Crystal and Molecular Structure of Tetraphenylphosphonium Tetrakis(dimethyldithiophosphinato)praseodymium(III)

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The title compound crystallises from ethanol in space group $Pca2_1$, with cell dimensions a = 19.857(15), b = 11.422(5), c = 19.077(12) Å, and Z = 4. The structure was solved by conventional Patterson and Fourier techniques, and refined to R 0.073. The praseodymium is co-ordinated to eight sulphur atoms which have a distorted tetragonal antiprismatic arrangement. Pr–S bond lengths range from 2.888(7) to 3.056(7) (mean 2.976 Å). The praseodymium atoms alone form an almost perfect hexagonal lattice.

FEW compounds of the lanthanoids with sulphur donor ligands have been reported. A few dithiocarbamate complexes have been characterised[1-5] but the only structural information was given by Brown *et al.*[3] who reported that the series of tetraethylammonium tetrakisdiethyldithiocarbamatolanthanoid(III) compounds which they had isolated was isostructural with the neptunium(III) analogue. This compound has an unusually asymmetric co-ordination polyhedron. Our recent preparation of the first dithiophosphinate complexes of the lanthanoids[6,7] has prompted a full structural investigation of a typical example, which we now report.

TABLE 1

Atom parameters, with standard deviations in parentheses

Atom	10^4x	10^4y	10^4z	10^4U_{11}	10^4U_{22}	10^4U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Pr	1 913(1)	2 535(1)	2 500(0)	354(6)	402(6)	331(5)	−4(1)	−6(1)	1(1)
P(1)	2 480(4)	4 848(7)	1 439(4)	430(47)	581(47)	343(35)	2(5)	1(4)	8(4)
P(2)	256(3)	3 387(7)	2 082(4)	341(47)	434(46)	514(42)	5(4)	−5(4)	−5(4)
P(3)	1 953(4)	1 838(6)	4 335(3)	506(51)	570(45)	329(36)	−12(5)	6(4)	−1(4)
P(4)	3 015(4)	100(7)	2 263(3)	606(55)	480(44)	314(37)	11(5)	−3(4)	2(3)
P(5)	5 269(3)	2 477(7)	3 855(3)	452(42)	365(34)	360(32)	9(5)	−4(3)	−14(5)
S(1)	2 782(4)	4 699(6)	2 467(5)	781(56)	546(43)	470(42)	−25(4)	−20(6)	14(5)
S(2)	2 031(4)	3 438(7)	1 091(4)	556(58)	432(51)	312(39)	−6(5)	18(4)	8(4)
S(3)	880(3)	4 365(5)	2 650(4)	470(43)	509(40)	457(51)	1(3)	5(4)	−17(4)
S(4)	575(4)	1 729(6)	1 982(4)	428(49)	464(47)	776(55)	−1(4)	−22(4)	−7(4)
S(5)	1 476(4)	854(6)	3 608(3)	546(53)	639(50)	471(45)	−24(5)	−9(4)	11(4)
S(6)	2 152(4)	3 459(8)	3 983(4)	776(68)	540(60)	355(44)	−15(5)	−8(5)	3(5)
S(7)	3 252(3)	1 565(6)	2 787(3)	334(47)	627(47)	668(51)	−1(4)	−6(4)	−8(4)
S(8)	2 179(4)	312(6)	1 699(4)	474(50)	519(48)	514(43)	1(4)	−7(4)	1(4)

	10^4x	10^4y	10^4z	10^4U		10^4x	10^4y	10^4z	10^4U
C(1)	1 922(15)	6 181(23)	1 332(16)	650(65)	C(17)	5 694	1 644	1 845	484(64)
C(2)	3 206(11)	5 255(26)	850(14)	506(63)	C(18)	5 203	2 213	1 449	293(67)
C(3)	−583(10)	3 404(21)	2 511(17)	642(60)	C(19)	4 907	2 876	1 782	436(66)
C(4)	94(12)	4 053(28)	1 219(13)	731(85)	C(20)	4 703	2 971	2 511	525(57)
C(5)	1 415(14)	1 926(26)	5 128(15)	657(76)	C(21)	6 137	2 519	4 124	342(55)
C(6)	2 707(12)	1 097(21)	4 669(12)	401(67)	C(22)	6 610	3 190	3 761	443(66)
C(7)	2 927(13)	−1 128(23)	2 867(15)	634(72)	C(23)	7 278	3 216	3 986	540(65)
C(8)	3 721(13)	−343(20)	1 697(14)	618(76)	C(24)	7 474	2 574	4 574	555(58)
C(9)	4 836	1 260	4 216	280(77)	C(25)	7 001	1 905	4 937	578(64)
C(10)	4 590	1 303	4 900	445(62)	C(26)	6 333	1 877	4 712	466(67)
C(11)	4 307	305	5 203	609(66)	C(27)	4 864	3 801	4 131	530(76)
C(12)	4 270	−734	4 822	585(66)	C(28)	4 163	3 806	4 181	418(66)
C(13)	4 516	−777	4 137	527(66)	C(29)	3 827	4 814	4 403	621(63)
C(14)	4 799	220	3 835	513(63)	C(30)	4 194	5 816	4 574	537(68)
C(15)	5 194	2 400	2 906	450(57)	C(31)	4 894	5 811	4 524	448(66)
C(16)	5 689	1 737	2 573	387(59)	C(32)	5 229	4 803	4 302	335(65)

Group *	10^4x	10^4y	10^4z	θ	ϕ	ψ
(1)	4 553(4)	263(9)	4 519(5)	80.2(6)	24.9(6)	111.7(6)
(2)	5 198(4)	2 307(7)	2 178(5)	89.6(4)	94.4(6)	90.6(3)
(3)	6 805(5)	2 547(9)	4 349(5)	91.9(5)	162.1(5)	178.0(6)
(4)	4 529(5)	4 809(9)	4 352(5)	90.6(5)	162.3(5)	59.8(5)

* The four groups are: (1) C(9)—(14), (2) C(15)—(20), (3) C(21)—(26), and (4) C(27)—(32).

EXPERIMENTAL

Preparation.†—$PrCl_3·6H_2O$ (0.50 g, 1.41 mmol) and $Na[S_2PMe_2]$ (0.75 g, 5.06 mmol) were heated under reflux in ethanol for 15 min. Ph_4PBr (0.65 g, 1.55 mmol) was added and after 15 min further heating, solvent was removed *in vacuo* and the residue extracted with hot ethanol. The

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† A large number of related anionic, neutral and cationic complexes have been prepared for all the lanthanoids (excluding Pm) and yttrium. Their syntheses and characterisation will be reported (ref. 7).

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product crystallised on cooling as soft, pale-green needles (0.74 g, 0.75 mmol, 59%) (Found: C, 38.70; H, 4.55; Pr, 14.30; S, 27.5. $C_{32}H_{44}P_5PrS_8$ requires C, 39.18; H, 4.52; Pr, 14.38; S, 26.15%).

Crystal Data.—$C_{32}H_{44}P_5PrS_8$, Orthorhombic, $M = 981.0$, $a = 19.857(15)$, $b = 11.422(5)$, $c = 19.077(12)$ Å, $D_m = 1.486$, $Z = 4$, $D_c = 1.511$, $F(000) = 1\,992$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 18.4 cm^{-1}; space group $Pca2_1$ or $Pcam$ by systematic absences, structure subsequently solved in the acentric space group.

TABLE 2

Bond lengths (Å) and angles (°), with standard deviations in parentheses

(*a*) Distances

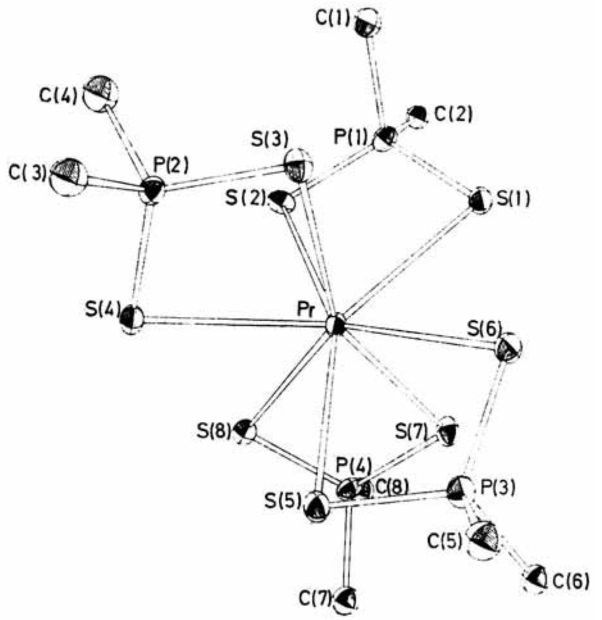
Pr–S(1)	3.015(7)	P(2)–S(3)	1.99(1)
Pr–S(2)	2.888(7)	P(2)–S(4)	2.01(1)
Pr–S(3)	2.942(7)	P(2)–C(3)	1.86(2)
Pr–S(4)	2.982(7)	P(2)–C(4)	1.84(3)
Pr–S(5)	2.985(7)	P(3)–S(5)	2.02(1)
Pr–S(6)	3.056(8)	P(3)–S(6)	2.01(1)
Pr–S(7)	2.932(7)	P(3)–C(5)	1.86(3)
Pr–S(8)	3.010(7)	P(3)–C(6)	1.83(3)
P(1)–S(1)	2.06(1)	P(4)–S(7)	2.01(1)
P(1)–S(2)	1.96(1)	P(4)–S(8)	1.99(1)
P(1)–C(1)	1.89(3)	P(4)–C(7)	1.82(3)
P(1)–C(2)	1.89(3)	P(4)–C(8)	1.84(3)

(*b*) Angles

S(1)–Pr–S(2)	69.0(2)	Pr–S(3)–P(2)	89.0(3)
S(1)–Pr–S(3)	79.6(2)	Pr–S(4)–P(2)	87.6(3)
S(1)–Pr–S(4)	139.2(2)	Pr–S(5)–P(3)	89.5(3)
S(1)–Pr–S(5)	135.1(2)	Pr–S(6)–P(3)	87.7(3)
S(1)–Pr–S(6)	69.3(2)	Pr–S(7)–P(4)	90.6(3)
S(1)–Pr–S(7)	78.2(2)	Pr–S(8)–P(4)	88.5(3)
S(1)–Pr–S(8)	125.5(2)	S(1)–P(1)–S(2)	112.9(4)
S(2)–Pr–S(3)	83.9(2)	S(1)–P(1)–C(1)	109.8(1.0)
S(2)–Pr–S(4)	82.7(2)	S(1)–P(1)–C(2)	111.4(9)
S(2)–Pr–S(5)	155.8(2)	S(2)–P(1)–C(1)	111.0(1.0)
S(2)–Pr–S(6)	136.5(2)	S(2)–P(1)–C(2)	110.4(1.0)
S(2)–Pr–S(7)	103.6(2)	C(1)–P(1)–C(2)	100.6(1.3)
S(2)–Pr–S(8)	79.3(2)	S(3)–P(2)–S(4)	112.7(4)
S(3)–Pr–S(4)	68.3(2)	S(3)–P(2)–C(3)	108.3(1.0)
S(3)–Pr–S(5)	100.7(2)	S(3)–P(2)–C(4)	111.4(1.0)
S(3)–Pr–S(6)	76.9(2)	S(4)–P(2)–C(3)	109.6(9)
S(3)–Pr–S(7)	151.9(2)	S(4)–P(2)–C(4)	111.1(1.0)
S(3)–Pr–S(8)	140.4(2)	C(3)–P(2)–C(4)	103.4(1.2)
S(4)–Pr–S(5)	77.1(2)	S(5)–P(3)–S(6)	112.0(4)
S(4)–Pr–S(6)	123.5(2)	S(5)–P(3)–C(5)	108.7(1.0)
S(4)–Pr–S(7)	138.9(2)	S(5)–P(3)–C(6)	111.4(9)
S(4)–Pr–S(8)	74.2(2)	S(6)–P(3)–C(5)	109.6(1.0)
S(5)–Pr–S(6)	67.1(2)	S(6)–P(3)–C(6)	112.4(9)
S(5)–Pr–S(7)	83.6(2)	C(5)–P(3)–C(6)	102.3(1.2)
S(5)–Pr–S(8)	82.4(2)	S(7)–P(4)–S(8)	111.3(5)
S(6)–Pr–S(7)	79.5(2)	S(7)–P(4)–C(7)	110.4(9)
S(6)–Pr–S(8)	137.2(2)	S(7)–P(4)–C(8)	110.1(9)
S(7)–Pr–S(8)	67.5(2)	S(8)–P(4)–C(7)	110.8(9)
Pr–S(1)–P(1)	85.4(3)	S(8)–P(4)–C(8)	110.5(9)
Pr–S(2)–P(1)	90.8(3)	C(7)–P(4)–C(8)	103.4(1.2)

The intensities of 3 938 unique reflections were measured with a Syntex $P2_1$ automated diffractometer by use of Mo-K_α radiation and ω scans. The dimensions of the crystal chosen were 0.30 × 0.08 × 0.08 mm. Scattering factors for the neutral atoms were taken from ref. 8. All computer programs used were taken from ref. 9. The stereoprojection was drawn by the program ORTEP.[10] No absorption correction was applied.

Solution of the Structure.—The praseodymium atom was found from a three-dimensional Patterson map. Owing to the pronounced hexagonal pseudosymmetry of the arrangement of the praseodymium atoms eight difference-Fourier syntheses were required to find all the phosphorus and sulphur atoms unequivocally. Two cycles of full-matrix least squares were used to refine the positional parameters of the fourteen medium and heavy atoms. Two more difference-Fourier syntheses were required to find the remaining non-hydrogen atoms. The phenyl groups were refined as ideal groups, assuming C–C 1.395 Å and C–C–C 120°. Final refinement by block-diagonal least squares was carried out in two parts: first non-carbon, then carbon atoms. The first cycles used individual isotropic temperature factors, and the final cycles individual anisotropic temperature factors for the non-carbon atoms. The last cycle gave the residual R 0.073. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2$, estimated standard deviations, σ, of the measured structure factors being derived from counting statistics and the variations in the standard reflections. Positional and thermal parameters for all non-hydrogen atoms are reported in Table 1. Bond lengths and angles for the complex anion are reported in Table 2. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21777 (7 pp., 1 microfiche).*



DISCUSSION AND DESCRIPTION OF THE STRUCTURE

A stereoprojection of the complex anion is shown in the Figure. The praseodymium is surrounded by eight sulphur atoms in a distorted tetragonal antiprismatic arrangement. The arrangement contrasts strongly with the unusual co-ordination polyhedron found for the [Np($S_2CNEt_2)_4$]$^-$ ion[3] (a plane pentagonal arrangement of sulphur atoms with one atom above and two below the plane). This may perhaps be due to an important covalent contribution to the bonding in the latter case, *vs.* a predominantly electrostatic model for the praseodymium compound. The two most common regular polyhedra for eight-co-ordination are the dodecahedron and the square

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

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antiprism. If the ligands are identical and bidentate there are a total of nine possible isomers.[11] By applying the condition that each ligand must span an identical polyhedral edge, the number of possible isomers is reduced to four. Blight and Kepert[12] have calculated the ligand–ligand repulsion energies for these as a function of b (defined in our case as the intraligand S–S distance divided by the Pr–S bond length) and report that the D_2 square antiprism is the form of lowest energy for $1.10 < b < 1.20$. The lowest energy for $b < 1.10$ was found for the D_{2d} dodecahedron, and for $b > 1.20$ for the D_2 dodecahedron or the S_4 square antiprism. We calculate a value of 1.12 for b in the present antiprismatic structure which thus agrees well with the predictions of the ligand–ligand repulsion model. The mean Pr–S distance (2.98 Å) is a little longer than that found for Np–S (2.86 Å) in the analogous diethyldithiocarbamatoneptunium complex. The increase in bond length may be explained by the increase in the ' bite ' of the ligand from 2.93 for the dithiocarbamate to 3.33 Å for the dithiophosphinate. The ' bite ' here is also greater than is the case for transition-metal complexes; *e.g.*, in $[V\{S_2P(OEt)_2\}_3]$ the S–S distance is 3.21 Å.[13] This may be discussed in terms of the much stronger bonding interaction, in the case of vanadium, diminishing the S–P–S angle (108.1 *vs.* 112.2°).

An interesting crystallographic feature is the arrangement of the praseodymium atoms alone. As was shown very clearly by precession photographs, the complex ions are arranged in a pseudohexagonal lattice with ideal symmetry $P6_3/mmc$. The ' hexagonal ' lattice parameters calculated from the pseudo-orthohexagonal cell are: $a = 11.422$, $b = 11.465$, $c = 19.077$ Å, and $\gamma = 119.91°$. The space group $Pca2_1$ in the given orientation is a subgroup of index 12 of $P6_3/mmc$. This additional symmetry of the arrangement of the heavy atoms was the cause of much confusion in the preliminary stages of structure solution, requiring many difference-Fourier syntheses before one single image could be chosen.

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