# Ligand Displacement from Tetrakis(*OO'*-diethyl phosphorodithioate)-lanthanoid(III) Anions by Triphenylphosphine Oxide. *X*-Ray Crystal Structure of $[La\{S_2P(OEt)_2\}_3(POPh_3)_2]$ and $[Sm\{S_2P(OEt)_2\}_2(POPh_3)_3]$-$[S_2P(OEt)_2]$

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Triphenylphosphine oxide reacts with the anionic complexes $[Ln\{S_2P(OEt)_2\}_4]^-$ (Ln = La—Lu, excluding Pm and Y) in ethanolic solution to displace one (La—Pr) or two (Nd—Lu and Y) ligands and form the neutral complexes $[Ln\{S_2P(OEt)_2\}_3(POPh_3)_2]$ or the cationic complexes $[Ln\{S_2P(OEt)_2\}_2(POPh_3)_2]^+$. The crystal structures of the lanthanum and samarium compounds have been determined.

The lanthanum compound crystallises in space group $P2_1/c$, with $a = 19.66(2)$, $b = 12.54(1)$, $c = 24.11(3)$ Å, $\beta = 94.16(8)°$, and $Z = 4$, and the samarium compound in space group $P2_1$, with $a = 17.90(2)$, $b = 16.84(1)$ $c = 12.54(2)$ Å, $\beta = 99.98(10)°$, and $Z = 2$. Both structures were solved by conventional Patterson and Fourier, methods and refined to $R$ 0.09 (La) and 0.08 (Sm).

The neutral lanthanum complex has a square antiprismatic structure. The cationic samarium complex has a pentagonal bipyramidal structure. The nature of the bonding is discussed.

We have recently reported the preparation of the first phosphorodithioate complexes of the rare earths,[1,2] which confirms that the 'hard' acid lanthanoid ions form well-defined complexes with 'soft' bases. We were interested to determine to what extent these ligands could be replaced by 'hard' bases, and to this end we have investigated the reaction of triphenylphosphine oxide with anionic tetrakis(*OO'*-diethyl phosphorodithioate) complexes of all tervalent lanthanoids (excluding Pm) and yttrium. It was noted that the tetrakis-anionic complexes react with triphenylphosphine oxide in ethanolic solution to form crystalline complexes of empirical formulae $LnL_3P_n$ [$L = S_2P(OEt)_2$; $P = POPh_3$; $n = 2$ for La–Pr, or 3 for Nd—Lu and Y].[1] In the light of previous work[3,4] and with respect to steric requirements we were surprised to find that the light earths crystallised with two molecules of phosphine oxide, and the heavy earths with three under the same conditions, *i.e.* an apparent increase in co-ordination number with decreasing ionic radius. A number of phosphine oxide complexes of the lanthanoids have been prepared in recent years;[3,4] however, very little structural data have been reported. For this reason, and in order to resolve the apparent anomalous increase

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[1] A. A. Pinkerton, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 495.

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

[3] D. R. Cousins and F. A. Hart, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1745.

[4] D. R. Cousins and F. A. Hart, *J. Inorg. Nuclear Chem.*, 1968, **30**, 3009.

in co-ordination number, the crystal structures of two representative complexes have been determined and are reported herein.

## EXPERIMENTAL

*Preparation of* [La{$S_2P(OEt)_2$}$_3$($POPh_3$)$_2$], (I).—A solution of Na[La{$S_2P(OEt)_2$}$_4$][1,2] (0.50 g, 0.55 mmol) in hot ethanol (10 ml) was mixed with $POPh_3$ (0.50 g, 1.81 mmol), also in hot ethanol (10 ml). The hot solution was concentrated to *ca.* 5 ml and cooled to 0 °C for 12 h. The resulting white crystals were washed with ethanol and ether, and dried *in vacuo* (0.64 g, 0.51 mmol, 93%) (Found: C, 46.15; H, 4.95; La, 11.10; S, 15.25. Calc. for $C_{48}H_{60}LaO_8P_5S_6$: C, 46.08; H, 4.83; La, 11.10; S, 15.27%).

TABLE 1

(*a*) Atomic and thermal * parameters (excluding phenyl and ethoxy groups) for (I) with standard deviations in parentheses

| Atom | $10^4x$ | $10^4y$ | $10^4z$ | $10^4U_{11}$ | $10^4U_{22}$ | $10^4U_{33}$ | $10^3U_{12}$ | $10^3U_{13}$ | $10^3U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| La | 2 418(1) | 377(1) | 1 854(1) | 338(6) | 316(6) | 360(6) | −2(1) | −3(1) | −1(1) |
| P(1) | 1 152(3) | 1 758(5) | 941(3) | 599(45) | 750(49) | 653(46) | 7(4) | −11(4) | 18(4) |
| P(2) | 1 575(3) | −1 486(5) | 2 708(3) | 696(49) | 670(48) | 635(49) | −21(4) | 17(4) | 2(4) |
| P(3) | 4 130(3) | 1 235(5) | 1 609(3) | 598(45) | 568(46) | 639(46) | −3(4) | 8(4) | 10(4) |
| P(4) | 2 858(3) | −2 102(4) | 979(2) | 410(37) | 369(35) | 393(36) | 0(3) | 0(3) | −1(3) |
| P(5) | 2 532(3) | 2 197(4) | 3 181(2) | 391(35) | 399(33) | 416(34) | 0(4) | 1(3) | 0(4) |
| S(1) | 1 590(3) | 419(6) | 722(2) | 771(44) | 749(44) | 615(40) | 9(5) | −24(3) | −7(4) |
| S(2) | 1 458(3) | 2 274(5) | 1 674(2) | 771(47) | 584(43) | 588(43) | 19(4) | 5(4) | 4(4) |
| S(3) | 1 101(3) | −595(6) | 2 131(3) | 551(40) | 1 037(60) | 783(47) | −31(4) | −6(4) | 13(4) |
| S(4) | 2 584(3) | −1 479(5) | 2 697(2) | 743(45) | 510(40) | 606(43) | 11(4) | 13(4) | 16(4) |
| S(5) | 3 947(3) | 350(5) | 2 257(2) | 424(35) | 608(36) | 526(36) | −7(4) | −8(3) | 9(4) |
| S(6) | 3 318(3) | 1 752(6) | 1 173(3) | 587(45) | 1 028(55) | 869(51) | −23(4) | −4(4) | 48(4) |
| O(7) | 2 772(6) | −1 093(9) | 1 290(5) | 529(91) | 332(85) | 391(88) | −3(8) | 7(7) | −10(7) |
| O(8) | 2 426(6) | 1 388(9) | 2 727(5) | 279(82) | 364(85) | 462(85) | 3(7) | 2(7) | −11(7) |

(*b*) Atomic and thermal † parameters for phenyl and ethoxy groups of (I) with standard deviations in parentheses

| Atom | $10^4x$ | $10^4y$ | $10^4z$ | $10^3U$ | Atom | $10^4x$ | $10^4y$ | $10^4z$ | $10^3U$ |
|---|---|---|---|---|---|---|---|---|---|
| O(1) | 297(8) | 1 669(13) | 939(7) | 107(5) | C(22) | 2 524 | −1 496 | −895 | 87(9) |
| O(2) | 1 194(8) | 2 655(12) | 466(6) | 83(5) | C(23) | 2 823 | −695 | −559 | 85(9) |
| O(3) | 1 375(8) | −1 109(12) | 3 314(6) | 85(5) | C(24) | 3 004 | −896 | 2 | 73(8) |
| O(4) | 1 257(13) | −2 709(21) | 2 639(10) | 182(11) | C(25) | 2 258 | −3 151 | 1 147 | 47(7) |
| O(5) | 4 610(8) | 2 215(12) | 1 850(6) | 93(5) | C(26) | 1 565 | −2 945 | 1 030 | 66(7) |
| O(6) | 4 656(10) | 638(17) | 1 226(8) | 153(8) | C(27) | 1 084 | −3 732 | 1 120 | 81(9) |
| C(1) | 9 908(18) | 1 214(27) | 451(13) | 146(13) | C(28) | 1 296 | −4 727 | 1 326 | 94(9) |
| C(2) | 9 256(20) | 1 584(30) | 439(15) | 201(16) | C(29) | 1 989 | −4 933 | 1 443 | 64(9) |
| C(3) | 1 850(12) | 3 025(19) | 320(9) | 82(8) | C(30) | 2 469 | −4 145 | 1 354 | 58(8) |
| C(4) | 1 706(13) | 1 001(21) | 4 926(11) | 113(10) | C(31) | 1 708 | 2 616 | 3 434 | 38(6) |
| C(5) | 9 257(23) | 4 518(40) | 1 508(19) | 255(21) | C(32) | 1 688 | 3 225 | 3 917 | 72(8) |
| C(6) | 9 391(18) | 4 519(32) | 1 047(15) | 183(15) | C(33) | 1 066 | 3 604 | 4 079 | 59(7) |
| C(7) | 8 826(27) | 1 571(44) | 2 154(21) | 268(26) | C(34) | 464 | 3 376 | 3 758 | 71(8) |
| C(8) | 9 240(17) | 715(28) | 2 211(13) | 130(14) | C(35) | 4 837 | 2 769 | 3 276 | 67(9) |
| C(9) | 4 795(16) | 3 103(25) | 1 402(12) | 143(12) | C(36) | 1 106 | 2 388 | 3 113 | 63(8) |
| C(10) | 5 556(16) | 3 181(24) | 1 532(12) | 146(12) | C(37) | 2 984 | 3 379 | 2 976 | 48(6) |
| C(11) | 5 380(17) | 4 818(30) | 4 058(13) | 159(13) | C(38) | 3 675 | 3 264 | 2 888 | 81(9) |
| C(12) | 4 745(15) | 4 429(24) | 4 281(11) | 125(11) | C(39) | 4 050 | 4 143 | 2 730 | 103(10) |
| C(13) | 3 711 | −2 659 | 1 106 | 49(7) | C(40) | 3 736 | 5 136 | 2 658 | 89(9) |
| C(14) | 4 038 | −3 234 | 709 | 63(8) | C(41) | 3 046 | 5 250 | 2 745 | 72(8) |
| C(15) | 4 667 | −3 716 | 849 | 87(9) | C(42) | 2 670 | 4 372 | 2 904 | 66(8) |
| C(16) | 4 968 | −3 622 | 1 389 | 63(8) | C(43) | 3 111 | 1 698 | 3 767 | 43(6) |
| C(17) | 4 641 | −3 047 | 1 787 | 67(7) | C(44) | 3 324 | 2 353 | 4 213 | 53(7) |
| C(18) | 4 012 | −2 565 | 1 647 | 50(7) | C(45) | 3 558 | 1 901 | 4 720 | 61(8) |
| C(19) | 2 884 | −1 899 | 226 | 39(7) | C(46) | 3 578 | 795 | 4 780 | 70(8) |
| C(20) | 2 586 | −2 701 | −112 | 56(7) | C(47) | 3 364 | 140 | 4 334 | 71(9) |
| C(21) | 2 405 | −2 500 | −671 | 77(8) | C(48) | 3 131 | 592 | 3 827 | 45(7) |

* In the form $\exp[-2\pi^2\Sigma h_ih_ja_i\sigma a_j\sigma U_{ij}]$. † In the form: $\exp[-8\pi^2U(\sin\theta/\lambda)^2]$. The following atoms were refined as ideal phenyl groups: C(13)—(18), C(19)—(24), C(25)—(30), C(31)—(36), C(37)—(42), C(43)—(48). Mean standard deviations of centres of gravity of the six groups: 0.009, 0.010, and 0.009 Å in *x*, *y*, and *z*; errors in Euler angles 0.4—1.9°.

Similar procedures have been used to prepare the Ce and Pr analogues.

*Preparation of* [Sm{$S_2P(OEt)_2$}$_2$($POPh_3$)$_3$][$S_2P(OEt)_2$], (II).—The foregoing procedure was used with Na[Sm{$S_2P(OEt)_2$}$_4$][1,2] (0.30 g, 0.33 mmol) and $POPh_3$ (0.30 g, 1.08 mmol) to give creamy white crystals (0.43 g, 0.28 mmol, 85%) (Found: C, 51.05; H, 4.60; S, 13.06; Sm, 9.75. Calc. for $C_{66}H_{75}O_9P_6S_6Sm$: C, 51.45; H, 4.91; S, 12.49; Sm, 9.76%).

The same method has been used to prepare the similar Nd and Eu—Lu and Y compounds.

*X-Ray Measurements*.—(*a*) *Crystal data for* (I). $C_{48}H_{60}LaO_8P_5S_6$, $M = 1\,251.2$, Monoclinic, $a = 19.66(2)$, $b = 12.54(1)$, $c = 24.11(3)$ Å, $\beta = 94.16(8)°$, $U = 5\,928.3$ Å$^3$, $D_m = 1.412$ (by flotation), $Z = 4$, $D_c = 1.408$. Space group $P2_1/c$ by systematic absences. Mo-$K_\alpha$ radiation, $\lambda = 0.710\,7$ Å; $\mu$(Mo-$K_\alpha$) = 11.2 cm$^{-1}$.

The intensities of 5 531 unique reflections were measured with a Syntex $P2_1$ automated four-circle diffractometer using graphite monochromatised Mo-$K_\alpha$ radiation and the ω scan technique to a maximum sinθ/λ 0.482. Intensities were corrected for absorption using the positions of the well-developed faces which were measured optically. The dimensions of the chosen crystal were 0.06 × 0.64 × 0.11 mm.

(*b*) *Crystal data for* (II). $C_{66}H_{75}O_9P_6S_6Sm$, $M = 1\,540.9$, Monoclinic, $a = 17.90(2)$, $b = 16.84(1)$, $c = 12.54(2)$ Å, $\beta = 99.98(10)°$, $U = 3\,722.8$ Å$^3$, $D_m = 1.392$ (by flotation),

$Z = 2$, $D_c = 1.383$. Space group $P2_1$ or $P2_1/m$ by systematic absences, structure subsequently solved in the acentric space group. Mo-$K_\alpha$ radiation, $\mu$(Mo-$K_\alpha$) = 11.4 cm$^{-1}$. The intensities of 5 080 unique reflections were measured as before to maximum $\sin\theta/\lambda$ 0.539. An absorption correction was applied. The dimensions of the chosen crystal were 0.08 × 0.36 × 0.22 mm.

Scattering factors for the neutral atoms were taken from ref. 5. All computer programs were taken from the '*X*-RAY '72' program system.[6] The stereoprojections were drawn by the program ORTEP.[7] Final observed and calculated structure factors for both compounds are listed in Supplementary Publication No. SUP 21807 (19 pp., 1 microfiche).*

*Solution of the Structures.—Structure of* (I). The lanthanum atom position was found from a three-dimensional Patterson map. All the medium-weight atoms were found from a difference Fourier synthesis. Two cycles of full-matrix least-squares were used to refine the positional parameters of the twelve medium and heavy atoms. Two more difference-Fourier syntheses were required to locate the remaining non-hydrogen atoms. The phenyl rings were refined as ideal groups with bond lengths 1.395 Å and angles 120°. Final refinement by block-diagonal least-squares was carried out in two parts: first non-carbon, and then carbon atoms. The first cycles used individual isotropic temperature factors for all atoms, and the final cycles individual anisotropic temperature factors for the non-carbon atoms except the ethoxy-oxygen atoms. The last cycle gave $R$ 0.09. The function minimised was $D = \Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2$, $\sigma$ of the measured structure factors being derived from counting statistics and the variations in the periodically measured standard reflections. The use of variable scan speeds gives similar $\sigma$ values for the medium and strong reflections. Positional parameters for all non-hydrogen atoms are reported in Table 1. Bond lengths and angles, excluding phenyl rings, are given in Table 2. A perspective drawing of the co-ordination polyhedron is shown in Figure 1.

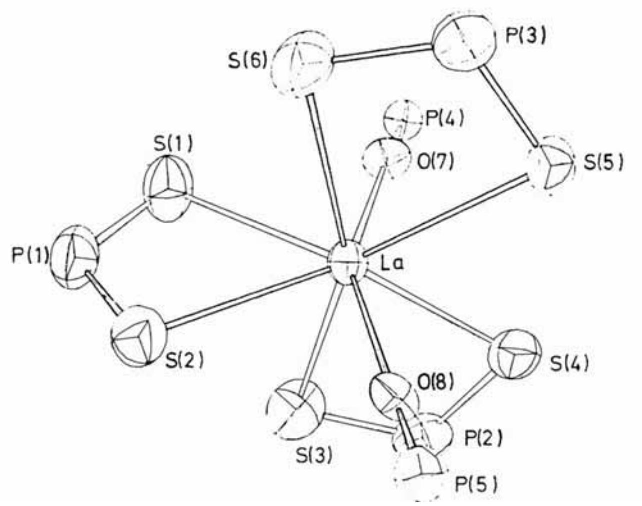

FIGURE 1 Inner co-ordination sphere of the lanthanum complex (I)

*Structure of* (II). The samarium atom position was found from a three-dimensional Patterson map. Five difference-Fourier syntheses were required to locate all the non-carbon atoms unequivocally because of the confusion caused by the presence of a pseudo-mirror plane perpendicular to the $b$ axis. The following atoms lie essentially on pseudo-mirror planes at height 0 or $\frac{1}{2}$: Sm, P(1), P(3), P(4), P(5), S(3), O(1), O(2), O(5)—(8). In addition the positions S(1) and S(2) as well as S(5) and S(6) are related by the same pseudo-symmetry element. Thus 16 out of 22 non-carbon atoms form a nearly centrosymmetric arrangement which would correspond to the space group

TABLE 2

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

(*a*) Distances

| | | | |
|---|---|---|---|
| La–S(1) | 3.076(6) | P(3)–S(5) | 1.971(8) |
| La–S(2) | 3.047(7) | P(3)–S(6) | 1.957(9) |
| La–S(3) | 2.982(7) | P(3)–O(5) | 1.630(16) |
| La–S(4) | 3.092(6) | P(3)–O(6) | 1.619(21) |
| La–S(5) | 3.092(6) | P(4)–O(7) | 1.487(13) |
| La–S(6) | 3.036(7) | P(5)–O(8) | 1.496(12) |
| La–O(7) | 2.422(12) | O(1)–C(1) | 1.47(4) |
| La–O(8) | 2.456(11) | O(2)–C(3) | 1.44(3) |
| S(1)–S(2) | 3.291(9) | O(3)–C(5) | 1.56(5) |
| S(3)–S(4) | 3.319(9) | O(4)–C(7) | 1.05(6) |
| S(5)–S(6) | 3.315(9) | O(5)–C(9) | 1.61(3) |
| P(1)–S(1) | 1.976(9) | O(6)–C(11) | 1.23(4) |
| P(1)–S(2) | 1.937(8) | C(1)–C(2) | 1.36(5) |
| P(1)–O(1) | 1.683(18) | C(3)–C(4) | 1.56(4) |
| P(1)–O(2) | 1.611(16) | C(5)–C(6) | 1.16(6) |
| P(2)–S(3) | 1.965(9) | C(7)–C(8) | 1.35(6) |
| P(2)–S(4) | 1.986(9) | C(9)–C(10) | 1.51(4) |
| P(2)–O(3) | 1.613(16) | C(11)–C(12) | 1.48(5) |
| P(2)–O(4) | 1.660(27) | | |

(*b*) Angles

| | | | |
|---|---|---|---|
| S(1)–La–S(2) | 65.0(2) | La–S(6)–P(3) | 90.3(3) |
| S(1)–La–S(3) | 78.1(2) | La–O(7)–P(4) | 168.2(8) |
| S(1)–La–S(4) | 128.3(2) | La–O(8)–P(5) | 165.7(7) |
| S(1)–La–S(5) | 136.0(2) | S(1)–P(1)–S(2) | 114.5(4) |
| S(1)–La–S(6) | 78.6(2) | S(1)–P(1)–O(1) | 113.4(7) |
| S(1)–La–O(7) | 70.7(3) | S(1)–P(1)–O(2) | 110.9(7) |
| S(1)–La–O(8) | 136.2(3) | S(2)–P(1)–O(1) | 105.6(7) |
| S(2)–La–S(3) | 79.2(2) | S(2)–P(1)–O(2) | 112.8(6) |
| S(2)–La–S(4) | 135.7(2) | O(1)–P(1)–O(2) | 98.5(8) |
| S(2)–La–S(5) | 129.2(2) | S(3)–P(2)–S(4) | 114.3(4) |
| S(2)–La–S(6) | 81.9(2) | S(3)–P(2)–O(3) | 109.9(7) |
| S(2)–La–O(7) | 135.5(3) | S(3)–P(2)–O(4) | 107.4(9) |
| S(2)–La–O(8) | 71.6(3) | S(4)–P(2)–O(3) | 108.7(6) |
| S(3)–La–S(4) | 66.2(2) | S(4)–P(2)–O(4) | 111.8(1.0) |
| S(3)–La–S(5) | 140.0(2) | O(3)–P(2)–O(4) | 104.2(1.1) |
| S(3)–La–S(6) | 154.5(2) | S(5)–P(3)–S(6) | 115.1(4) |
| S(3)–La–O(7) | 96.0(3) | S(5)–P(3)–O(5) | 106.0(6) |
| S(3)–La–O(8) | 88.3(3) | S(5)–P(3)–O(6) | 110.6(8) |
| S(4)–La–S(5) | 74.4(2) | S(6)–P(3)–O(5) | 111.7(6) |
| S(4)–La–S(6) | 138.2(2) | S(6)–P(3)–O(6) | 112.1(8) |
| S(4)–La–O(7) | 77.0(3) | O(5)–P(3)–O(6) | 100.1(1.0) |
| S(4)–La–O(8) | 80.3(3) | P(1)–O(1)–C(1) | 119.2(1.7) |
| S(5)–La–S(6) | 65.5(2) | P(1)–O(2)–C(3) | 119.5(1.3) |
| S(5)–La–O(7) | 81.7(3) | P(2)–O(3)–C(5) | 130.5(1.9) |
| S(5)–La–O(8) | 77.9(3) | P(2)–O(4)–C(7) | 114.9(3.4) |
| S(6)–La–O(7) | 85.8(3) | P(3)–O(5)–C(9) | 115.7(1.4) |
| S(6)–La–O(8) | 101.7(3) | P(3)–O(6)–C(11) | 133.5(2.2) |
| O(7)–La–O(8) | 152.8(4) | O(1)–C(1)–C(2) | 108.6(2.7) |
| La–S(1)–P(1) | 89.5(3) | O(2)–C(3)–C(4) | 106.0(1.8) |
| La–S(2)–P(1) | 91.0(3) | O(3)–C(5)–C(6) | 120.4(3.9) |
| La–S(3)–P(2) | 90.9(3) | O(4)–C(7)–C(8) | 138.6(4.9) |
| La–S(4)–P(2) | 87.4(3) | O(5)–C(9)–C(10) | 100.0(2.1) |
| La–S(5)–P(3) | 88.5(2) | O(6)–C(11)–C(12) | 117.5(2.9) |

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

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

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

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

TABLE 3

(*a*) Atomic and thermal * parameters (excluding phenyl and ethoxy groups) for (II) with standard deviations in parentheses

| Atom | $10^4x$ | $10^4y$ | $10^4z$ | $10^4U_{11}$ | $10^4U_{22}$ | $10^4U_{33}$ | $10^3U_{12}$ | $10^3U_{13}$ | $10^3U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Sm | 3 224(1) | 0 000 | 1 182(1) | 267(7) | 256(6) | 282(6) | 1(2) | 3(1) | 3(1) |
| P(1) | 3 928(5) | −51(10) | −1 285(6) | 471(54) | 519(60) | 318(38) | 8(9) | 8(4) | −[illegible](7) |
| P(2) | 2 663(6) | 1 431(6) | 2 937(8) | 506(75) | 406(64) | 613(62) | −6(6) | 7(6) | −11(6) |
| P(3) | 1 124(6) | 4 865(8) | 5 323(7) | 440(59) | 570(93) | 468(48) | 5(6) | 9(4) | 4(6) |
| P(4) | 5 250(4) | −5(9) | 2 744(5) | 301(42) | 508(47) | 326(38) | −20(9) | 1(3) | −13(8) |
| P(5) | 1 197(4) | 45(9) | −414(6) | 391(45) | 486(51) | 410(40) | 0(9) | −5(4) | 3(8) |
| P(6) | 2 821(6) | −2 074(5) | 2 068(7) | 420(63) | 267(48) | 464(52) | −8(5) | 5(5) | 5(4) |
| S(1) | 3 714(7) | 965(7) | −477(9) | 969(95) | 560(64) | 875(74) | −1(7) | 40(7) | 4(6) |
| S(2) | 3 701(6) | −959(5) | −516(6) | 573(69) | 413(45) | 457(45) | 0(5) | 26(5) | −1(4) |
| S(3) | 2 591(6) | 256(5) | 3 161(7) | 676(68) | 654(76) | 462(47) | −4(5) | 23(5) | −2(4) |
| S(4) | 3 170(7) | 1 709(6) | 1 735(8) | 823(84) | 452(61) | 646(61) | −1(6) | 20(6) | −8(5) |
| S(5) | 1 210(8) | 3 775(7) | 5 695(9) | 889(103) | 696(72) | 798(81) | −2(8) | 16(8) | 14(7) |
| S(6) | 1 741(7) | 5 641(7) | 6 285(9) | 769(88) | 781(81) | 697(69) | −12(7) | −7(7) | 8(7) |

(*b*) Atomic and thermal † parameters for phenyl and ethoxy-groups of (II)

| Atom | $10^4x$ | $10^4y$ | $10^4z$ | $10^3U$ | Atom | $10^4x$ | $10^4y$ | $10^4z$ | $10^3U$ |
|---|---|---|---|---|---|---|---|---|---|
| O(1) | 3 549(8) | −24(16) | −2 538(10) | 58(4) | C(30) | 6 605 | −580 | 2 117 | 51(9) |
| O(2) | 4 790(8) | 49(14) | −1 547(10) | 56(4) | C(31) | 1 085 | −667 | −1 540 | 91(9) |
| O(3) | 1 842(11) | 1 732(11) | 2 795(13) | 53(6) | C(32) | 1 577 | −1 314 | −1 348 | 54(9) |
| O(4) | 3 116(11) | 1 862(11) | 4 006(14) | 85(6) | C(33) | 1 475 | −1 971 | −2 035 | 16(7) |
| O(5) | 1 228(9) | 4 991(16) | 4 064(11) | 74(4) | C(34) | 880 | −1 980 | −2 917 | 74(10) |
| O(6) | 219(8) | 5 107(14) | 5 164(10) | 70(4) | C(35) | 388 | −1 334 | −3 111 | 87(14) |
| O(7) | 4 437(7) | −41(12) | 2 160(9) | 45(4) | C(36) | 491 | −677 | −2 422 | 77(11) |
| O(8) | 1 993(7) | 70(14) | 218(9) | 45(3) | C(37) | 439 | −74 | 323 | 36(8) |
| O(9) | 2 961(9) | −1 276(10) | 1 610(12) | 61(5) | C(38) | −13 | −754 | 169 | 63(7) |
| C(1) | 5 416(17) | 99(32) | −673(22) | 116(9) | C(39) | −522 | −916 | 866 | 87(11) |
| C(2) | 6 151(16) | −190(17) | −976(19) | 91(9) | C(40) | −580 | −399 | 1 717 | 115(14) |
| C(3) | 2 721(15) | −220(14) | −2 797(19) | 60(8) | C(41) | −128 | 281 | 1 871 | 65(10) |
| C(4) | 2 506(18) | −645(18) | −3 911(22) | 82(10) | C(42) | 381 | 443 | 1 174 | 62(9) |
| C(5) | 1 569(18) | 2 622(19) | 2 597(24) | 104(10) | C(43) | 960 | 936 | −1 269 | 57(10) |
| C(6) | 1 103(23) | 2 487(26) | 1 549(30) | 192(14) | C(44) | 1 535 | 1 500 | −1 244 | 105(11) |
| C(7) | 2 828(19) | 1 711(21) | 5 008(25) | 130(11) | C(45) | 1 365 | 2 251 | −1 692 | 98(7) |
| C(8) | 3 087(18) | 2 270(20) | 5 849(23) | 106(10) | C(46) | 622 | 2 438 | −2 164 | 95(12) |
| C(9) | 33(21) | 5 948(23) | 4 794(28) | 92(12) | C(47) | 47 | 1 875 | −2 189 | 141(13) |
| C(10) | −767(21) | 5 971(26) | 4 227(26) | 151(13) | C(48) | 216 | 1 124 | −1 741 | 185(14) |
| C(11) | 1 952(22) | 4 913(43) | 3 748(30) | 122(14) | C(49) | 2 103 | −2 060 | 2 880 | 60(11) |
| C(12) | 1 862(16) | 4 965(25) | 2 516(20) | 109(9) | C(50) | 1 580 | −1 439 | 2 710 | 64(8) |
| C(13) | 5 602 | 977 | 2 719 | 43(9) | C(51) | 1 019 | −1 375 | 3 352 | 53(8) |
| C(14) | 5 259 | 1 521 | 1 947 | 141(20) | C(52) | 981 | −1 933 | 4 164 | 62(9) |
| C(15) | 5 548 | 2 289 | 1 930 | 90(12) | C(53) | 1 504 | −2 554 | 4 333 | 48(7) |
| C(16) | 6 180 | 2 513 | 2 685 | 64(8) | C(54) | 2 065 | −2 617 | 3 692 | 44(10) |
| C(17) | 6 524 | 1 969 | 3 456 | 82(17) | C(55) | 2 560 | −2 817 | 963 | 43(9) |
| C(18) | 6 234 | 1 201 | 3 472 | 56(9) | C(56) | 1 819 | −3 102 | 686 | 87(12) |
| C(19) | 5 348 | −335 | 5 855 | 41(8) | C(57) | 1 633 | −3 627 | −179 | 98(11) |
| C(20) | 4 769 | −95 | 4 688 | 86(9) | C(58) | 2 187 | −3 868 | −768 | 62(7) |
| C(21) | 4 779 | −332 | 5 756 | 95(16) | C(59) | 2 927 | −3 583 | −491 | 81(10) |
| C(22) | 5 367 | −809 | 6 281 | 93(10) | C(60) | 3 114 | −3 058 | 374 | 80(8) |
| C(23) | 5 945 | −1 050 | 5 737 | 63(11) | C(61) | 3 649 | −2 506 | 2 916 | 60(9) |
| C(24) | 5 936 | −812 | 4 669 | 73(14) | C(62) | 4 022 | −2 055 | 3 780 | 64(8) |
| C(25) | 5 838 | −700 | 2 147 | 42(7) | C(63) | 4 604 | −2 393 | 4 527 | 63(7) |
| C(26) | 5 481 | −1 396 | 1 724 | 54(13) | C(64) | 4 812 | −3 182 | 4 410 | 85(11) |
| C(27) | 5 890 | −1 972 | 1 271 | 66(9) | C(65) | 4 439 | −3 633 | 3 545 | 101(8) |
| C(28) | 6 658 | −1 852 | 1 241 | 76(13) | C(66) | 3 857 | −3 295 | 2 798 | 165(16) |
| C(29) | 7 016 | −1 156 | 1 664 | 76(5) | | | | | |

* In the form: $\exp[-2\pi^2\Sigma h_ih_ja_i^*a_j^*U_{ij}]$. † In the form: $\exp[-2\pi^2U(\sin\theta/\lambda)^2]$. The following atoms were refined as ideal phenyl groups: C(13)—(18), C(19)—(24), C(25)—(30), C(31)—(36), C(37)—(42), C(43)—(48), C(49)—(54), C(55)—(60), C(61)—(66). Mean standard deviations of centres of gravity of the six groups: 0.01 Å in *x*, *y*, and *z*; errors in Euler angles 0.7—1.4°.

$P2_1/m$. Two cycles of full-matrix least-squares were used to refine the positional parameters of the 22 non-carbon atoms. Two more difference-Fourier syntheses were required to find all the atoms of the phenyl rings. A further refinement cycle was carried out followed by a final difference-Fourier synthesis to find the carbon atoms of the ethoxy-groups.

Final refinement was carried out as before. The last cycle gave *R* 0.08. Positional parameters for all non-hydrogen atoms are reported in Table 3, and bond lengths and angles of the complex cation, excluding the phenyl rings, in Table 4. A perspective drawing of the inner co-ordination polyhedron of the cationic complex is shown in Figure 2. In both cases, the ethoxy-groups were badly defined and hence did not refine well. This is reflected in their standard deviations. Refinement was stopped at *R* 9 and 8% respectively due to prohibitive computing costs.

## DISCUSSION

*Lanthanum Complex*, (I).—The lanthanum atom is co-ordinated to six sulphur and two oxygen atoms in a distorted square antiprismatic arrangement. The bulky phosphine oxides are located on opposite sides of the molecule, as would be expected from steric considerations. Although there is no crystallographically required symmetry, the co-ordination polyhedron does have nearly $C_2$ symmetry.

*Samarium Complex*, (II).—The samarium atom is co-ordinated to four sulphur and three oxygen atoms in a pentagonal bipyramidal arrangement. The pentagonal plane consists of four sulphur atoms and one oxygen. The phosphorus atoms of the phosphorodithioate ligands and that of the equatorial phosphine oxide also lie in the same plane. The remaining two phosphine oxides are co-ordinated perpendicular to the pentagonal plane. The structure also contains discrete unco-ordinated $[S_2P(OEt)_2]^-$ ions.

TABLE 4

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

(*a*) Distances

| | | | |
|---|---|---|---|
| Sm–S(1) | 2.89(1) | P(3)–S(6) | 1.98(2) |
| Sm–S(2) | 2.92(1) | P(3)–O(5) | 1.63(2) |
| Sm–S(3) | 2.93(1) | P(3)–O(6) | 1.65(2) |
| Sm–S(4) | 2.97(1) | P(4)–O(7) | 1.51(1) |
| Sm–O(7) | 2.30(1) | P(5)–O(8) | 1.51(1) |
| Sm–O(8) | 2.32(1) | P(6)–O(9) | 1.50(2) |
| Sm–O(9) | 2.28(2) | O(1)–C(3) | 1.50(3) |
| S(1)–S(2) | 3.24(1) | O(2)–C(1) | 1.43(3) |
| S(3)–S(4) | 3.30(1) | O(3)–C(5) | 1.58(4) |
| S(5)–S(6) | 3.33(2) | O(4)–C(7) | 1.46(4) |
| P(1)–S(1) | 2.06(2) | O(5)–C(11) | 1.42(5) |
| P(1)–S(2) | 1.89(2) | O(6)–C(9) | 1.51(4) |
| P(1)–O(1) | 1.60(1) | C(1)–C(2) | 1.51(5) |
| P(1)–O(2) | 1.64(2) | C(3)–C(4) | 1.56(4) |
| P(2)–S(3) | 2.01(1) | C(5)–C(6) | 1.45(5) |
| P(2)–S(4) | 1.95(2) | C(7)–C(8) | 1.43(4) |
| P(2)–O(3) | 1.53(2) | C(9)–C(10) | 1.44(5) |
| P(2)–O(4) | 1.61(2) | C(11)–C(12) | 1.53(5) |
| P(3)–S(5) | 1.89(2) | | |

(*b*) Angles

| | | | |
|---|---|---|---|
| S(1)–Sm–S(2) | 67.8(3) | S(1)–P(1)–O(1) | 112.1(1.2) |
| S(1)–Sm–S(3) | 137.4(3) | S(1)–P(1)–O(2) | 106.0(1.1) |
| S(1)–Sm–S(4) | 69.5(3) | S(2)–P(1)–O(1) | 115.6(1.2) |
| S(1)–Sm–O(7) | 91.4(4) | S(2)–P(1)–O(2) | 118.5(1.1) |
| S(1)–Sm–O(8) | 88.6(5) | O(1)–P(1)–O(2) | 93.1(8) |
| S(1)–Sm–O(9) | 149.9(5) | S(3)–P(2)–S(4) | 113.3(7) |
| S(2)–Sm–S(3) | 154.7(3) | S(3)–P(2)–O(3) | 105.0(1.0) |
| S(2)–Sm–S(4) | 137.2(3) | S(3)–P(2)–O(4) | 111.3(9) |
| S(2)–Sm–O(7) | 90.2(4) | S(4)–P(2)–O(3) | 113.3(9) |
| S(2)–Sm–O(8) | 91.1(5) | S(4)–P(2)–O(4) | 107.5(1.0) |
| S(2)–Sm–O(9) | 75.5(4) | O(3)–P(2)–O(4) | 106.3(1.2) |
| S(3)–Sm–S(4) | 68.1(3) | S(5)–P(3)–S(6) | 118.5(7) |
| S(3)–Sm–O(7) | 91.2(4) | S(5)–P(3)–O(5) | 110.2(1.2) |
| S(3)–Sm–O(8) | 87.9(4) | S(5)–P(3)–O(6) | 107.8(1.1) |
| S(3)–Sm–O(9) | 79.3(4) | S(6)–P(3)–O(5) | 111.0(1.1) |
| S(4)–Sm–O(7) | 88.3(5) | S(6)–P(3)–O(6) | 110.0(1.0) |
| S(4)–Sm–O(8) | 90.3(6) | O(5)–P(3)–O(6) | 97.2(9) |
| S(4)–Sm–O(9) | 147.3(5) | P(1)–O(1)–C(3) | 116.2(1.4) |
| O(7)–Sm–O(8) | 178.6(7) | P(1)–O(2)–C(1) | 119.5(1.6) |
| O(7)–Sm–O(9) | 93.5(6) | P(2)–O(3)–C(5) | 126.5(1.8) |
| O(8)–Sm–O(9) | 87.4(7) | P(2)–O(4)–C(7) | 115.7(1.8) |
| Sm–S(1)–P(1) | 89.6(5) | P(3)–O(5)–C(11) | 121.2(1.9) |
| Sm–S(2)–P(1) | 92.3(5) | P(3)–O(6)–C(9) | 115.5(1.9) |
| Sm–S(3)–P(2) | 89.0(5) | O(1)–C(3)–C(4) | 112.1(2.2) |
| Sm–S(4)–P(2) | 89.2(5) | O(2)–C(1)–C(2) | 112.9(2.4) |
| Sm–O(7)–P(4) | 174.8(1.2) | O(3)–C(5)–C(6) | 96.2(2.5) |
| Sm–O(8)–P(5) | 175.5(1.6) | O(4)–C(7)–C(8) | 113.6(2.8) |
| Sm–O(9)–P(6) | 171.2(1.0) | O(5)–C(11)–C(12) | 109.5(2.6) |
| S(1)–P(1)–S(2) | 110.3(6) | O(6)–C(9)–C(10) | 100.6(3.0) |

The structures resolve the apparent anomalous increase in co-ordination number for the heavy earths by showing that in fact the co-ordination number decreases from eight to seven. This is a more logical phenomenon, as steric effects must become more important for the heavy earths with their smaller ionic radius, the co-ordination numbers of seven and eight being quite common for the lanthanoids. A precedent for the formation of cationic lanthanoid complexes in this way is demonstrated by the isolation[3] of $[Ln(NO_3)_2(POPh_3)_4][NO_3]$ by Cousins and Hart who inferred the presence of free nitrate ions from i.r. spectra.

We observe that the M–S bond lengths are a function of the ionic radius and the charge on the central metal ion. The decrease from 3.08 in the lanthanum complex (I) to 2.92 Å for samarium complex (II) corresponds to 0.05 Å more than the change in the ionic radii. We attribute this to the residual positive charge on the samarium atom being only partly compensated by the donation of electrons from the extra molecule of phosphine oxide, leading to a stronger bond in this case. We have made a similar observation in the case of praseodymium. In the anion $[Pr(S_2PMe_2)_4]^-$ (eight-co-ordinate, square antiprismatic) the M–S bond length is 2.97 Å,[8] but on reducing the now negative residual charge on the central ion by forming the neutral tris-complex $[Pr\{S_2P(C_6H_{11})_2\}_3]$ [9] (six-co-ordinate, trigonal prismatic) the value decreases to 2.84 Å.

Although a lower co-ordination number reduces the effect of ligand–ligand repulsion and would thus also lead to a shorter M–S bond, we believe that this is less important than the effect of the changing charge. This is especially so in the case of the two aforementioned praseodymium compounds where the large bulk of the cyclohexyl ligands must offset the reduction in co-ordination number.

It is interesting to compare the M–S bond lengths found for the lanthanoids with those of a few analogous transition-metal complexes, as this must be a function of the bonding interaction. Table 5 lists M–S bond lengths for the rare-earth compounds and several transition-metal analogues[8–13] as well as the value remaining when the radius of the metal ion has been subtracted. The values show that the bonding is weaker for the lan-

TABLE 5

Comparison of bond data for phosphorodithioate complexes

| Compound | $d_{M-S}$ (Å) | $d_{M-S} - r_{M^{n+}}$ (Å) | $\widehat{SPS}$ (°) |
|---|---|---|---|
| $[S_2P(OEt)_2]^-$ [a] | | | 118.5 |
| $[La\{S_2P(OEt)_2\}_3(POPh_3)_2]$ [a] | 3.08 | 1.93 | 114.6 |
| $[Sm\{S_2P(OEt)_2\}_2(POPh_3)_3]^+$ [a] | 2.92 | 1.88 | 111.8 |
| $[Pr(S_2PMe_2)_4]^-$ [b] | 2.97 | 1.88 | 112.2 |
| $[Pr\{S_2P(C_6H_{11})_2\}_3]$ [c] | 2.84 | 1.75 | 112.9 |
| $[V\{S_2P(OEt)_2\}_3]$ [d] | 2.46 | 1.72 | 108.1 |
| $[Ni\{S_2P(OEt)_2\}_2]$ [e] | 2.23 | 1.51 | 103.1 |
| $[Zn\{S_2PEt_2\}_2]$ [g] | 2.42 | 1.68 | 109.6 |
| $[Ni\{S_2P(OEt)_2\}_2]\cdot 2py$ [h] | 2.49 | 1.77 | 110.4 |

[a] This work. [b] Ref. 8. [c] Ref. 9. [d] Ref. 10. [e] Ref. 11. [g] Ref. 12. [h] Ref. 13.

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thanoids; however the difference may be qualitatively explained by the possibility of $d_\pi$–$d_\pi$ supplementary bonding for the transition metals.

In the same way as that by which we compared M–S bond lengths to obtain an indication of bonding interactions, we may consider changes in the S–P–S angle of the chelates. The value in the free $[S_2P(OEt)_2]^-$ ion (118.5°) is known from the samarium structure. In the present two complexes the value falls to 114.6 (La) and 111.8° (Sm) in agreement with the foregoing arguments. The same rationale seems to break down in the case of $[Pr(S_2PMe_2)_4]^-$ (ref. 8) and $[Pr\{S_2P(C_6H_{11})_2\}_3]$ (ref. 9) where the angles are 112.2 and 112.9°; however it is to be expected that the angle is also sensitive to the substituents at phosphorus. In order to compare the lanthanoids with the transition metals we have included in Table 5 some values for this angle. Again, the stronger interaction with the transition metals is evident, especially where $d_\pi$–$d_\pi$ bonding may be important.

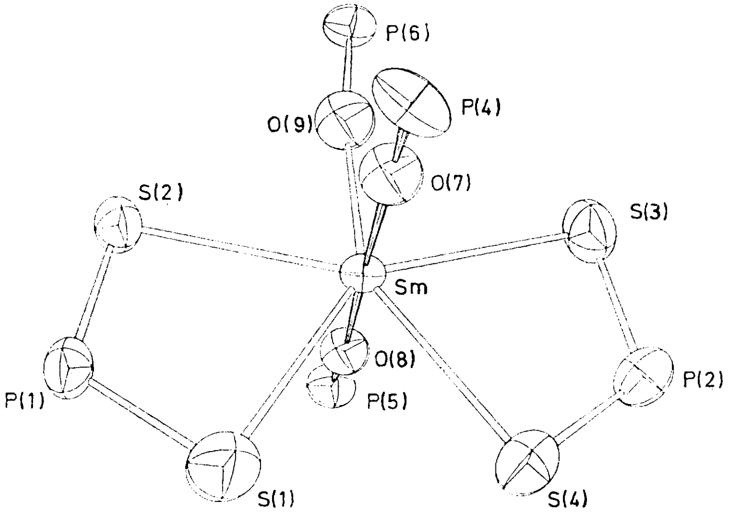

FIGURE 2 Inner co-ordination sphere of the samarium cation of (II)

The validity of the foregoing arguments is shown by comparing the nickel[11] complex $[Ni\{S_2P(OEt)_2\}_2]$ with its bispyridine addition complex[13] which is reported to have weaker Ni–S bonds which are 0.26 Å longer and S–P–S angles 7.3° larger than the parent compound.

The La–O bond length (mean 2.44 Å) is the same as that found in $[La_2O_2\{N(SiMe_3)_2\}_4(POPh_3)_2]$.[14] The decrease to a mean of 2.30 Å for samarium is consistent with the smaller ionic radius. The mean $Ce^{IV}$–O distance of 2.22 Å in $[Ce(NO_3)_4(POPh_3)_2]$[15] may also be in part due to the decrease in the size of the ion. However, the existence of $p_\pi$–$d_\pi$ bonding was suggested in this case, based on the length of the P=O bond (1.53 Å), which is 0.07 Å longer than in the free phosphine oxide (1.46 Å).[16] Cerium(IV) must be a stronger acceptor of electrons than tervalent lanthanum and samarium, which is consistent with the observation that the P=O bond length in complexes (I) and (II) is 1.50, 0.04 Å longer than in the free ligand. This may indicate some $\pi$ interaction in these cases also.

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