4)	10.987(2)	10.569(1)
c (Å)	13.524(1)	15.001(7)	11.317(2)	17.639(1)
α (°)	88.25(2)	90	77.68(2)	90
β (°)	88.01(1)	90	89.53(2)	95.97(2)
γ (°)	80.24(1)	90	75.60(1)	90
V (Å^3)	1683.2(3)	2316.2(15)	1229.6(3)	3245.7(4)
Z	2	4	2	4
D_{calc} (Mg m^{-3})	1.546	1.833	1.685	1.518
μ (mm^{-1})	1.671	2.171	2.333	1.910
Crystal size (mm)	0.26 × 0.23 × 0.17	0.42 × 0.22 × 0.20	0.33 × 0.32 × 0.28	0.58 × 0.55 × 0.27
θ_{max} (°)	27.0	27.0	25.0	30.0
Reflections collected	7377	2873	4383	9472
Reflections unique	6540 [$R_{int} = 0.0363$]	2514 [$R_{int} = 0.0253$]	4138 [$R_{int} = 0.0453$]	8302 [$R_{int} = 0.0164$]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0508$, $wR_2 = 0.1127$	$R_1 = 0.0465$, $wR_2 = 0.1152$	$R_1 = 0.0484$, $wR_2 = 0.1318$	$R_1 = 0.0288$, $wR_2 = 0.0564$
R indices (all data)	$R_1 = 0.0706$, $wR_2 = 0.1405$	$R_1 = 0.0634$, $wR_2 = 0.1356$	$R_1 = 0.0632$, $wR_2 = 0.1595$	$R_1 = 0.0421$, $wR_2 = 0.0613$
Goodness-of-fit on F^2	1.172	1.141	1.070	1.043
ρ max./min. (e Å^{-3})	2.5, −4.5	2.37, −2.55	1.45, −1.77	0.54, −0.74

2.543(39), 2.600(39) and 2.803(38) Å. The N–Pr–N 'bite' angles are 59.1(2)°, 60.4(2)° and 61.8(2)°, averaging 60.4°, similar to the value of 60.0° in [Pr(bipy)$(O_2CCMe_3)_3$]$_2$ which also has nine-coordinate praseodymium with similar Pr–N bond lengths [10].

3.2. The structure of Pr(bipy)$_2$(NO$_3$)$_3$ (2)

Compound **2** is isomorphous and isostructural with the La, Nd and Lu analogues, containing isolated Pr(N,N'-bipy)$_2$(O,O'-NO$_3$)$_3$ molecules (Fig. 2) in which praseodymium has a co-ordination number of 10. The average Pr–N bond length of 2.625 Å and Pr–O distance of 2.570 Å can be compared with the respective values of 2.596 and 2.549 Å in the neodymium analogue; a difference of just under 0.02 Å would be predicted from ionic radius considerations [14]. Comparisons of the Pr–O bond length can be drawn with other 10-coordinate praseodymium nitrate complexes; in [Pr(H$_2$O)$_4$(NO$_3$)$_3$]·2H$_2$O, the average Pr–O(nitrate) distance is 2.617 Å (and the average Pr–OH$_2$ distance 2.467 Å) [15] whilst in [Pr(phenyl-12-crown-4)(NO$_3$)$_3$], the average Pr–O(nitrate) distance is 2.519 Å [16]. The Pr–N(bipy) bond length is 0.08 Å shorter than that in the nine-coordinate thiocyanate complex and 0.03 Å shorter than in the eight-coordinate chloride. The O–Pr–O bite angle of 49.53(12)° falls between the values of 48.0(3)° and 50.5(3)° in the La and Lu analogues, respectively [3], the angle increasing with decreasing ionic radius of the lanthanide ion (as expected); similarly, the N–Pr–N bite angle of 62.0(1)° falls between the respective values of 60.1(3)° and 66.5(4)° for the lanthanum and lutetium compounds. The co-ordination polyhedron in these compounds has been variously described as a bicapped dodecahedron or as another 10-vertex polyhedron, a sphenocorona [3].

3.3. The structure of Pr(bipy)$_2$Cl$_3$(OH$_2$)·EtOH

Crystals of **3** contain neutral Pr(bipy)$_2$Cl$_3$(OH$_2$) molecules with a molecule of uncoordinated EtOH in the lattice (Fig. 3). Presumably a Pr(bipy)$_2$Cl$_3$ species is not coordinatively saturated and a water molecule coordinates in preference to EtOH at least in part on grounds of the higher hydration energy. Average bond lengths are Pr–Cl 2.805, Pr–N 2.653 and Pr–O 2.486 Å; the N–Pr–N 'bite' angles are 60.7(2)° and 61.8(2)°, averaging 61.25 Å. This compound is isostructural with [Ln(bipy)$_2$Cl$_3$(OH$_2$)]·EtOH (Ln = Nd, Eu) characterised by Semenova and White [17]. Under the crystallisation conditions that they employed, Semenova and White also obtained a praseodymium complex [Pr(bipy)$_2$-Cl$_3$(OH$_2$)]·0.5EtOH in which the Pr–Cl, Pr–N and Pr–O distances are 2.79, 2.656 and 2.501 Å, respectively, very similar to the corresponding distances in our Pr(bipy)$_2$Cl$_3$(OH$_2$)·EtOH. The structure of a related eight-coordinate complex, La(phen)$_2$Cl$_3$(OH$_2$), has been determined [18] in which average bond lengths are La–Cl 2.820, La–N 2.734 and La–OH$_2$ 2.520 Å. Subtracting the ionic radius difference [14] between eight-

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

	1		**2**		**3**		**4**
Bond lengths							
Pr–N1	2.714(6)	Pr–N1	2.623(5)	Pr–N1	2.659(6)	Pr–N1	2.655(2)
Pr–N2	2.743(6)	Pr–N2	2.626(4)	Pr–N2	2.687(7)	Pr–N2	2.664(2)
Pr–N1A	2.741(6)			Pr–N1A	2.617(7)		
Pr–N2A	2.699(6)			Pr–N2A	2.648(7)		
Pr–N1B	2.685(6)						
Pr–N2B	2.632(6)						
Pr–N11	2.527(6)	Pr–O1	2.543(5)	Pr–Cl1	2.852(2)	Pr–S1	2.884(1)
Pr–N12	2.492(7)	Pr–O3	2.556(4)	Pr–Cl2	2.766(2)	Pr–S2	2.903(1)
Pr–N13	2.506(7)	Pr–O4	2.602(4)	Pr–Cl3	2.797(2)	Pr–S3	2.897(1)
				Pr–O1	2.486(6)	Pr–S4	2.951(1)
						Pr–S5	2.940(1)
						Pr–S6	2.858(1)
Bond angles							
N12–Pr–N13	152.3(2)	O1#1–Pr–O1	50.2(3)	O1–Pr–N1A	151.6(2)	N1–Pr–N2	61.3(1)
N12–Pr–N11	79.8(2)	O1#1–Pr–O3	71.8(2)	O1–Pr–N2A	146.6(2)	N1–Pr–S6	88.0(1)
N13–Pr–N11	77.4(2)	O1–Pr–O3	70.5(2)	N1A–Pr–N2A	61.8(2)	N2–Pr–S6	72.3(1)
N12–Pr–N2B	124.0(2)	O1–Pr–O3#1	71.8(2)	O1–Pr–N1	73.7(2)	N1–Pr–S1	80.0(1)
N13–Pr–N2B	77.4(2)	O3–Pr–O3#1	138.2(2)	N1A–Pr–N1	129.8(2)	N2–Pr–S1	129.2(1)
N11–Pr–N2B	154.8(2)	O1#1–Pr–O4	66.6(2)	N2A–Pr–N1	78.3(2)	S6–Pr–S1	141.6(1)
N12–Pr–N1B	78.4(2)	O1–Pr–O4	102.7(2)	O1–Pr–N2	110.9(2)	N1–Pr–S3	154.5(1)
N13–Pr–N1B	129.3(2)	O3–Pr–O4	49.5(1)	N1A–Pr–N2	76.6(2)	N2–Pr–S3	141.0(1)
N11–Pr–N1B	139.2(2)	O3#1–Pr–O4	125.4(1)	N2A–Pr–N2	69.1(2)	S6–Pr–S3	89.4(1)
N2B–Pr–N1B	61.8(2)	O1–Pr–O4#1	66.6(2)	N1–Pr–N2	60.7(2)	S1–Pr–S3	86.4(1)
N12–Pr–N2A	86.7(2)	O3–Pr–O4#1	125.4(1)	O1–Pr–Cl2	73.2(2)	N1–Pr–S2	85.4(1)
N13–Pr–N2A	71.9(2)	O4–Pr–O4#1	168.8(2)	N1A–Pr–Cl2	82.9(2)	N2–Pr–S2	82.3(1)
N11–Pr–N2A	73.3(2)	O1–Pr–N1#1	137.5(1)	N2A–Pr–Cl2	134.2(2)	S6–Pr–S2	153.8(1)
N2B–Pr–N2A	97.8(2)	O3–Pr–N1#1	74.1(1)	N1–Pr–Cl2	108.2(2)	S1–Pr–S2	61.8(1)
N1B–Pr–N2A	138.6(2)	O4–Pr–N1#1	69.4(1)	N2–Pr–Cl2	75.2(2)	S3–Pr–S2	107.0(1)
N12–Pr–N1	75.3(2)	O1#1–Pr–N1	137.5(1)	O1–Pr–Cl3	84.9(2)	N1–Pr–S5	79.7(1)
N13–Pr–N1	110.1(2)	O1–Pr–N1	135.3(2)	N1A–Pr–Cl3	77.0(2)	N2–Pr–S5	119.7(1)
N11–Pr–N1	68.7(2)	O3–Pr–N1	147.6(2)	N2A–Pr–Cl3	113.3(2)	S6–Pr–S5	61.7(1)
N2B–Pr–N1	121.8(2)	O3#1–Pr–N1	74.1(2)	N1–Pr–Cl3	151.0(2)	S1–Pr–S5	80.2(1)
N1B–Pr–N1	72.6(2)	O4–Pr–N1	120.5(1)	N2–Pr–Cl3	147.7(2)	S3–Pr–S5	76.8(1)
N2A–Pr–N1	140.1(2)	O4#1–Pr–N1	69.4(1)	Cl2–Pr–Cl3	83.3(2)	S2–Pr–S5	141.1(1)
N12–Pr–N1A	67.7(2)	N1#1–Pr–N1	73.8(2)	O1–Pr–Cl1	81.9(2)	N1–Pr–S4	144.5(1)
N13–Pr–N1A	113.3(2)	O1–Pr–N2#1	84.5(2)	N1A–Pr–Cl1	115.1(2)	N2–Pr–S4	84.1(1)
N11–Pr–N1A	123.5(2)	O3–Pr–N2#1	71.0(1)	N2A–Pr–Cl1	75.1(2)	S6–Pr–S4	89.0(1)
N2B–Pr–N1A	66.9(2)	O4–Pr–N2#1	110.7(1)	N1–Pr–Cl1	79.0(2)	S1–Pr–S4	121.2(1)
N1B–Pr–N1A	78.2(2)	N1–Pr–N2#1	90.0(2)	N2–Pr–Cl1	130.0(2)	S3–Pr–S4	60.8(1)
N2A–Pr–N1A	60.4(2)	O1#1–Pr–N2	84.5(2)	Cl2–Pr–Cl1	150.4(2)	S2–Pr–S4	81.9(1)
N1–Pr–N1A	136.5(2)	O1–Pr–N2	128.8(2)	Cl3–Pr–Cl1	78.7(2)	S5–Pr–S4	128.7(1)
N12–Pr–N2	129.4(2)	O3–Pr–N2	122.3(1)				
N13–Pr–N2	70.9(2)	O3#1–Pr–N2	71.0(1)				
N11–Pr–N2	101.1(2)	O4–Pr–N2	72.8(1)				
N2B–Pr–N2	71.4(2)	O4#1–Pr–N2	110.7(1)				
N1B–Pr–N2	68.5(2)	N1#1–Pr–N2	90.0(2)				
N2A–Pr–N2	142.7(2)	N1–Pr–N2	62.0(1)				
N1–Pr–N2	59.1(2)	N2#1–Pr–N2	145.9(2)				
N1A–Pr–N2	135.3(2)						

#1 = $1-x$, y, $3/2-z$.

coordinate La (1.160 Å) and eight-coordinate Pr (1.126 Å), these would correspond to Pr–Cl, Pr–N and Pr–O distances of 2.786, 2.700 and 2.486 Å, respectively corresponding well to the values actually obtained. In the $[Pr(terpy)Cl(OH_2)_5]^{2+}$ ion [19], where the co-ordination number of praseodymium is 9, Pr–Cl is 2.876(2) Å, Pr–N averages 2.628(4) Å and Pr–O averages 2.513(3) Å. Other average Pr–Cl distances are 2.789(1) Å in seven-coordinate [20] $[PrCl_3(thf)_2]_n$ and 2.723(3) Å in six-coordinate [21] $PrCl_3(hmpa)_3$; the average Pr–O distance [22] in the nine-coordinate $[Pr(OH_2)_9]^{3+}$ ion is 2.507(3) Å (six at 2.470(2) and three at 2.583(3).

In the hydrated chloride $[Pr(OH_2)_6Cl_2]\cdot Cl$, where praseodymium is eight-coordinate [23], Pr–O averages

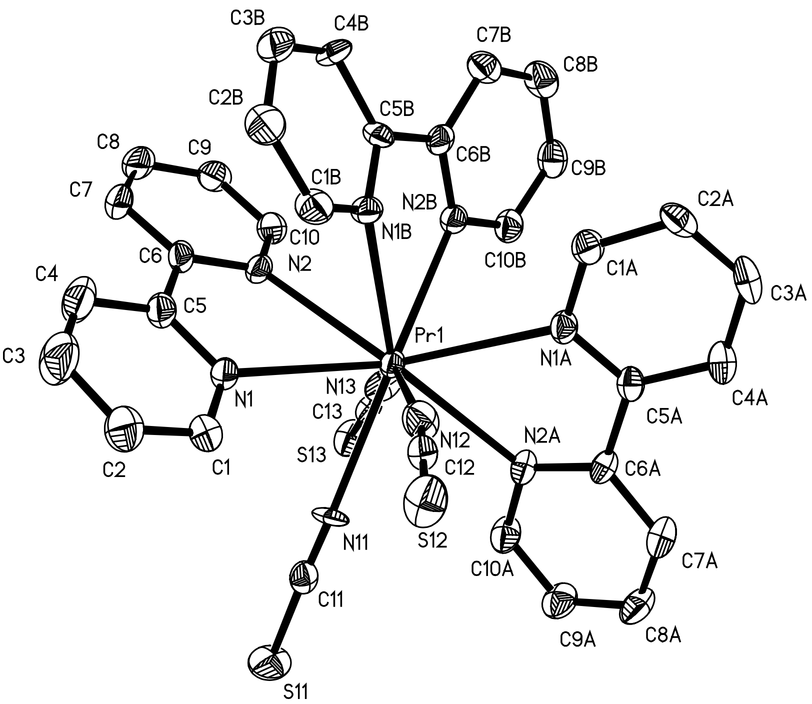

Fig. 1. Molecular structure of Pr(bipy)$_3$(NCS)$_3$ (**1**). Displacement ellipsoids are shown at the 30% probability level.

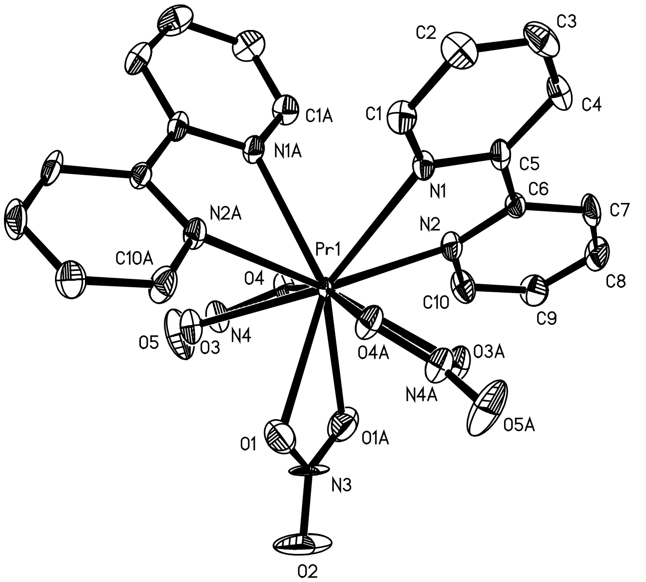

Fig. 2. Molecular structure of Pr(bipy)$_2$(NO$_3$)$_3$ (**2**). Displacement ellipsoids are shown at the 30% probability level.

2.472(6) and Pr–Cl 2.834(2) Å whilst in [(H$_2$O)$_7$Pr(μ-Cl)$_2$Pr(OH$_2$)$_7$]Cl$_4$, where praseodymium is nine-coordinate [24], Pr–O averages 2.511(4) and Pr–Cl 2.906(1) Å.

3.4. The structure of [Pr(bipy)(S$_2$CNEt$_2$)$_3$]

Crystals of **4** contain neutral molecules (Fig. 4) with eight-coordinate praseodymium. The co-ordination geometry approximates to a distorted dodecahedron, similar to that found [2] in the isostructural Er(bipy)(S$_2$CNEt$_2$)$_3$. The average Er–S and Er–N bond distances in the latter are 2.801 and 2.532 Å, respectively. If an allowance for the ionic radius difference of 0.122 Å between eight-coordinate Er^{3+} and Pr^{3+} is made, values of Pr–S and Pr–N of 2.923 and 2.654 Å are predicted which compares with the observed average values of Pr–S 2.905 and Pr–N 2.659 Å. The N–Pr–N bite angle is 61.28(2)°, compared with 64.4° in the Er analogue; the S–Pr–S and S–Er–S bite angle are 61.39(2)° and 63.16°, respectively, the bite angles thus decreasing with increasing ionic radius, as expected. There is evidence of weak intermolecular contacts between H22A and S6B and between H22B and S6A.

4. Conclusions

In transition metal complexes, where the co-ordination number for a particular combination of metal ion and oxidation state is often constrained to a particular value, the bond length can reflect the strength of the metal–ligand interaction. In lanthanide complexes, where the bonding is regarded as being substantially ionic, the co-ordination number is determined by packing considerations, this in turn determining the bond lengths between the central metal ion and the atoms surrounding it.

Fig. 5 shows the expected trend of increasing Pr–Cl distance with increasing co-ordination number for a

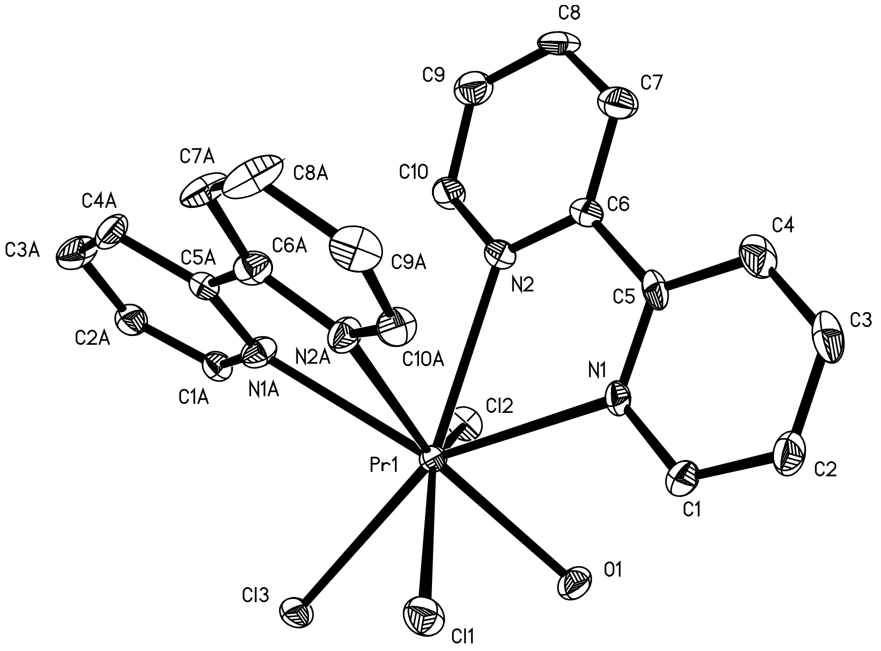

Fig. 3. Molecular structure of $Pr(bipy)_2Cl_3(OH_2)\cdot EtOH$ (**3**). Displacement ellipsoids are shown at the 30% probability level.

number of praseodymium complexes with chlorine as a ligand. The expectation that Pr–N bond length will similarly increase with increasing co-ordination number of the praseodymium ion is fulfilled in a comparison of eight-coordinate $[Pr(bipy)_2Cl_3(OH_2)]\cdot EtOH$ (**3**) (2.653 Å) and $[Pr(bipy)(S_2CNEt_2)_3]$ (**4**) (2.659 Å) and the nine-coordinate $[Pr(bipy)_3(NCS)_3]$ (**1**) (2.702 Å) and $[Pr(bipy)(O_2CCMe_3)_3]_2$ (2.693 Å).

The Pr–N distance in 10-coordinate $[Pr(bipy)_2(NO_3)_3]$ (**2**) (2.625 Å) is in fact shorter than any of these and may be due to efficient packing of the bidentate ligands on account of the small bite angle of nitrates, partly a consequence of the small radius of oxygen. The short Pr–N bond could, conceivably, arise at the expense of a long Pr–O bond (the bipy 'squeezing out' the nitrate). This, however, seems unlikely in view of the oxophilic tendencies of the lanthanide ions and also because of the unwillingness of Ln^{3+} ions to form complexes with bipy and other N-donors [25]. In fact the average Pr–O bond length in $[Pr(bipy)_2(NO_3)_3]$ (**2**) is, as noted above, shorter than that in $[Pr(H_2O)_4(NO_3)_3]$, also 10-coordinate.

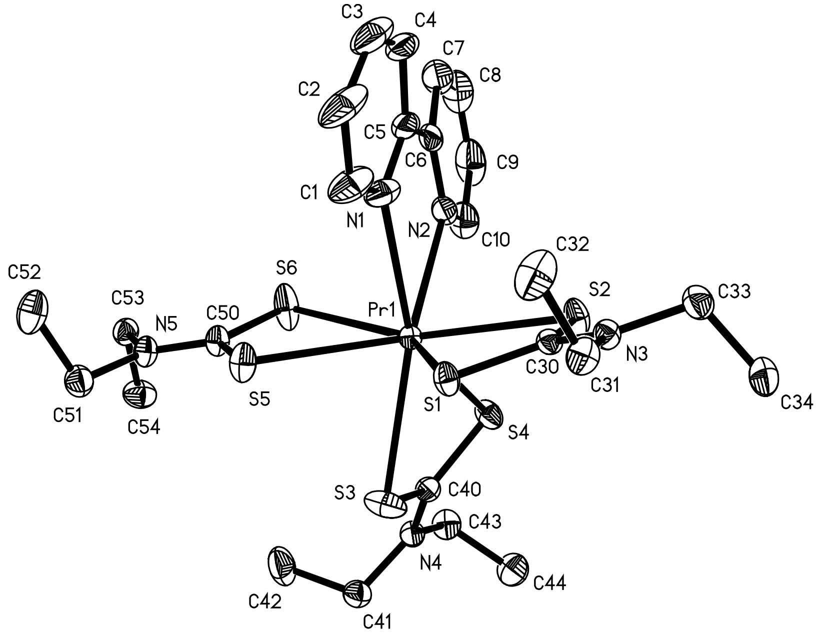

Fig. 4. Molecular structure of $Pr(bipy)(S_2CNEt_2)_3$ (**4**). Displacement ellipsoids are shown at the 30% probability level.

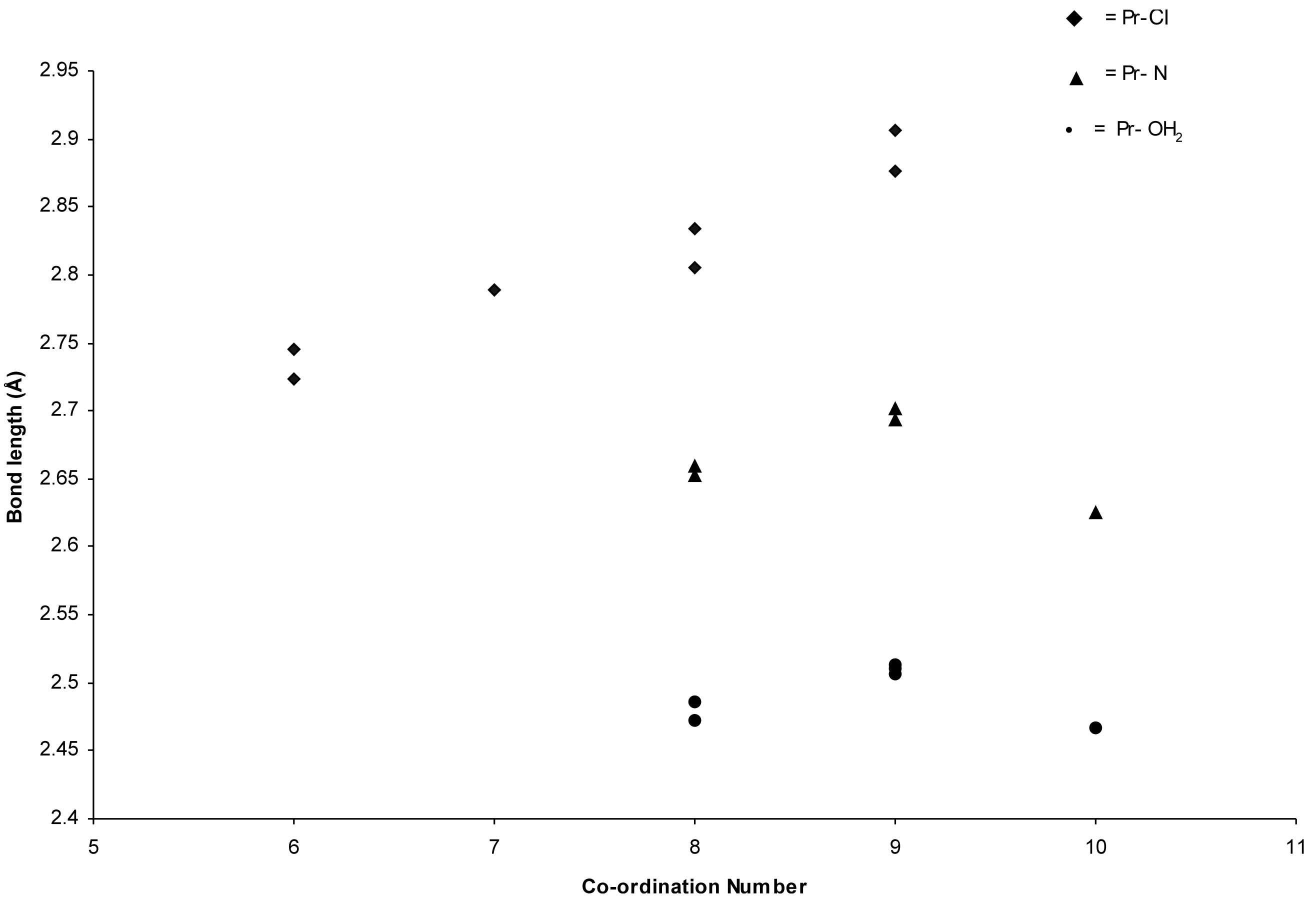

Fig. 5. Relationship between bond length and co-ordination number for a number of praseodymium complexes.

Turning now to the Pr–O(OH$_2$) distances, a similar trend emerges. In the eight-coordinate [Pr(OH$_2$)$_6$Cl$_2$]·Cl, where praseodymium is 8-coordinate [23], Pr–O averages 2.472(6) Å. In nine-coordinate [Pr(terpy)-Cl(OH$_2$)$_5$]$^{2+}$ ion [19], Pr–O averages 2.513(3) Å; similarly in the nine-coordinate [Pr(OH$_2$)$_9$]$^{3+}$ ion, the average Pr–O distance [22] is 2.507(2) Å and in [(H$_2$O)$_7$Pr(μ-Cl)$_2$Pr(OH$_2$)$_7$]Cl$_4$, where praseodymium is nine-coordinate [24], Pr–O averages 2.511(4) Å. However, the Pr–OH$_2$ bond length (2.467 Å) in [Pr(H$_2$O)$_4$(NO$_3$)$_3$] is, similarly, the exception to the pattern of increasing Pr–O bond length with increasing co-ordination number, so that, once again, it is the nitrate complex that has the shortest praseodymium–ligand bond length despite having the highest co-ordination number. A similar effect can be seen in other nitrate complexes, compare the average Sc–OH$_2$ distance at 2.271 Å in the nine-coordinate [Sc(H$_2$O)$_9$]$^{3+}$ ions in the hydrated triflate [26] Sc(O$_3$CSF$_3$)$_3$·9H$_2$O with the Sc–OH$_2$ distances in the nine-coordinate [Sc(NO$_3$)$_3$(H$_2$O)$_3$] complex with 18-crown-6, where Sc–O distances are 2.120(6), 2.221(6) and 2.303(15) Å, averaging 2.215 Å [27].

Recent ab initio quantum mechanical calculations [28] on Ln(NO$_3$)$_n$ and Ln(NO$_3$)$_n$(H$_2$O)$_m$ ($n = 1$–3, $m = 4$–6) species indicate that the adoption of either mono- and bidentate binding of nitrate groups is a delicately balanced, possibly being affected by the phase and by the other ligands bound, and complexes of terpyridyl with lanthanide nitrates clearly demonstrate the balance [29,30]. The ability of a bidentate nitrate group to approach closely to a lanthanide ion and facilitate close attachment of other ligands has implications in the role of lanthanide nitrates in the separation of lanthanides from actinides in spent fuel rods from nuclear reactors [30].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 167515–167518 for compounds **1**, **2**, **3** and **4**. Copies of this information may be obtained free of charge 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).

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