Crystal and Molecular Structures of the Tris(dicyclohexyldithiophosphinato)-complexes of Praseodymium and Samarium

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The compound $[Pr\{(C_6H_{11})_2PS_2\}_3]$ is triclinic, space group $P\bar{1}$, with cell dimensions: $a = 10.416(5)$, $b = 12.327(4)$, $c = 18.275(8)$ Å, $\alpha = 73.20(3)$, $\beta = 79.50(4)$, and $\gamma = 85.14(3)°$, $Z = 2$. The analogous samarium compound $[Sm\{(C_6H_{11})_2PS_2\}_3]$ is also triclinic, space group $P\bar{1}$ with cell dimensions: $a = 9.664(3)$, $b = 11.499(13)$, $c = 20.612(19)$ Å, $\alpha = 85.87(8)$, $\beta = 77.59(6)$, $\gamma = 84.61(7)°$, $Z = 2$.

The structures were determined from *X*-ray diffraction data collected with an automatic diffractometer and the model refined to *R* 0.052 (Pr, 3 617 reflections) and 0.079 (Sm, 2 467 reflections). Both Pr and Sm are co-ordinated to six sulphur atoms at mean distances of 2.84 and 2.79 Å. The co-ordination polyhedra are distorted trigonal prisms with different distortions. The Pr compound is isomorphous with the Nd analogue, and the Sm complex with those formed by Eu—Lu and Y.

We have recently reported the first examples of dithiophosphinate complexes of the tervalent lanthanoids.[1,2] Our initial work was confined to eight-co-ordinate anionic tetrakis(dithiophosphinate) complexes, $[Ln(S_2PR_2)_4]^-$ (Ln = La—Lu excluding Pm, and Y, R = Me or OEt) and their substitution reactions with triphenylphosphine oxide to form the neutral or cationic complexes $[LnL_3P_2]$ (Ln = La—Nd) and $[LnL_2P_3]^+$ (Ln = Sm—Lu and Y) where L = $S_2P(OEt)_2$ and P = Ph_3PO. The crystal structures of $[Ph_4P][Pr(S_2PMe_2)_4]$, $[La\{S_2P(OEt)_2\}_3(Ph_3PO)_2]$ and $[Sm\{S_2P(OEt)_2\}_2(Ph_3PO)_3][S_2P(OEt)_2]$ have been determined[3,4] and show that the co-ordination of sulphur (a 'soft' base) to the rare-earth ion (a 'hard' acid) is strong.

Although Brown *et al.*[5] were able to prepare neutral tris(diethyldithiocarbamate) complexes of the lanthanoids, our initial attempts to prepare the analogous dimethyl and diethoxy dithiophosphinate complexes were not successful. In the belief that steric effects should play an important role in determining the co-ordination number, we have treated the ammonium salt of dicyclohexyldithiophosphinic acid with hydrated lanthanoid(III) chlorides in ethanol solution, and thus isolated complexes of the desired stoicheiometry. The chemistry and spectral properties of these compounds will be reported later;[6] however, a preliminary *X*-ray examination by use of powder diffraction patterns showed that there were two series of isostructural compounds, Pr—Nd, and Sm—Lu and Y respectively.

As part of our continuing study of dithiophosphinate complexes of tervalent lanthanoid ions, we now report the *X*-ray crystal structure of tris(dicyclohexyldithiophosphinato)praseodymium(III) and of its samarium analogue.

EXPERIMENTAL

Preparation of $[Pr\{(C_6H_{11})_2PS_2\}_3]$.—$PrCl_3\cdot 6H_2O$ (0.50 g, 1.41 mmol) and $[NH_4][S_2P(C_6H_{11})_2]$ (1.18 g, 4.23 mmol) were dissolved in ethanol (*ca.* 50 ml) to give a clear green solution which was set aside at room temperature for 4 days. A number of suitable crystals which had then formed were washed with ethanol and dried *in vacuo* (Found: C, 46.83; H, 7.20; Pr, 15.15; S, 20.90. $C_{36}H_{66}P_3S_6Pr$ requires C, 46.74; H, 7.19; Pr, 15.23; S, 20.79%). Higher yields in microcrystalline form may be obtained from hot ethanolic solutions. The Nd analogue may be prepared similarly.†

Preparation of $[Sm\{(C_6H_{11})_2PS_2\}_3]$.—$SmCl_3\cdot 6H_2O$ was treated similarly but in a larger volume of hot ethanol (*ca.* 200 ml). Setting aside at room temperature rapidly produced a microcrystalline product, but after 7 days it was possible to isolate small crystals suitable for an *X*-ray study (Found: C, 46.0; H, 7.0; S, 20.75; Sm, 16.09. $C_{36}H_{66}P_3S_6Sm$ requires C, 46.27; H, 7.12; S, 20.59; Sm, 16.09%). The Eu–Lu and Y analogues may be prepared similarly.

Crystal Structure of $[Pr\{(C_6H_{11})_2PS_2\}_3]$.—A crystal with dimensions *ca.* 0.21 × 0.26 × 0.17 mm was measured on an automatic four-circle diffractometer (Syntex $P2_1$) using graphite monochromatized Mo-K_α radiation ($\lambda = 0.710\,7$ Å).

Crystal Data.—$C_{36}H_{66}P_3PrS_6$, $M = 925.14$, Triclinic, $a = 10.416(5)$, $b = 12.327(4)$, $c = 18.275(8)$ Å, $\alpha = 73.20(3)$, $\beta = 79.50(4)$, $\gamma = 85.14(3)°$, $U = 2\,207.4$ Å^3, $D_m = 1.39$ g cm^{-3} by flotation, $Z = 2$, $D_c = 1.39$ g cm^{-3}, $F(000) = 964$. Space group $P\bar{1}$ from successful refinement. Mo-K_α *X*-radiation $\lambda = 0.710\,69$ Å. $\mu(\text{Mo-}K_\alpha) = 15.0$ cm^{-1}. The intensities of 4 141 unique reflections were measured by the θ—2θ scan technique in half the reciprocal sphere ($+h \pm k \pm l$) with $2\theta \leqslant 40°$, 524 of which had $I < 3\sigma(I)$ estimated from counting statistics. A numerical absorption correction was applied to the measurements by use of a crystal form accurately measured by means of a special telescope mounted on the 2θ arm of the diffractometer.

Crystal Structure of $[Sm\{(C_6H_{11})_2PS_2\}_3]$.—The chosen crystal had dimensions *ca.* 0.14 × 0.11 × 0.09 mm and was measured similarly with the same equipment, by use of Mo *X*-radiation and balanced Nb filters.

Crystal Data.—$C_{36}H_{66}P_3S_6Sm$, $M = 934.58$, Triclinic, $a = 9.664(3)$, $b = 11.499(13)$, $c = 20.612(19)$ Å, $\alpha = 85.87(8)$, $\beta = 77.59(6)$, $\gamma = 84.61(7)°$, $U = 2\,240.0$ Å^3, $D_m = 1.41$ g cm^{-3} by flotation, $Z = 2$, $D_c = 1.40$ g cm^{-3}, $F(000) = 970$.

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† The same reaction with La or Ce, and under some conditions also Pr and Nd, yields the anionic tetrakis-complexes.

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[2] A. A. Pinkerton, C. Rieder, and Y. Meseri, to be published.

[3] A. A. Pinkerton and D. Schwarzenbach, *J.C.S. Dalton*, 1976, 2464.

[4] A. A. Pinkerton and D. Schwarzenbach, *J.C.S. Dalton*, 1976, 2466.

[5] D. Brown, D. G. Holah, and C. E. F. Rickard, *J. Chem. Soc.* (*A*), 1970, 786.

[6] Y. Meseri and A. A. Pinkerton, unpublished results.

Space group $P\bar{1}$ from successful refinement. μ(Mo-K_α) = 17.46 cm^{-1}.

The intensities of 4 797 unique reflections ($+h \pm k \pm l$, $2\theta \leqslant 40°$) of which 2 030 had $I < 3\sigma(I)$ were measured by the step-scan technique.[7] An absorption correction was applied as already described.

Structure Solution.—The computer programs used for data reduction and the structure analyses were taken from the '*X*-RAY '72' program system.[8] Scatterings factors for the neutral atoms were taken from ref. 9.

TABLE 1 (*a*)

Atomic co-ordinates * for [Pr{(C_6H_{11})$_2$PS_2}$_3$], with standard deviations in parentheses (excluding carbon atoms)

Atom	10^4x	10^4y	10^4z	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Pr	1 921(1)	923(1)	2 265(0)	29.7(4)	34.3(4)	43.3(4)	0.9(3)	−0.8(3)	4.9(3)
S(1)	676(3)	2 582(2)	1 167(2)	38(2)	36(2)	58(2)	−8(2)	−15(2)	−6(2)
S(2)	3 192(3)	3 012(2)	1 965(2)	40(2)	44(2)	53(2)	−3(2)	−19(2)	−7(2)
S(3)	3 398(3)	−486(2)	1 417(2)	37(2)	56(2)	44(2)	3(2)	−13(2)	−20(2)
S(4)	4 097(3)	3(2)	3 024(2)	39(2)	48(2)	41(2)	6(2)	−9(2)	−18(2)
S(5)	−388(3)	−364(2)	2 559(2)	41(2)	48(2)	38(2)	−7(2)	−2(2)	−18(1)
S(6)	555(3)	965(2)	3 729(2)	40(2)	47(2)	45(2)	−12(2)	−3(2)	−20(1)
P(1)	1 924(3)	3 710(2)	1 234(2)	30(2)	34(2)	43(2)	−3(1)	−7(2)	−6(1)
P(2)	4 672(3)	−765(2)	2 174(2)	28(2)	38(2)	39(2)	1(2)	−6(2)	−12(1)
P(3)	−803(3)	−2(2)	3 588(2)	29(2)	34(2)	36(2)	−5(1)	0(1)	−10(1)

(*b*)

Atom	10^4x	10^4y	10^4z	10^3U/Å^2 †
C(1)	2 864(10)	4 330(8)	263(6)	38(3)
C(2)	1 928(11)	4 943(10)	−312(6)	47(3)
C(3)	2 778(12)	5 452(10)	−1 137(7)	60(4)
C(4)	3 631(12)	4 495(10)	−1 419(7)	60(4)
C(5)	4 520(12)	3 899(9)	−837(7)	55(3)
C(6)	3 710(12)	3 357(9)	−10(6)	53(3)
C(7)	930(10)	4 863(8)	1 540(6)	38(3)
C(8)	1 762(11)	5 901(9)	1 461(6)	50(3)
C(9)	818(13)	6 843(10)	1 714(7)	63(4)
C(10)	100(13)	6 376(10)	2 572(7)	66(4)
C(11)	−675(13)	5 323(10)	2 655(7)	64(4)
C(12)	239(12)	4 380(9)	2 399(6)	52(3)
C(13)	6 292(11)	−277(8)	1 651(6)	41(3)
C(14)	6 205(11)	1 035(9)	1 265(6)	51(3)
C(15)	7 602(12)	1 430(10)	831(7)	59(4)
C(16)	8 144(13)	797(10)	207(7)	67(4)
C(17)	8 205(13)	−502(11)	605(7)	70(4)
C(18)	6 804(12)	−933(9)	1 033(6)	54(3)
C(19)	4 840(10)	−2 307(8)	2 616(6)	38(3)
C(20)	5 876(11)	−2 553(9)	3 158(6)	47(3)
C(21)	5 936(13)	−3 879(10)	3 587(7)	64(4)
C(22)	4 566(13)	−4 264(10)	4 032(7)	62(4)
C(23)	3 573(13)	−4 051(10)	3 466(7)	65(4)
C(24)	3 441(12)	−2 736(9)	3 054(6)	53(3)
C(25)	−2 418(10)	712(8)	3 681(6)	37(3)
C(26)	−2 797(11)	888(9)	4 515(6)	52(3)
C(27)	−4 188(13)	1 498(10)	4 585(7)	66(4)
C(28)	−4 152(14)	2 678(11)	3 959(7)	73(4)
C(29)	−3 775(13)	2 507(10)	3 131(7)	62(4)
C(30)	−2 389(11)	1 894(9)	3 048(6)	49(3)
C(31)	−890(10)	−1 315(8)	4 394(6)	37(3)
C(32)	415(11)	−2 010(9)	4 323(6)	46(3)
C(33)	347(12)	−3 099(9)	5 050(6)	52(3)
C(34)	−854(13)	−3 797(10)	5 109(7)	62(4)
C(35)	−2 148(13)	−3 074(10)	5 161(7)	66(4)
C(36)	−2 091(11)	−1 993(9)	4 411(6)	48(3)

* The expression for the temperature factors has the form $\exp[-2\pi^2\Sigma h_ih_ja_i^*a_j^*U_{ij}]$. † The expression for the temperature factors has the form $\exp[-8\pi^2U(\sin\theta/\lambda)^2]$.

(*a*) [Pr{(C_6H_{11})$_2$PS_2}$_3$]. All the Pr, P, and S atoms were found by interpretation of a three-dimensional Patterson map assuming a centrosymmetric structure. A difference-Fourier synthesis phased with these atoms revealed all the carbon atom positions. Subsequent block-diagonal least-squares refinement yielded a final *R* of 0.052 in the space group $P\bar{1}$. The non-carbon atoms were refined anisotropically in blocks containing all positional and thermal parameters for a single atom. All the carbon atoms belonging to the same cyclohexyl group were refined isotropically in a single block. No hydrogen atoms were included in the model. The minimised function was $D = \Sigma\frac{1}{\sigma^2}(|F_o| - |F_c|)^2$ where σ is the estimated standard deviation of the structure factor derived from counting statistics.* During the final stage of refinement, an isotropic extinction factor was included in the calculation, according to the method of Zachariasen[10] (no shifts $>0.3\sigma$ were observed in the last cycle). Final positional and thermal parameters for all non-hydrogen atoms are listed in Table 1, bond lengths and angles in Table 2. Final observed and calculated structure factors for both compounds are listed in Supplementary Publication No. SUP 21891 (38 pp., 1 microfiche).†

(*b*) [Sm{(C_6H_{11})$_2$PS_2}$_3$]. In this case also the Sm, P, and S atoms were found directly from a Patterson map, and the carbon atoms from a subsequent difference Fourier synthesis. Refinement was carried out as before to *R* 0.079. A final difference Fourier showed six peaks (0.6—0.9 eÅ^{-3}) which were interpreted as ripples resulting from the heavy Sm atom. Some of the hydrogen atoms were also found, but no attempt was made to include them in our calculations. Final positional and thermal parameters for non-hydrogen atoms are listed in Table 3, bond lengths and angles in Table 4.

From Table 3 we note that the Sm atom has co-ordinates near $\frac{1}{4}$,0,$\frac{1}{4}$. This gives a nearly *B*-centred cell which thus explains the large number of weak reflections for which $h + l = 2n + 1$ and also the difference observed between the powder diffraction patterns of the two different series of isostructural compounds.

Description of the Structures.—A perspective drawing of the neutral praseodymium complex prepared by the program ORTEP[11] and viewed along the pseudo-three-fold axis is

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* Variable scan-speeds were chosen to give similar weights to the strong and medium reflections.

† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

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[8] J. M. Stewart, F. A. Kundell, and J. C. Baldwin, '*X*-RAY '72' system, version of June 1972, Technical Report TR 192, Computing Science Center, University of Maryland (as modified by D. Schwarzenbach).

[9] D. Cromer and J. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[10] W. H. Zachariasen, *Acta Cryst.*, 1967, **23**, 558.

[11] C. K. Johnson, Report ORNL 3794, Oak Ridge National Laboratory, 1971.

TABLE 2

Bond lengths (Å) and angles (°) with standard deviations in parentheses for $[Pr\{(C_6H_{11})_2PS_2\}_3]$ *

(*a*) Distances

Pr–S(1)	2.832(3)	P(2)–S(4)	2.020(5)
Pr–S(2)	2.860(3)	P(2)–C(13)	1.837(11)
Pr–S(3)	2.833(3)	P(2)–C(19)	1.846(10)
Pr–S(4)	2.854(3)	P(3)–S(5)	2.021(5)
Pr–S(5)	2.877(3)	P(3)–S(6)	2.021(5)
Pr–S(6)	2.804(3)	P(3)–C(25)	1.835(11)
P(1)–S(1)	2.024(5)	P(3)–C(31)	1.843(9)
P(1)–S(2)	2.014(4)	S(1) · · · S(2)	3.369(5)
P(1)–C(1)	1.844(9)	S(3) · · · S(4)	3.375(5)
P(1)–C(7)	1.845(10)	S(5) · · · S(6)	3.359(5)
P(2)–S(3)	2.028(5)		

(*b*) Angles

S(1)–Pr–S(2)	72.56(9)	Pr–S(6)–P(3)	88.5(1)
S(1)–Pr–S(3)	105.04(9)	S(1)–P(1)–S(2)	113.1(2)
S(1)–Pr–S(4)	153.02(8)	S(1)–P(1)–C(1)	109.3(4)
S(1)–Pr–S(5)	86.15(9)	S(1)–P(1)–C(7)	107.4(4)
S(1)–Pr–S(6)	106.32(9)	S(2)–P(1)–C(1)	108.4(4)
S(2)–Pr–S(3)	110.59(9)	S(2)–P(1)–C(7)	110.7(4)
S(2)–Pr–S(4)	82.94(9)	C(1)–P(1)–C(7)	107.8(4)
S(2)–Pr–S(5)	151.71(9)	S(3)–P(2)–S(4)	113.0(2)
S(2)–Pr–S(6)	95.40(9)	S(3)–P(2)–C(13)	109.7(4)
S(3)–Pr–S(4)	72.83(9)	S(3)–P(2)–C(19)	108.4(4)
S(3)–Pr–S(5)	92.52(10)	S(4)–P(2)–C(13)	109.4(4)
S(3)–Pr–S(6)	144.00(8)	S(4)–P(2)–C(19)	109.0(4)
S(4)–Pr–S(5)	120.62(8)	C(13)–P(2)–C(19)	107.1(5)
S(4)–Pr–S(6)	86.72(9)	S(5)–P(3)–S(6)	112.5(2)
S(5)–Pr–S(6)	72.50(9)	S(5)–P(3)–C(25)	109.8(5)
Pr–S(1)–P(1)	87.5(1)	S(5)–P(3)–C(31)	110.6(4)
Pr–S(2)–P(1)	86.9(1)	S(6)–P(3)–C(25)	109.9(4)
Pr–S(3)–P(2)	87.2(1)	S(6)–P(3)–C(31)	107.5(4)
Pr–S(4)–P(2)	86.8(1)	C(25)–P(3)–C(31)	106.5(4)
Pr–S(5)–P(3)	86.5(1)		

* For cyclohexyl groups C–C 1.52(2)—1.61(1) Å, C–C–C angles 108.1(9)—113.0(8)°.

shown in Figure 1, and the same view of the samarium analogue in Figure 2.

The metal ions are surrounded by six sulphur atoms in the form of a distorted trigonal prism. Both the praseodymium and samarium atoms lie nearly in the plane defined by the three phosphorus atoms at distances of 0.15 and 0.06 Å respectively.

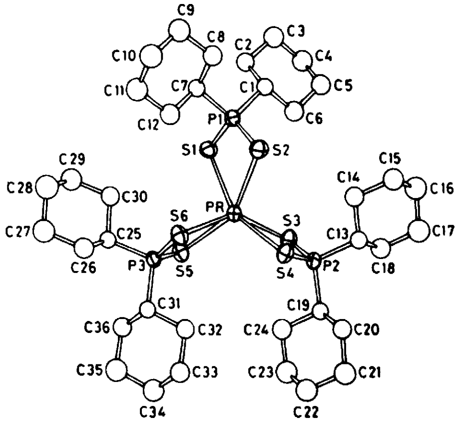

FIGURE 1 The $[Pr\{(C_6H_{11})_2PS_2\}_3]$ molecule viewed along the pseudo-three-fold axis

The four-membered chelate rings defined by the metal atom, one P, and two S atoms are all planar; angles between their normals and the direction perpendicular to the plane of the three phosphorus atoms are listed in Table 5. The samarium compound has nearly perfect trigonal symmetry; however, in the case of praseodymium, the inclination of one of the normals differs from the other two, thus destroying the trigonal symmetry in this particular case.

TABLE 3 (*a*)

Atomic co-ordinates * for $[Sm\{(C_6H_{11})_2PS_2\}_3]$ with standard deviations in parentheses (excluding carbon atoms)

Atom	10^4x	10^4y	10^4z	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Sm	2 607(2)	70(1)	2 492(1)	38.3(7)	33.2(5)	38.6(5)	−5.9(5)	1.8(5)	−8.1(4)
S(1)	3 992(7)	744(6)	1 212(3)	40(4)	70(4)	38(3)	−10(3)	−6(3)	−4(3)
S(2)	5 466(7)	52(5)	2 545(3)	45(4)	65(4)	32(3)	−7(3)	−12(3)	1(3)
S(3)	1 224(7)	2 302(5)	2 636(3)	70(5)	40(3)	36(3)	13(3)	−7(3)	−4(2)
S(4)	1 804(7)	361(5)	3 857(3)	57(4)	36(3)	37(3)	12(3)	−4(3)	0(2)
S(5)	390(7)	−676(5)	1 997(3)	45(4)	37(3)	62(4)	2(3)	−20(3)	11(3)
S(6)	2 738(6)	−2 363(5)	2 703(3)	44(4)	37(3)	61(4)	−4(3)	−12(3)	−7(3)
P(1)	5 790(6)	552(5)	1 562(3)	38(4)	47(3)	26(3)	−3(3)	1(3)	−5(2)
P(2)	949(6)	1 953(5)	3 627(3)	49(4)	30(3)	34(3)	5(3)	−7(3)	−3(2)
P(3)	1 030(7)	−2 327(5)	2 292(3)	48(4)	29(3)	41(3)	−7(3)	−4(3)	−2(2)

(*b*)

Atom	10^4x	10^4y	10^4z	10^3U/Å^2 †	Atom	10^4x	10^4y	10^4z	10^3U/Å^2 †
C(1)	7 053(23)	−544(17)	1 102(10)	37(5)	C(19)	−977(27)	2 077(21)	4 002(12)	59(6)
C(2)	6 370(23)	−1 723(18)	1 162(10)	42(5)	C(20)	−1 253(24)	2 017(9)	4 763(11)	49(6)
C(3)	7 463(27)	−2 662(21)	792(12)	58(7)	C(21)	−2 869(28)	2 102(22)	5 055(12)	64(7)
C(4)	7 925(28)	−2 307(22)	61(12)	61(7)	C(22)	−3 675(32)	1 173(25)	4 782(14)	78(8)
C(5)	8 548(26)	−1 100(20)	−13(11)	55(6)	C(23)	−3 329(30)	1 223(24)	4 017(13)	71(8)
C(6)	7 498(26)	−151(20)	348(11)	53(6)	C(24)	−1 739(26)	1 101(20)	3 738(11)	52(6)
C(7)	6 599(24)	1 937(18)	1 428(10)	44(5)	C(25)	−432(22)	−2 921(17)	2 895(9)	35(5)
C(8)	8 086(28)	1 778(22)	1 570(12)	62(7)	C(26)	−783(25)	−2 160(19)	3 522(11)	50(6)
C(9)	8 785(30)	3 013(24)	1 434(13)	71(7)	C(27)	−2 030(30)	−2 680(23)	4 059(13)	69(7)
C(10)	7 816(30)	3 996(24)	1 842(13)	70(8)	C(28)	−3 560(31)	−2 800(27)	3 755(15)	82(9)
C(11)	6 386(32)	4 047(26)	1 701(14)	79(8)	C(29)	−2 960(29)	−3 580(23)	3 145(13)	74(7)
C(12)	5 589(28)	2 865(22)	1 835(12)	60(7)	C(30)	−1 706(26)	−3 021(20)	2 600(11)	52(6)
C(13)	1 719(24)	3 042(18)	4 001(10)	45(5)	C(31)	1 423(23)	−3 264(17)	1 586(10)	39(5)
C(14)	3 380(28)	2 937(22)	3 712(12)	68(7)	C(32)	1 738(24)	−4 545(19)	1 783(11)	51(6)
C(15)	4 038(30)	3 891(24)	4 047(13)	77(8)	C(33)	2 032(27)	−5 330(22)	1 165(12)	61(7)
C(16)	3 410(30)	5 102(23)	3 921(13)	68(7)	C(34)	3 274(33)	−4 826(26)	610(14)	78(9)
C(17)	1 758(29)	5 193(23)	4 213(13)	68(7)	C(35)	2 971(28)	−3 526(22)	418(12)	61(7)
C(18)	1 093(27)	4 273(22)	3 906(12)	59(7)	C(36)	2 652(26)	−2 825(21)	1 053(12)	54(6)

*, † See footnotes to Table 1.

TABLE 4

Bond lengths (Å) and angles (°), with standard deviations in parentheses for $[Sm\{(C_6H_{11})_2PS_2\}_3]$ *

(*a*) Distances

Sm–S(1)	2.781(6)	P(2)–S(4)	2.005(8)
Sm–S(2)	2.787(7)	P(2)–C(13)	1.81(2)
Sm–S(3)	2.785(6)	P(2)–C(19)	1.85(2)
Sm–S(4)	2.790(6)	P(3)–S(5)	2.033(8)
Sm–S(5)	2.790(7)	P(3)–S(6)	2.007(9)
Sm–S(6)	2.796(6)	P(3)–C(25)	1.82(2)
P(1)–S(1)	2.007(9)	P(3)–C(31)	1.83(2)
P(1)–S(2)	2.032(8)	S(1) · · · S(2)	3.371(9)
P(1)–C(1)	1.83(2)	S(3) · · · S(4)	3.346(8)
P(1)–C(7)	1.82(2)	S(5) · · · S(6)	3.349(9)
P(2)–S(3)	2.018(8)		

(*b*) Angles

S(1)–Sm–S(2)	74.5(2)	Sm–S(6)–P(3)	87.3(2)
S(1)–Sm–S(3)	89.9(2)	S(1)–P(1)–S(2)	113.1(3)
S(1)–Sm–S(4)	152.4(2)	S(1)–P(1)–C(1)	110.2(8)
S(1)–Sm–S(5)	90.6(2)	S(1)–P(1)–C(7)	108.5(8)
S(1)–Sm–S(6)	111.7(2)	S(2)–P(1)–C(1)	108.1(7)
S(2)–Sm–S(3)	111.8(2)	S(2)–P(1)–C(7)	109.0(6)
S(2)–Sm–S(4)	90.8(2)	C(1)–P(1)–C(7)	107.7(9)
S(2)–Sm–S(5)	152.5(2)	S(3)–P(2)–S(4)	112.5(3)
S(2)–Sm–S(6)	90.2(2)	S(3)–P(2)–C(13)	110.1(7)
S(3)–Sm–S(4)	73.8(2)	S(3)–P(2)–C(19)	109.0(9)
S(3)–Sm–S(5)	90.6(2)	S(4)–P(2)–C(13)	109.2(8)
S(3)–Sm–S(6)	153.0(2)	S(4)–P(2)–C(19)	109.7(8)
S(4)–Sm–S(5)	111.3(2)	C(13)–P(2)–C(19)	106.0(11)
S(4)–Sm–S(6)	91.1(2)	S(5)–P(3)–S(6)	112.0(4)
S(5)–Sm–S(6)	73.7(2)	S(5)–P(3)–C(25)	108.4(7)
Sm–S(1)–P(1)	86.5(2)	S(5)–P(3)–C(31)	110.0(7)
Sm–S(2)–P(1)	85.8(3)	S(6)–P(3)–C(25)	109.4(8)
Sm–S(3)–P(2)	86.8(2)	S(6)–P(3)–C(31)	109.8(8)
Sm–S(4)–P(2)	86.9(2)	C(25)–P(3)–C(31)	107.0(10)
Sm–S(5)–P(3)	87.0(3)		

* For cyclohexyl groups C–C 1.47(4)—1.61(3) Å, C–C–C angles 106(2)—117(2)°.

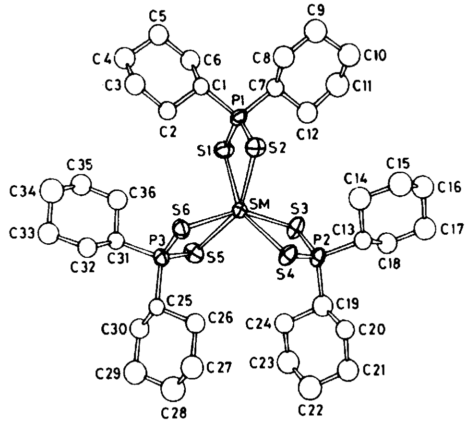

FIGURE 2 The $[Sm\{(C_6H_{11})_2PS_2\}_3]$ molecule viewed along the ' three-fold ' axis

The distortion from a trigonal prism in the samarium case may be expressed as a twist, θ, between upper and lower triangular faces. Expressed as the angle between corresponding opposing edges of the triangular faces, θ is 26.3, 26.2, and 26.8° for the three possible angles. The three-fold axis is thus shown to be preserved. A similar calculation for the praseodymium compound gave the values 29.1, 16.8, and 28.7°, showing again the departure from trigonal symmetry. This is caused by an additional rotation of one of the ligands about its two-fold axis, perpendicular to the ' trigonal ' axis.

TABLE 5

Angles (°) between the Ln-S-P-S rings and the plane of the three-P atoms

Pr, S(1), P(1), S(2)	59.3	Sm, S(1), P(1), S(2)	72.7
Pr, S(3), P(2), S(4)	80.3	Sm, S(3), P(2), S(4)	71.2
Pr, S(5), P(3), S(6)	78.9	Sm, S(5), P(3), S(6)	71.5

DISCUSSION

The effect of changing ionic radius of the central ion is marked with the $[(C_6H_{11})_2PS_2]^-$ ligand. For the large light-earths (La—Nd), the eight-co-ordinate tetrakis-complexes are formed. Praseodymium and neodymium also form six-co-ordinate tris-complexes which are isomorphous; however, the smaller heavy earths (Sm—Lu and Y) form a second isomorphous series of tris-complexes.

The difference originates in the packing of the complexes. In the Pr compound each molecule has fourteen nearest-neighbours, the centres of which lie approximately on the vertices of a rhombic dodecahedron. By contrast, the Sm complex has only twelve nearest-neighbours approximately forming a cubo-octahedron (*i.e.* pseudo-cubic close packing).

The molecular structures of $[Pr\{S_2P(C_6H_{11})_2\}_3]$ and $[Sm\{S_2P(C_6H_{11})_2\}_3]$ are interesting from two points of view. The M–S bond lengths (mean 2.843 and 2.788 Å) are the shortest lanthanoid–sulphur bonds which we have so far observed, and the trigonal prismatic co-ordination polyhedron is unknown for other tris(dithiophosphinato)-complexes.

In a previous paper,[4] we discussed the variation in M–S bond length in dithiophosphinato-complexes and suggested that most of the values we had observed for lanthanoid complexes were longer than those for transition metals, even when taking account of the changing ionic radii of the metal ions, and thus indicative of weaker bonding. Again, taking account of the changing ionic radii, we find only small differences between those for the present case and for several transition metals (see Table 6).[12-16] This indicates that there may be little difference

TABLE 6

A comparison of bond length data (Å) for some dithiophosphinate complexes

Compound	d(M–S)	$d(M–S) - r(M^{n+})$
$[Pr\{S_2P(C_6H_{11})_2\}_3]$ [a]	2.84	1.75
$[Sm\{S_2P(C_6H_{11})_2\}_3]$ [a]	2.79	1.75
$[V\{S_2P(OEt)_2\}_3]$ [b]	2.46	1.72
$[Ni\{S_2P(OEt)_2\}_2]$ [c]	2.23	1.51
$[Cr\{S_2P(OEt)_2\}_3]$ [d]	2.43	1.74
$[Co\{S_2P(OMe)_2\}_3]$ [e]	2.32	1.69
$[Zn(S_2PEt_2)_2]$ [f]	2.42	1.68

[a] Present work. [b] Ref. 12. [c] Ref. 13. [d] Ref. 14. [e] Ref. 15. [f] Ref. 16.

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in M–S bond type between the lanthanoids and the transition metals except where the possibility exists for supplementary d_π–d_π interactions.

The longer M–S bond (2.97 Å) found for the anion $[Pr(S_2PMe_2)_4]^-$ is explained by electrostatic repulsion due to the added negative charge.[3,4] The increase in co-ordination number (6 to 8) would have the same effect although the smaller size of the methyl ligand would tend to reduce its importance.

The only tris(dithiophosphinate) compounds whose structures have been reported are octahedral complexes with a trigonal distortion.[12,14,15] However, these were of first-row transition metals which are small. Kepert[17] has calculated ligand–ligand repulsion energies for three bidentate ligands with changes in the 'bite', *b*, of the ligand (*b* is defined as the intraligand S ··· S distance divided by the M–S bond length), and shown that for large values of *b*, an octahedral arrangement is preferred, and that for smaller values of *b*, a trigonal distortion is expected. The twist, θ, between the upper and lower triangular faces is 60° for an octahedron, and 0° for a trigonal prism. For the samarium compound θ is 26.4°, for *b* 1.20, and for the praseodymium case 24.6° and 1.18; however, θ here is less meaningful owing to the secondary distortion already described. These values agree qualitatively with the predictions of Kepert. It would be interesting to see whether the heavier members of the series with their smaller ionic radii will tend more towards an octahedral arrangement.

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