Inorganica Chimica Acta, *128* (1987) 283–287

The Preparation and Crystal Structures of [$Ln(S_2PEt_2)_4$][Ph_4As] (Ln = La, Er)

A. ALAN PINKERTON

Department of Chemistry, University of Toledo, Toledo, Ohio 43606, U.S.A.

DIETER SCHWARZENBACH

Institut de Cristallographie, BSP, 1015 Lausanne-Dorigny, Switzerland

and STAVROS SPILIADIS

Institut de Chimie Minérale et Analytique, 3 place du Château, 1005 Lausanne, Switzerland

(Received September 18, 1986)

Abstract

The title compounds were prepared from the metal chlorides, NaS_2PEt_2 and Ph_4AsCl in ethanol. The crystal structures have been determined from diffractometer data. [$La(S_2PEt_2)_4$][Ph_4As]: triclinic, space group $P\bar{1}$, with $a = 10.748(3)$, $b = 15.028(6)$, $c = 16.544(6)$ Å, $\alpha = 84.86(3)$, $\beta = 84.04(3)$, $\gamma = 84.73(4)°$, $R = 0.069$.

[$Er(S_2PEt_2)_4$][Ph_4As]: isomorphous to above with $a = 10.715(3)$, $b = 15.084(2)$, $c = 16.410(3)$ Å, $\alpha = 85.11(1)$, $\beta = 84.59(2)$, $\gamma = 83.94(2)°$, $R = 0.066$.

The metal ions are surrounded by eight sulphur atoms (La–S = 2.981 Å, Er–S = 2.859 Å) in an almost perfect D_{2d} dodecahedral arrangement. Only minor distortion towards a square antiprism is observed.

Introduction

We have prepared and characterized a number of complexes of the tervalent lanthanides with the chelating sulphur donor dithiophosphinate, $R_2PS_2^-$, and dithiophosphate, $(RO)_2PS_2^-$, ligands [1]. From our previous studies of the eight coordinate tetrakis complexes, it appeared that the phosphate ligands (OMe, OEt, OPr^i) strongly favoured dodecahedral coordination, whereas phosphinate ligands (Me) produced significant distortion towards a square antiprism (albeit still best described as dodecahedra).

In order to determine whether the origin of the latter distortion lies in electronic or steric factors, we have prepared diethyldithiophosphinate ($Et_2PS_2^-$) complexes which should have electronic properties similar to the methyl analogues but with some difference in the steric requirements. We report herein the structures of the lanthanum and erbium complexes.

Experimental

The two complexes were prepared by a similar route to that used for the methyl analogues [2] from $LnCl_3$, NaS_2PEt_2 and Ph_4AsCl. The lanthanum complex requires no special precautions, however, the erbium analogue was prepared under argon using anhydrous materials. Crystals suitable for X-ray analysis were grown from isopropanol solutions. The lanthanum compound was studied in the air and the erbium analogue in a sealed capillary under argon.

X-ray Measurements and Structure Determination

X-ray intensity measurements were carried out with an Enraf-Nonius CAD4 automatic diffractometer and corrected for absorption as before [3]. Crystal data, measurement methods, structure determination and refinement are summarized in Table I. Scattering factors for the neutral atoms were taken from Cromer and Mann [4] and anomalous scattering coefficients from Cromer and Liberman [5]. Computer programs for data reduction and structure solution were taken from the XRAY-72 program system [6]. The figure was prepared with the aid of ORTEP [7] and the coordination polyhedra analyzed with the program POLY [8].

The structure of the lanthanum complex was solved by conventional Patterson and Fourier methods and refined by least squares in two blocks. The erbium analogue is isomorphous, hence, starting parameters were taken from the previous structure and refined in the same way. In the final cycles, all heavy atoms were refined with anisotropic thermal parameters and the carbon atoms with isotropic ones. No hydrogen atoms were included in the model.

Final atomic coordinates are given in Tables II and III. Derived bond lengths and angles are reported in Table IV. A perspective view of one of the complexes is given in Fig. 1 with the carbon atoms reduced in

0020-1693/87/$3.50

TABLE I. Summary of Crystal Data, Intensity Measurements, Structure Solution and Refinement for $[Ln(S_2PEt_2)_4][Ph_4As]$

Formula	$LaS_8P_4AsC_{40}H_{60}$	$ErS_8P_4AsC_{40}H_{60}$
Molecular weight	1135.16	1163.51
Crystal dimensions (mm)	0.28 x 0.15 x 0.12	0.30 x 0.16 x 0.13
Crystal system	triclinic	triclinic
a (Å)	10.748(3)	10.715(3)
b (Å)	15.028(6)	15.084(2)
c (Å)	16.544(6)	16.410(3)
α (°)	84.86(3)	85.11(1)
β (°)	84.04(3)	84.59(2)
γ (°)	84.73(4)	83.94(2)
U (Å^3)	2637.7	2616.5
Space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
D_c (g cm^{-3})	1.43	1.48
$F(000)$	1156	1178
Radiation	Mo Kα	Mo Kα
λ (Å)	0.71069	0.71069
μ (cm^{-1})	18.84	27.05
Scan method	$2\theta-\theta$	$2\theta-\theta$
$(\sin\theta/\lambda)_{max}$	0.55	0.53
No. unique reflections	7348	6393
No. reflections < 3σ	2698	3684
No. observations/No. variables	22.0^a	17.0^a
Structure solution	Patterson & Fourier	refinement only
Refinement method	blocked matrix least-squares	blocked matrix least-squares
Function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
w	$1/\sigma^2$	$1/\sigma^2$
R	0.069	0.066
R_w	0.088	0.063
Goodness of fit	2.34	1.31

^{a}Only those reflections of $I < 3\sigma$ with $|F_c| > |F_o|$ were included in the refinement.

size for clarity. Tables of observed and calculated structure factors and thermal parameters are available as supplementary material.

Results and Discussion

As anticipated from previous studies of the reactions of dithiophosphinate and dithiophosphate ligands with tervalent lanthanide ions [1] the tetrakis complexes are formed in alcoholic solution. With the ethyl substituted ligands, complexes of the heavy ions are moisture sensitive and must be prepared from anhydrous starting materials under argon as previously observed for the methyl [2, 9] and methoxy [1] analogues.

We chose to study two molecules as representative of light and heavy lanthanides because, although we have yet to observe such behaviour in the solid, NMR studies have shown them to have different structures in solution [9–11].

The crystal structures confirm the expected coordination number of eight. The average Ln–S bond lengths are 2.981 (La) and 2.859 (Er) Å, close to values obtained for similar eight coordinate complexes [1]. As expected from the calculations of Blight and Kepert [12], and in agreement with our previous observations on complexes of this type [1], the coordination polyhedra are best described as a D_{2d} dodecahedron (*mmmm* isomer). For ligands with normalized 'bites', b, between 1.00 and 1.15 (here b = 1.11 (La) and 1.14 (Er)) we may anticipate a distortion towards a D_2 square antiprism (*ssss* isomer) [12]. We have analyzed the polyhedra using the program POLY [8] based on the least squares approach of Dollase [13]. In the present two structures there is only minor distortion, the rms deviations from the ideal dodecahedron are 0.052 (La) and 0.044 (Er) in agreement with previous findings for this type of molecule [1]. The more significant deviation in the case of the methyl analogues [14] is thus likely to be due to steric effects rather than electronic. We note, however, that analogous complexes of thorium(IV) (R = Me, C_6H_{11}) do not exhibit this distortion either [15].

The ideal polyhedron has point symmetry D_{2d}, thus there are two different coordination sites, A and B. Here the A sites are occupied by S1, S3, S6, S7 and the B sites by S2, S4, S5, S8. It is to be noted that the M–L_A bond lengths are longer than M–L_B as

TABLE II. Atomic Coordinates for $[La(S_2PEt_2)_4][Ph_4As]$

Atom	*x*	*y*	*z*
As	0.9390(1)	0.68939(9)	0.26005(9)
La	0.30837(8)	0.22940(5)	0.24448(5)
P(1)	0.3181(4)	0.1266(3)	0.4484(2)
P(2)	0.4485(5)	0.1796(3)	0.0467(3)
P(3)	−0.0061(5)	0.1881(3)	0.2221(4)
P(4)	0.4733(5)	0.4226(3)	0.2568(3)
S(1)	0.4252(4)	0.0802(3)	0.3534(2)
S(2)	0.2173(5)	0.2411(3)	0.4192(3)
S(3)	0.4727(5)	0.0992(3)	0.1463(3)
S(4)	0.3304(5)	0.2866(3)	0.0665(3)
S(5)	0.1250(5)	0.0924(3)	0.2472(3)
S(6)	0.0476(4)	0.3088(3)	0.2183(3)
S(7)	0.2893(5)	0.4273(3)	0.2605(4)
S(8)	0.5529(4)	0.2976(4)	0.2521(4)
C(1)	0.409(2)	0.140(1)	0.530(1)
C(2)	0.501(2)	0.209(1)	0.507(1)
C(3)	0.213(2)	0.038(1)	0.491(1)
C(4)	0.125(3)	0.070(2)	0.558(2)
C(5)	0.618(3)	0.212(2)	0.008(2)
C(6)	0.597(3)	0.269(2)	−0.059(2)
C(7)	0.400(2)	0.119(1)	−0.032(1)
C(8)	0.277(2)	0.081(2)	−0.008(1)
C(9)	−0.062(3)	0.177(2)	0.122(2)
C(10)	−0.088(3)	0.078(2)	0.109(2)
C(11)	−0.144(4)	0.168(2)	0.294(2)
C(12)	−0.136(3)	0.191(2)	0.371(2)
C(13)	0.522(3)	0.464(2)	0.355(2)
C(14)	0.451(4)	0.558(2)	0.371(2)
C(15)	0.526(3)	0.499(2)	0.165(2)
C(16)	0.649(5)	0.496(3)	0.149(3)
C(17)	0.794(1)	0.7676(8)	0.2544(8)
C(18)	0.801(1)	0.8613(9)	0.2432(8)
C(19)	0.683(1)	0.913(1)	0.2421(9)
C(20)	0.575(1)	0.879(1)	0.2478(9)
C(21)	0.564(2)	0.786(1)	0.259(1)
C(22)	0.681(1)	0.7285(9)	0.2622(9)
C(23)	0.993(1)	0.6463(9)	0.1569(8)
C(24)	1.106(2)	0.596(1)	0.149(1)
C(25)	1.149(2)	0.564(1)	0.073(1)
C(26)	1.077(2)	0.587(1)	0.007(1)
C(27)	0.962(2)	0.639(1)	0.016(1)
C(28)	0.915(2)	0.667(1)	0.093(1)
C(29)	1.067(1)	0.756(1)	0.290(1)
C(30)	1.129(2)	0.808(1)	0.227(1)
C(31)	1.217(2)	0.866(1)	0.251(1)
C(32)	1.243(2)	0.861(1)	0.331(1)
C(33)	1.184(2)	0.807(1)	0.388(1)
C(34)	1.090(2)	0.751(1)	0.372(1)
C(35)	0.903(1)	0.5961(9)	0.3425(9)
C(36)	0.839(2)	0.618(1)	0.415(1)
C(37)	0.813(2)	0.553(1)	0.478(1)
C(38)	0.856(2)	0.462(1)	0.462(1)
C(39)	0.917(2)	0.442(1)	0.390(1)
C(40)	0.945(2)	0.506(1)	0.327(1)

TABLE III. Atomic Coordinates for $[Er(S_2PEt_2)_4][Ph_4As]$

Atom	*x*	*y*	*z*
As	0.9346(2)	0.6838(1)	0.2612(1)
Er	0.3180(1)	0.22845(5)	0.24666(5)
P(1)	0.3252(6)	0.1297(3)	0.4460(3)
P(2)	0.4604(6)	0.1875(4)	0.0526(3)
P(3)	0.0145(7)	0.1802(4)	0.2201(3)
P(4)	0.4708(6)	0.4177(4)	0.2618(3)
S(1)	0.4375(6)	0.0852(3)	0.3516(3)
S(2)	0.2241(5)	0.2425(3)	0.4120(2)
S(3)	0.4868(6)	0.1059(3)	0.1520(3)
S(4)	0.3321(5)	0.2891(3)	0.0790(3)
S(5)	0.1594(7)	0.0926(3)	0.2403(3)
S(6)	0.0624(5)	0.3033(3)	0.2224(3)
S(7)	0.2871(6)	0.4201(3)	0.2645(3)
S(8)	0.5517(6)	0.2934(3)	0.2581(3)
C(1)	0.414(2)	0.148(1)	0.533(1)
C(2)	0.503(2)	0.218(1)	0.511(1)
C(3)	0.229(2)	0.037(1)	0.487(1)
C(4)	0.123(2)	0.070(2)	0.548(1)
C(5)	0.618(3)	0.227(2)	0.012(2)
C(6)	0.597(4)	0.283(2)	−0.052(2)
C(7)	0.413(2)	0.127(1)	−0.029(1)
C(8)	0.293(2)	0.085(1)	−0.006(1)
C(9)	−0.043(2)	0.169(1)	0.118(1)
C(10)	−0.067(3)	0.071(2)	0.107(2)
C(11)	−0.141(3)	0.157(2)	0.287(2)
C(12)	−0.133(3)	0.179(2)	0.364(2)
C(13)	0.524(2)	0.464(1)	0.355(1)
C(14)	0.447(3)	0.558(2)	0.365(2)
C(15)	0.521(3)	0.490(2)	0.165(2)
C(16)	0.648(3)	0.488(2)	0.157(2)
C(17)	0.783(2)	0.763(1)	0.2558(8)
C(18)	0.795(2)	0.856(1)	0.245(1)
C(19)	0.678(2)	0.914(1)	0.2402(9)
C(20)	0.567(2)	0.876(1)	0.2451(9)
C(21)	0.559(2)	0.785(1)	0.2565(9)
C(22)	0.669(2)	0.728(1)	0.2611(9)
C(23)	0.986(2)	0.639(1)	0.153(1)
C(24)	1.105(2)	0.586(1)	0.150(1)
C(25)	1.150(2)	0.559(1)	0.070(1)
C(26)	1.082(2)	0.589(1)	0.003(1)
C(27)	0.962(2)	0.640(1)	0.011(1)
C(28)	0.910(2)	0.667(1)	0.089(1)
C(29)	1.064(2)	0.748(1)	0.2901(9)
C(30)	1.126(2)	0.803(1)	0.231(1)
C(31)	1.212(2)	0.858(1)	0.254(1)
C(32)	1.240(2)	0.859(1)	0.334(1)
C(33)	1.176(2)	0.802(1)	0.390(1)
C(34)	1.087(2)	0.747(1)	0.375(1)
C(35)	0.900(2)	0.593(1)	0.3393(9)
C(36)	0.838(2)	0.617(1)	0.4164(9)
C(37)	0.813(2)	0.548(1)	0.479(1)
C(38)	0.851(2)	0.459(1)	0.465(1)
C(39)	0.917(2)	0.434(1)	0.389(1)
C(40)	0.939(2)	0.500(1)	0.327(1)

frequently observed [8]. This asymmetry is not reflected in the P–S bond lengths.

The four membered chelate rings are essentially planar, the average bend about the S——S direction being 4.9° (La) and 5.3° (Er). The angles at sulphur are all close to 90°.

TABLE IV. Selected Bond Lengths and Angles in $[Ln(S_2PEt_2)_4][Ph_4As]$ with Estimated Standard Deviations in Parentheses

	La	Er
Ln–S(1)	3.013(4)	2.911(5)
Ln–S(2)	2.969(4)	2.821(4)
Ln–S(3)	2.987(5)	2.889(5)
Ln–S(4)	2.983(5)	2.821(4)
Ln–S(5)	2.972(5)	2.812(6)
Ln–S(6)	3.002(4)	2.898(5)
Ln–S(7)	2.996(5)	2.911(5)
Ln–S(8)	2.926(5)	2.811(6)
P(1)–S(1)	1.987(6)	1.988(7)
P(1)–S(2)	1.997(6)	1.987(7)
P(1)–C(1)	1.79(2)	1.84(2)
P(1)–C(3)	1.87(2)	1.87(2)
P(2)–S(3)	1.979(7)	1.982(7)
P(2)–S(4)	1.984(7)	1.996(7)
P(2)–C(5)	1.97(3)	1.90(3)
P(2)–C(7)	1.80(2)	1.82(2)
P(3)–S(5)	1.967(6)	1.964(6)
P(3)–S(6)	1.947(6)	1.982(6)
P(3)–C(9)	1.85(3)	1.87(2)
P(3)–C(11)	1.83(4)	1.96(3)
P(4)–S(7)	1.967(7)	1.961(8)
P(4)–S(8)	1.996(7)	1.984(8)
P(4)–C(13)	1.93(3)	1.90(2)
P(4)–C(15)	1.89(3)	1.92(3)
As–C(17)	1.87(1)	1.91(2)
As–C(23)	1.90(1)	1.96(2)
As–C(29)	1.91(2)	1.89(2)
As–C(35)	1.90(1)	1.84(1)
S(1)–S(2)	3.316(6)	3.266(7)
S(3)–S(4)	3.313(7)	3.265(7)
S(5)–S(6)	3.286(6)	3.236(6)
S(7)–S(8)	3.286(7)	3.245(8)
S(1)–Ln–S(2)	67.3(1)	69.5(1)
S(1)–Ln–S(3)	69.1(1)	68.4(1)
S(1)–Ln–S(4)	136.3(1)	138.0(1)
S(1)–Ln–S(5)	79.2(1)	78.6(2)
S(1)–Ln–S(6)	136.5(1)	136.4(1)
S(1)–Ln–S(7)	128.6(2)	129.2(2)
S(1)–Ln–S(8)	80.5(1)	79.4(2)
S(2)–Ln–S(3)	136.2(1)	137.7(1)
S(2)–Ln–S(4)	156.4(1)	152.5(1)
S(2)–Ln–S(5)	85.3(1)	88.1(2)
S(2)–Ln–S(6)	83.2(1)	80.7(1)
S(2)–Ln–S(7)	77.6(1)	76.0(1)
S(2)–Ln–S(8)	96.8(2)	97.2(2)
S(3)–Ln–S(4)	67.4(1)	69.7(1)
S(3)–Ln–S(5)	82.7(1)	80.5(2)
S(3)–Ln–S(6)	128.5(1)	130.3(2)
S(3)–Ln–S(7)	136.5(1)	136.5(2)
S(3)–Ln–S(8)	79.9(2)	78.4(2)
S(4)–Ln–S(5)	99.2(1)	98.2(2)
S(4)–Ln–S(6)	77.5(1)	76.7(1)
S(4)–Ln–S(7)	83.1(2)	81.3(1)
S(4)–Ln–S(8)	88.0(2)	88.9(2)
S(5)–Ln–S(6)	66.7(1)	69.0(2)
S(5)–Ln–S(7)	135.0(1)	136.8(2)
S(5)–Ln–S(8)	156.9(1)	153.9(2)
S(6)–Ln–S(7)	70.1(1)	68.8(2)
S(6)–Ln–S(8)	136.3(1)	137.0(1)
S(7)–Ln–S(8)	67.4(1)	69.1(2)
Ln–S(1)–P(1)	89.3(2)	88.5(2)
Ln–S(2)–P(1)	90.4(2)	91.1(2)
Ln–S(3)–P(2)	89.5(2)	89.0(2)
Ln–S(4)–P(2)	89.5(2)	90.7(2)
Ln–S(5)–P(3)	89.6(2)	91.8(3)
Ln–S(6)–P(3)	89.1(2)	88.9(2)
Ln–S(7)–P(4)	89.5(2)	88.8(2)
Ln–S(8)–P(4)	90.9(2)	91.3(3)
S(1)–P(1)–S(2)	112.7(3)	110.5(3)
S(1)–P(1)–C(1)	111.4(6)	111.9(7)
S(1)–P(1)–C(3)	107.8(7)	106.8(7)
S(2)–P(1)–C(1)	110.0(6)	109.7(6)
S(2)–P(1)–C(3)	110.5(7)	114.1(7)
C(1)–P(1)–C(3)	104.1(9)	103.7(9)
S(3)–P(2)–S(4)	113.4(3)	110.4(3)
S(3)–P(2)–C(5)	104(1)	107.9(9)
S(3)–P(2)–C(7)	110.6(7)	110.4(6)
S(4)–P(2)–C(5)	111.9(9)	112.0(8)
S(4)–P(2)–C(7)	110.9(7)	110.7(7)
C(5)–P(2)–C(7)	106(1)	105(1)
S(5)–P(3)–S(6)	114.3(3)	110.2(4)
S(5)–P(3)–C(9)	110.7(9)	110.9(7)
S(5)–P(3)–C(11)	107(1)	114.7(9)
S(6)–P(3)–C(9)	106.5(9)	108.4(7)
S(6)–P(3)–C(11)	114(1)	114.4(9)
C(9)–P(3)–C(11)	104(2)	97(1)
S(7)–P(4)–S(8)	112.1(3)	110.6(4)
S(7)–P(4)–C(13)	110.2(8)	113.0(8)
S(7)–P(4)–C(15)	106(1)	106(1)
S(8)–P(4)–C(13)	105.5(8)	106.8(7)
S(8)–P(4)–C(15)	113(1)	111.2(8)
C(13)–P(4)–C(15)	111(1)	110(1)
C(17)–As–C(23)	110.7(6)	109.6(7)
C(17)–As–C(29)	107.4(6)	109.0(7)
C(17)–As–C(35)	107.4(6)	106.9(7)
C(23)–As–C(29)	108.2(6)	108.0(7)
C(23)–As–C(35)	113.0(6)	112.0(7)
C(29)–As–C(35)	110.0(6)	111.3(7)

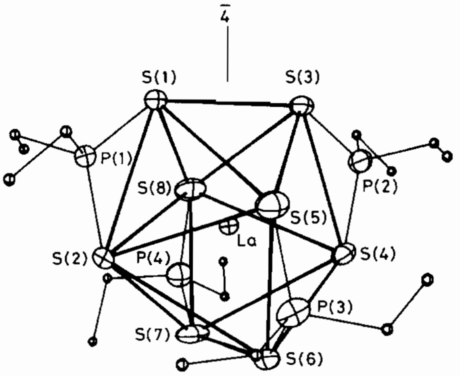

Fig. 1. A perspective view of the complex $[La(S_2PEt_2)_4]^-$ showing the dodecahedral geometry.

The tetraphenylarsonium counterions are unremarkable. They are tetrahedral with bond lengths and angles as expected.

Acknowledgements

We thank the Swiss National Science Foundation and the College of Arts and Sciences of the University of Toledo for financial support.

References

1 S. Spiliadis, A. A. Pinkerton and D. Schwarzenbach, *Inorg. Chim. Acta, 75,* 115 (1983) and refs. therein.

2 A. A. Pinkerton, Y. Meseri and Ch. Rieder, *J. Chem. Soc., Dalton Trans.,* 85 (1978).

3 A. A. Pinkerton and D. Schwarzenbach, *J. Chem. Soc., Dalton Trans.,* 1300 (1980).

4 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A, 34,* 321 (1968).

5 D. T. Cromer and D. Liberman, *J. Chem. Phys., 53,* 1891 (1970).

6 J. M. Stewart, F. A. Kundell and J. C. Baldwin, 'XRAY-72' program system (as modified locally), *Technical Report TR-192,* Computing Science Center, University of Maryland, June, 1972.

7 C. K. Johnson, 'ORTEP', *Report ORNL-3794,* Oak Ridge National Laboratory, Oak Ridge, Tenn., 1971.

8 M. G. B. Drew, *Coord. Chem. Rev., 24,* 179 (1977).

9 S. Spiliadis and A. A. Pinkerton, *J. Chem. Soc., Dalton Trans.,* 1815 (1982).

10 A. A. Pinkerton and W. L. Earl, *J. Chem. Soc., Dalton Trans.,* 267 (1978).

11 S. Spiliadis and A. A. Pinkerton, *Inorg. Chim. Acta, 75,* 125 (1983).

12 D. G. Blight and D. L. Kepert, *Inorg. Chem., 11,* 1556 (1972).

13 W. A. Dollase, *Acta Crystallogr., Sect. A, 30,* 513 (1974).

14 S. Spiliadis, A. A. Pinkerton and D. Schwarzenbach, *J. Chem. Soc., Dalton Trans.,* 1809 (1982).

15 A. A. Pinkerton, A. E. Storey and J. M. Zellweger, *J. Chem. Soc., Dalton Trans.,* 1475 (1981).