Studies in Six-co-ordination of the Lanthanides with Bidentate Ligands. The Crystal and Molecular Structures of Tris(dicyclohexyldithiophosphinato)dysprosium(III) and Tris(dicyclohexyldithiophosphinato)lutecium(III)

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The crystal structures of $[Dy\{P(C_6H_{11})_2S_2\}_3]$ and $[Lu\{P(C_6H_{11})_2S_2\}_3]$ have been determined from diffractometer data. The co-ordination polyhedra are intermediate between trigonal prismatic and octahedral, the smaller Lu ion having the more octahedral environment. The structures are significantly different from those expected from calculated ligand–ligand repulsions. The origin of this distortion is discussed and compared with that found in analogous praseodymium and samarium compounds. $[Dy\{P(C_6H_{11})_2S_2\}_3]$ crystallizes in the triclinic space group $P\bar{1}$, with a = 9.661(2), b = 11.449(2), c = 20.553(3) Å, α = 85.88(1), β = 77.32(1), and γ = 84.76(1)°. The R value was 0.042. $[Lu\{P(C_6H_{11})_2S_2\}_3]$ also crystallizes in the triclinic space group $P\bar{1}$, with a = 9.659(2), b = 11.399(1), c = 20.532(3) Å, α = 85.89(1), β = 77.09(1), and γ = 84.80(1)°. The R value was 0.039.

CO-ORDINATION polyhedra may often be predicted using simple arguments concerning ligand–ligand repulsions. This has been quantified over the past few years by Kepert [1] for a number of different ligand types and co-ordination numbers. For the specific case of [M(bidentate)$_3$] the structures are intermediate between octahedral and trigonal prismatic if the ligands are not of the dithiolene type.[2] The ideal co-ordination geometry may be described by the twist angle, θ, between opposite triangular faces where $\theta = 0°$ for a trigonal prism and $\theta = 60°$ for an octahedron. Consideration of ligand–ligand repulsions predicts small values of θ for ligands with a small ' bite ', b, and more octahedral geometry for ligands with larger values of b. This type of discussion was extended by Avdeef and Fackler [3] and a large number of examples were presented to illuminate the discussion which spanned a large number of ligands, central ions, and charge types. We thus thought it worthwhile to examine a series of compounds which are iso-electronic (excluding f electrons), have the same ligand, the same total charge, and only differ in the radius of the central ion.

We have recently reported the preparation [4] of the series $[Ln\{P(C_6H_{11})_2S_2\}_3]$ for Ln = Pr—Lu and determined the structures of the praseodymium and samarium compounds.[5] X-Ray powder diffraction patterns showed that the complexes for Sm–Lu are isomorphous, hence the structural changes along the series promised to be small. This offered the possibility of studying the effect of systematically changing the ionic radius of the central ion, and hence the ratio of ligand bite to bond length, on the twist angle θ. This series of compounds have the added advantage that they are well described in this way as they have almost perfect D_3 symmetry, whereas many similar compounds would be better described in terms of rotations about the individual ligand two-fold axes.[6]

A further stimulus to carry out this investigation was the fact that there exist few examples of structures with θ between 0 and 30°, *i.e.* the trigonal prismatic extreme and the midpoint of the D_{3d}—D_{3h} reaction co-ordinate as pointed out by Muetterties and Guggenberger.[7]

We thus report the structures of the title compounds herein, and their comparison with the known structures of the praseodymium and samarium analogues.[5]

EXPERIMENTAL

Suitable crystals for X-ray studies were prepared by allowing the metal ions as the chloride to diffuse towards the ammonium salt of the ligand, $P(C_6H_{11})_2S_2^-$,[8] in ethanol solution, the initial solutions being in opposite arms of a U tube arrangement. After 2—3 weeks crystals with linear dimensions up to 1 mm had formed and were isolated by decantation, washed with ethanol, then diethyl ether and dried *in vacuo*.

TABLE 1

Crystallographic data for $[Ln\{P(C_6H_{11})_2S_2\}_3]$

Compound	$[Dy\{P(C_6H_{11})_2S_2\}_3]$	$[Lu\{P(C_6H_{11})_2S_2\}_3]$
M	946.7	959.3
Crystal size/mm	0.15 × 0.23 × 0.26	0.16 × 0.21 × 0.28
Crystal system	Triclinic	Triclinic
a/Å	9.661(2)	9.659(2)
b/Å	11.449(2)	11.399(1)
c/Å	20.553(3)	20.532(3)
α/°	85.88(1)	85.89(1)
β/°	77.32(1)	77.09(1)
γ/°	84.76(1)	84.80(1)
U/Å^3	2 205.5(6)	2 191.2(6)
Space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
D_c/g cm^{-3}	1.43	1.45
F(000)	978	988
Wavelength/Å	0.710 69	0.710 69
Reflections measured	4 920 ($+h$, $\pm k$, $\pm l$)	5 785 ($+h$, $\pm k$, $\pm l$)
Reflections $I < 3\sigma$	597	629
$(\sin\theta/\lambda)_{max.}$	0.50	0.54
μ/cm^{-1}	21.6	27.7
R	0.042	0.039
R'	0.058	0.055
Goodness of fit	3.8	3.8

X-Ray measurements were carried out with a Syntex $P2_1$ automatic four-circle diffractometer using niobium-filtered Mo radiation (λ = 0.710 69 Å). Intensities were measured using θ—2θ scans and backgrounds estimated by analysis of the scan profile.[9] A numerical absorption correction was applied using a crystal form accurately measured by means of a special telescope mounted on the 2θ arm of the diffractometer.

Crystal data are presented in Table 1. Computer programs for data reduction and structure analysis were taken from the ' *X*-ray '72 ' program system.[10] The prespective drawing was prepared with the program ORTEP.[11] Scattering factors for the neutral atoms were taken from Cromer and Mann,[12] and anomalous scattering coefficients from Cromer and Liberman.[13]

The structures were solved using the published atomic co-ordinates for the analogous samarium compound [5] as the starting model and refining these by block-diagonal least squares. The function minimised was $D = \Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2$, σ being the estimated standard deviation of the structure factor derived from counting statistics. In the final cycle non-carbon atoms were refined anisotropically, and carbon atoms isotropically. Hydrogen atoms were not included in the model. The resulting atomic co-ordinates are reported in Table 2 and calculated bond lengths and angles in Table 3. Tables of temperature factors and observed and calculated structure factors are available as Supplementary Publication No. SUP 22753 (44 pp.).*

TABLE 2

Atomic co-ordinates for $[Dy\{P(C_6H_{11})_2S_2\}_3]$ and $[Lu\{P(C_6H_{11})_2S_2\}_3]$ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
(*a*) $[Dy\{P(C_6H_{11})_2S_2\}_3]$			
Dy	0.260 50(4)	0.006 52(3)	0.249 19(2)
P(1)	0.576 8(2)	0.053 8(2)	0.157 0(1)
S(1)	0.395 5(2)	0.070 8(2)	0.122 3(1)
S(2)	0.540 4(2)	0.005 0(2)	0.255 3(1)
P(2)	0.096 4(2)	0.194 2(2)	0.361 5(1)
S(3)	0.127 0(3)	0.228 6(2)	0.262 0(1)
S(4)	0.181 3(2)	0.033 1(2)	0.384 2(1)
P(3)	0.103 1(2)	−0.230 2(2)	0.230 1(1)
S(5)	0.041 1(2)	−0.065 2(2)	0.200 5(1)
S(6)	0.276 6(2)	−0.233 5(2)	0.270 0(1)
C(1)	0.704(1)	−0.055 9(9)	0.110 5(5)
C(2)	0.637(1)	−0.176(1)	0.118 2(6)
C(3)	0.747(1)	−0.270(1)	0.081 7(7)
C(4)	0.795(1)	−0.232(1)	0.006 7(7)
C(5)	0.858(1)	−0.112(1)	−0.002 0(6)
C(6)	0.749(1)	−0.015(1)	0.035 2(6)
C(7)	0.658(1)	0.195 2(9)	0.142 2(5)
C(8)	0.809(1)	0.180(1)	0.158 1(6)
C(9)	0.877(1)	0.303(1)	0.143 8(6)
C(10)	0.779(2)	0.396(1)	0.186 2(7)
C(11)	0.628(2)	0.411(1)	0.169 2(7)
C(12)	0.559(1)	0.288(1)	0.183 4(7)
C(13)	0.178(1)	0.304(1)	0.398 7(5)
C(14)	0.338(1)	0.299(1)	0.369 8(6)
C(15)	0.409(1)	0.390(1)	0.403 4(7)
C(16)	0.337(2)	0.514(1)	0.392 6(7)
C(17)	0.178(1)	0.521(1)	0.420 2(6)
C(18)	0.107(1)	0.428(1)	0.386 8(6)
C(19)	−0.095(1)	0.206 9(9)	0.397 6(5)
C(20)	−0.124(1)	0.201(1)	0.475 6(6)
C(21)	−0.288(1)	0.213(1)	0.504 4(6)
C(22)	−0.331(2)	0.119(1)	0.401 9(7)
C(23)	−0.362(2)	0.117(1)	0.478 8(7)
C(24)	−0.169(1)	0.109(1)	0.373 0(6)
C(25)	−0.043(1)	−0.291 6(9)	0.291 6(5)
C(26)	−0.081(1)	−0.217(1)	0.352 8(6)
C(27)	−0.206(1)	−0.270(1)	0.406 5(7)
C(28)	−0.336(2)	−0.277(1)	0.376 9(7)
C(29)	−0.298(2)	−0.354(1)	0.314 1(7)
C(30)	−0.175(1)	−0.301(1)	0.260 9(6)
C(31)	0.142(1)	−0.321 5(9)	0.157 6(5)
C(32)	0.174(1)	−0.454(1)	0.178 1(6)
C(33)	0.202(1)	−0.529(1)	0.114 4(6)
C(34)	0.324(1)	−0.481(1)	0.061 1(7)
C(35)	0.292(1)	−0.350(1)	0.041 5(7)
C(36)	0.265(1)	−0.276(1)	0.104 5(6)

TABLE 2 (*Continued*)

(*b*) $[Lu\{P(C_6H_{11})_2S_2\}_3]$			
Lu	0.260 80(3)	0.006 28(3)	0.249 04(2)
P(1)	0.574 2(2)	0.052 8(2)	0.157 67(9)
S(1)	0.392 5(2)	0.066 9(2)	0.123 4(1)
S(2)	0.535 1(2)	0.004 8(2)	0.256 20(9)
P(2)	0.098 6(2)	0.193 0(2)	0.360 37(9)
S(3)	0.132 8(2)	0.226 4(2)	0.260 3(1)
S(4)	0.182 0(2)	0.030 1(2)	0.382 12(9)
P(3)	0.104 0(2)	−0.228 0(2)	0.230 4(1)
S(5)	0.042 2(2)	−0.061 4(2)	0.202 3(1)
S(6)	0.278 5(2)	−0.230 5(2)	0.269 2(1)
C(1)	0.702 5(8)	−0.057 6(6)	0.111 3(4)
C(2)	0.637 9(9)	−0.177 3(7)	0.118 5(4)
C(3)	0.747 5(9)	−0.271 4(7)	0.081 9(4)
C(4)	0.796(1)	−0.232 9(8)	0.006 5(5)
C(5)	0.859(1)	−0.111 8(7)	−0.001 9(4)
C(6)	0.747 7(9)	−0.015 1(7)	0.036 2(4)
C(7)	0.655 6(8)	0.194 5(6)	0.142 6(4)
C(8)	0.805 6(9)	0.180 8(7)	0.158 4(4)
C(9)	0.872(1)	0.304 6(7)	0.145 0(4)
C(10)	0.773(1)	0.398 3(9)	0.186 3(5)
C(11)	0.624(1)	0.411 4(9)	0.168 6(5)
C(12)	0.556(1)	0.289 1(8)	0.182 6(5)
C(13)	0.178 6(8)	0.303 2(6)	0.398 0(4)
C(14)	0.340 9(9)	0.297 3(7)	0.369 5(4)
C(15)	0.410(1)	0.389 7(8)	0.403 1(4)
C(16)	0.340(1)	0.514 2(8)	0.392 1(5)
C(17)	0.180(1)	0.520 4(8)	0.419 8(4)
C(18)	0.108 3(9)	0.427 6(7)	0.386 2(4)
C(19)	−0.094 1(8)	0.207 2(6)	0.396 5(4)
C(20)	−0.123 3(9)	0.201 1(7)	0.474 7(4)
C(21)	−0.287 2(9)	0.214 6(7)	0.503 4(4)
C(22)	−0.330(1)	0.120 6(8)	0.401 0(5)
C(23)	−0.361(1)	0.117 5(8)	0.478 1(5)
C(24)	−0.166 6(9)	0.108 1(7)	0.372 2(4)
C(25)	−0.042 7(8)	−0.291 6(6)	0.292 0(4)
C(26)	−0.080 4(9)	−0.216 0(7)	0.353 9(4)
C(27)	−0.204(1)	−0.271 3(8)	0.407 7(5)
C(28)	−0.336(1)	−0.276 8(8)	0.378 6(5)
C(29)	−0.298(1)	−0.354 2(9)	0.315 1(5)
C(30)	−0.174 3(9)	−0.298 9(7)	0.261 9(4)
C(31)	0.140 8(8)	−0.319 2(6)	0.157 6(4)
C(32)	0.172 2(9)	−0.452 0(7)	0.177 7(4)
C(33)	0.199(1)	−0.525 9(8)	0.113 7(4)
C(34)	0.323(1)	−0.479 3(8)	0.060 3(5)
C(35)	0.293(1)	−0.348 7(8)	0.040 8(5)
C(36)	0.266 7(9)	−0.273 2(7)	0.103 7(4)

RESULTS AND DISCUSSION

In all three complexes, $[Ln\{P(C_6H_{11})_2S_2\}_3]$ where Ln = Sm, Dy, or Lu, the metal atoms are bonded to six sulphur atoms as shown in Figure 1. The metal–sulphur bond lengths (Table 3) decrease with the ionic radius of the metal ion, the bond to lutecium being the shortest Ln–S bond observed to date (2.629 Å). This bond shortening is accompanied by a concomitant reduction in the S–P–S angles of the chelate rings (112.8 to 111.8 to 110.7°) while the angles at sulphur remain essentially unchanged. The metal atom is in the plane described by the three phosphorus atoms of the ligands. The four-membered chelate rings defined by the metal, one phosphorus and two sulphur atoms are planar and are tilted with respect to the metal–phosphorus plane (Table 4). The similarity of these three tilt angles in each case serves to demonstrate the presence of the almost perfect three-fold axis to be discussed below.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

The co-ordination polyhedron may best be described as intermediate between an octahedron and a trigonal prism, having nearly D_3 symmetry. In previous discussions of the expected geometry of [M(bidentate)$_3$] compounds where the ligands are not dithiolene in character, it has proved possible to predict the deviation from octahedral symmetry with reasonable precision by calculating the minimum ligand–ligand repulsion energy.[2,3]

TABLE 3

Bond lengths (Å) and angles (°) with standard deviations in parentheses for [Ln{P(C$_6$H$_{11}$)$_2$S$_2$}$_3$] where Ln = Sm, Dy, and Lu

	Ln = Sm	Ln = Dy [a]	Ln = Lu [b]
(*a*) Distances			
Ln–S(1)	2.781(6)	2.730(2)	2.681(2)
Ln–S(2)	2.787(7)	2.733(2)	2.685(2)
Ln–S(3)	2.785(6)	2.747(2)	2.696(2)
Ln–S(4)	2.790(6)	2.743(2)	2.694(2)
Ln–S(5)	2.790(7)	2.745(3)	2.698(2)
Ln–S(6)	2.796(6)	2.746(2)	2.697(2)
P(1)–S(1)	2.007(9)	2.019(3)	2.021(3)
P(1)–S(2)	2.032(8)	2.020(3)	2.018(3)
P(1)–C(1)	1.83(2)	1.84(1)	1.840(7)
P(1)–C(7)	1.82(2)	1.84(1)	1.836(8)
P(2)–S(3)	2.018(8)	2.016(3)	2.020(3)
P(2)–S(4)	2.005(8)	2.016(3)	2.017(3)
P(2)–C(13)	1.81(2)	1.84(1)	1.832(9)
P(2)–C(19)	1.85(2)	1.84(1)	1.840(8)
P(3)–S(5)	2.033(8)	2.022(3)	2.021(3)
P(3)–S(6)	2.007(9)	2.018(4)	2.016(3)
P(3)–C(25)	1.82(2)	1.83(1)	1.841(7)
P(3)–C(31)	1.83(2)	1.83(1)	1.833(8)
S(1) · · · S(2)	3.371(9)	3.345(3)	3.326(3)
S(3) · · · S(4)	3.346(8)	3.340(3)	3.320(3)
S(5) · · · S(6)	3.349(9)	3.341(3)	3.321(3)
(*b*) Angles			
S(1)–Ln–S(2)	74.5(2)	75.52(7)	76.60(6)
S(1)–Ln–S(3)	89.9(2)	89.45(7)	89.19(6)
S(1)–Ln–S(4)	152.4(2)	153.54(7)	154.97(7)
S(1)–Ln–S(5)	90.6(2)	89.78(7)	89.42(7)
S(1)–Ln–S(6)	111.7(2)	110.98(7)	110.03(6)
S(2)–Ln–S(3)	111.8(2)	111.27(8)	110.69(7)
S(2)–Ln–S(4)	90.8(2)	90.18(7)	89.69(6)
S(2)–Ln–S(5)	152.5(2)	153.29(7)	154.68(6)
S(2)–Ln–S(6)	90.2(2)	89.44(7)	88.94(6)
S(3)–Ln–S(4)	73.8(2)	74.94(6)	76.03(6)
S(3)–Ln–S(5)	90.6(2)	90.38(7)	89.78(7)
S(3)–Ln–S(6)	153.0(2)	154.37(7)	155.60(6)
S(4)–Ln–S(5)	111.3(2)	111.15(7)	110.27(6)
S(4)–Ln–S(6)	91.1(2)	90.64(6)	90.23(6)
S(5)–Ln–S(6)	73.7(2)	74.95(7)	75.99(6)
Ln–S(1)–P(1)	86.5(2)	86.4(1)	86.30(9)
Ln–S(2)–P(1)	85.8(3)	86.3(1)	86.26(9)
Ln–S(3)–P(2)	86.8(2)	86.55(9)	86.59(8)
Ln–S(4)–P(2)	86.9(2)	86.66(9)	86.70(8)
Ln–S(5)–P(3)	87.0(3)	86.7(1)	86.6(1)
Ln–S(6)–P(3)	87.3(2)	86.73(9)	86.72(9)
S(1)–P(1)–S(2)	113.1(3)	111.8(1)	110.8(1)
S(1)–P(1)–C(1)	110.2(8)	109.9(4)	109.8(3)
S(1)–P(1)–C(7)	108.5(8)	108.5(4)	109.4(3)
S(2)–P(1)–C(1)	108.1(7)	109.0(4)	109.3(2)
S(2)–P(1)–C(7)	109.0(6)	109.9(4)	110.1(3)
C(1)–P(1)–C(7)	107.7(9)	107.6(5)	107.3(3)
S(3)–P(2)–S(4)	112.5(3)	111.8(1)	110.7(1)
S(3)–P(2)–C(13)	110.1(7)	109.5(3)	109.8(2)
S(3)–P(2)–C(19)	109.0(9)	108.8(4)	109.3(3)
S(4)–P(2)–C(13)	109.2(8)	108.9(4)	109.8(3)
S(4)–P(2)–C(19)	109.7(8)	110.0(3)	110.4(2)
C(13)–P(2)–C(19)	106(1)	107.7(5)	106.9(3)
S(5)–P(3)–S(6)	112.0(4)	111.6(1)	110.7(1)
S(5)–P(3)–C(25)	108.4(7)	109.5(3)	109.6(2)
S(5)–P(3)–C(31)	110.0(7)	108.6(4)	109.2(3)
S(6)–P(3)–C(25)	109.4(8)	109.5(4)	110.3(3)
S(6)–P(3)–C(31)	109.8(8)	109.8(4)	110.2(3)
C(25)–P(3)–C(31)	107(1)	107.8(5)	106.8(3)

[a] For cyclohexyl rings C–C 1.51(2)—1.59(2) Å and C–C–C 108(1)—113(1)°. [b] For cyclohexyl rings C–C 1.52(1)—1.59(1) Å and C–C–C 108.7(6)—112.9(7)°.

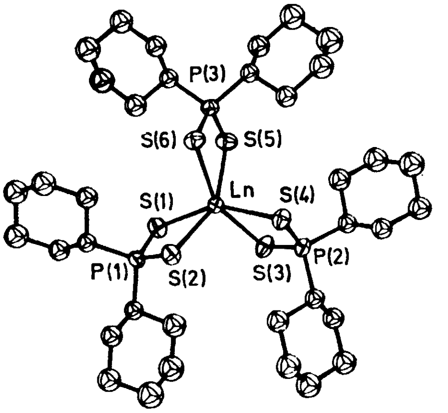

FIGURE 1 The [Ln{P(C$_6$H$_{11}$)$_2$S$_2$}$_3$] molecule viewed along the 'three-fold' axis

The most important parameter to determine the distortion is the ratio of the ligand 'bite', *b*, to the M–S bond length, *a*. This is quoted as *b*/*a* in Table 5 where a number of other parameters as proposed by Avdeef and Fackler[3] are presented. The distortion is expressed as the trigonal-twist angle, θ, measured as the angle between opposite triangular faces of edge *s*, which has a value of 0° for a trigonal prism, and 60° for a regular octahedron.

TABLE 4

Angles (°) between the Ln–S–P–S rings and the LnP$_3$ plane

	Ln = Sm	Ln = Dy	Ln = Lu
Ln, S(1), P(1), S(2)	72.7	72.2	71.4
Ln, S(3), P(2), S(4)	71.2	70.9	70.3
Ln, S(5), P(3), S(6)	71.5	70.9	70.0

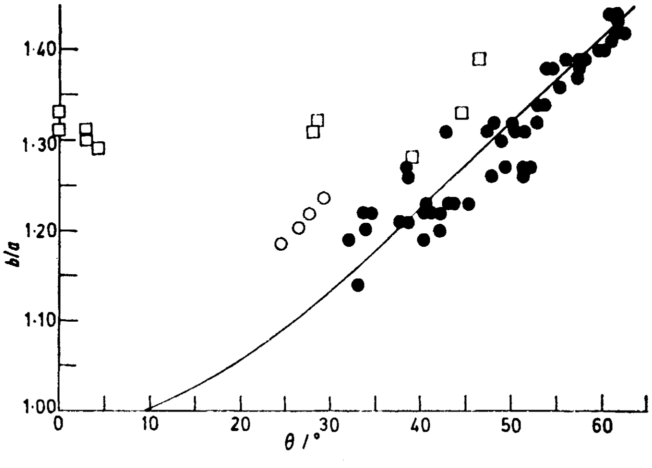

FIGURE 2 Trigonal twist angle, θ, as a function of *b*/*a*: minimum repulsion energy (—), normal tris bidentates (●), 1,2-dithiolene complexes (□), this work (○)

The solid line in Figure 2 shows the correlation between *b*/*a* and θ for the minimum repulsion calculated using the expression given by Avdeef and Fackler.[3] The fit of experimental results is demonstrated by the solid points, and the non-fit of dithiolene complexes by the squares (all results are taken from ref. 3). The open circles represent the four structures under discussion and, although they have the same slope as the theoretical curve, they lie too far to the left. The calculated and observed values of θ for the observed values of b/a are also reported in Table 5. We thus observe that the experimental value for θ is *ca.* 12° lower than the theoretical value in each case.

This is a large discrepancy, being double the maximum deviation from the theoretical curve previously observed for a non-dithiolene ligand.[2,3] It is significant that deviations of this type have been used as evidence in the literature to infer the existence of supplementary π bonding. For example the 1,2-dithiolene complex $[Zr(S_2C_6H_4)_3]^{2-}$ [14] is not trigonal prismatic where strong π bonding is to be accepted,[15] but rather, distorted towards an octahedron. However, the trigonal-twist angle is less than expected from ligand–ligand repulsions by 11°. This was interpreted as evidence for some residual π contribution to the M–S bonds as had previously been proposed for $[Mo\{S_2C_2(CN)_2\}_3]^{2-}$ and $[W\{S_2C_2(CN)_2\}_3]^{2-}$.[16] While the above reasoning may indeed be correct, we must point out that the same situation exists in the present case where π bonding is not allowed if we accept the normal molecular-orbital description of the π orbitals of 1,1-dithiolatoligands.[17]

TABLE 5

Structural parameters for $[Ln\{P(C_6H_{11})_2S_2\}_3]$ *

Ln	a	b	s	h	t	d	s/h	$\theta_{obs.}$	$\theta_{calc.}$	b/a	s/a
Sm	2.788	3.355	3.965	3.188	4.611	5.417	1.244	26.4	37.6	1.203	1.422
Dy	2.741	3.342	3.875	3.166	4.521	5.338	1.224	27.7	39.3	1.219	1.414
Lu	2.692	3.322	3.791	3.133	4.419	5.257	1.210	29.2	40.9	1.234	1.408

* Parameters are as defined in ref. 3.

One might suggest that the 12° discrepancy here is due to steric interaction between adjacent cyclohexyl rings, however molecular models show that deviations with opposite sign would be more likely. It is tempting to attribute the distortion to the effect of packing forces on the disc-like molecules tending to flatten the molecule as a whole. This process would produce the desired effect and should not require excessive energy as the minimum in the repulsion potential is rather flat for small values of b/a, especially on the low θ side. However, there are no very close contacts between neighbouring molecules to confirm this.

It is interesting to comment at this point on the previously published structure of $[Pr\{P(C_6H_{11})_2S_2\}_3]$.[5] Although the structure may be discussed in terms of the average twist angle and be considered as part of the same series as above, it is better considered in terms of the individual ligand distortions from a trigonal prism. To form a regular octahedron requires a twist of 35.3° around the two-fold axis of each ligand. In the molecules discussed above which have effective D_3 symmetry the ligands are twisted on average by 18.2, 18.7, and 19.4° for Sm, Dy, and Lu respectively. However, in the praseodymium compound one of the ligands is twisted by 30.7° which is close to the octahedral limit and the other two are twisted by only 9.7 and 11.1° respectively which is close to the trigonal prismatic limit of 0°.

We are currently investigating the structures of similar complexes of the lanthanides and actinides, and their early transition-metal analogues in the hope of finding the origin of the rather unexpected geometry found for the above series of complexes.

We thank the Swiss National Science Foundation for financial support.

[9/1516 *Received, 24th September*, 1979]

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