

Binuclear complexes of lanthanides with 1,4-bis(diphenylphosphino)butane dioxide

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Abstract

A series of binuclear complexes of a general formula $[(\text{dppbO}_2)\text{Ln}(\text{NO}_3)_3(\mu\text{-dppbO}_2)\text{Ln}(\text{NO}_3)_3(\text{dppbO}_2)]$ ($\text{Ln} = \text{Pr}$ (1), Nd (2), Sm (3), Dy (4), Lu (5)) were prepared by reacting bis(diphenylphosphino)butane dioxide (dppbO_2) with lanthanide nitrates under solvothermal conditions. All compounds were characterized by analytical and spectroscopic techniques, such as infrared spectroscopy and mass spectrometry with electrospray ionization, and their molecular structures were determined by single crystal X-ray diffraction analysis in four cases. In contrast to the majority of lanthanide complexes with bis(diphenylphosphino)ethane dioxide which were previously reported as 2D polymeric networks, the present compounds are strictly molecular. This is evidently manifestation of the longer and flexible ligand backbone that allows a chelating binding mode.

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1. Introduction

Recently we have studied the reactivity of bis(diphenylphosphino)ethane dioxide $\text{Ph}_2\text{P}(\text{O})\text{--CH}_2\text{CH}_2\text{--P}(\text{O})\text{Ph}_2$ (dppeO_2) with lanthanide salts [1]. While bis(diphenylphosphino)methane dioxide (dppmO_2) had already been known to form a range of various chelates with lanthanide cations [2], we have prepared a series of coordination polymers with its one-carbon longer homologue. We have observed different coordination geometries and polymeric architectures, depending on the ancillary non-bridging ligands and the reaction conditions involved.

Our current investigation was targeted on the reactivity of diphosphine dioxide ligands with longer central chains. There have been several publications studying the steric properties of the bidentate diphosphine ligands

in connection with the structural and catalytic features of resulting complexes [3–5]. The $\text{Ph}_2\text{P}(\text{O})\text{--}(\text{CH}_2)_n\text{--P}(\text{O})\text{Ph}_2$ series in particular, provided the opportunity to study the steric effects by the simple variations in n , without significantly affecting the electronic properties of ligands [6]. The oxidized series, $\text{Ph}_2\text{P}(\text{O})\text{--}(\text{CH}_2)_n\text{--P}(\text{O})\text{Ph}_2$, seemed suitable for similar investigations on lanthanides, which are generally coordinated by phosphorus to a lesser extent.

We will show in the following, that in contrast to the observed polymeric nature of dppeO_2 complexes, the reversal to the molecular character was featured in lanthanide complexes of bis(diphenylphosphino)butane dioxide (dppbO_2). These were prepared by the solvothermal reactions of dppbO_2 with lanthanide nitrates and characterized structurally and spectroscopically. Electrospray ionization technique has been used successfully to ionize both non-volatile and thermally labile inorganic compounds for mass spectrometric detection [7] and it proved a valuable tool in the characterization of the prepared lanthanide complexes 1–6.

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2. Results and discussion

The solvothermal synthesis is a variation to the well-known hydrothermal process, in which water is substituted by a general solvent. The hydrothermal and solvothermal methods are widely used in material design and crystal engineering, with the view to obtain the products of desired structure, texture and crystallinity [8–11]. Using solvothermal synthesis, we have successfully prepared good quality crystals of coordination polymers of dppeO₂ with lanthanides [1]. We have therefore used the reaction in an autoclave for the preparation of coordination compounds of dppbO₂. One-day heating of the ligand with a respective lanthanide nitrate in methanol yielded block-shaped crystals of excellent quality. In all cases, the single crystal X-ray diffraction analysis revealed the binuclear complexes of a general formula [(dppbO₂)₂-Ln(NO₃)₃-(μ-dppbO₂)-Ln(NO₃)₃(dppbO₂)] (Ln = Pr (1), Nd (2), Sm (3), Dy (4)) (see Fig. 1). The reaction with Lu(NO₃)₃ · 2H₂O led to a microcrystalline solid, which decomposed to powder on exposure to air, most probably because of a loss of the solvent of crystallization. Even though the lutetium complex was not studied by the X-ray diffraction, its binuclear nature is apparent from the electrospray mass spectra (see Table 3).

The molecular structures of 1–4 are similar to the binuclear complex [(dppeO₂)Lu(NO₃)₃-(μ-dppeO₂)-Lu(NO₃)₃(dppeO₂)] (6), which was isolated as the only molecular compound from the solvothermal reaction of dppeO₂ with lanthanide nitrates [1]. The fact that all other dppeO₂ complexes with lighter lanthanides were polymeric, we ascribed to the effect of the lanthanide contraction. The formation of binuclear com-

pounds with dppbO₂ is obvious throughout the whole rare earth metal series, thus the longer ligand backbone is clearly responsible for the transition from polymeric to molecular complexes.

All compounds combine chelating as well as bridging bonding modes for the bidentate dppbO₂. While the bridging ligands have their P=O groups in an *anti* conformation as they do in their uncoordinated form [12], in chelate rings they naturally adopt the *syn* conformation. Mean deviations from P1–O1–P2–O2 planes are 0.049, 0.049, 0.047, and 0.043 Å for 1–4, respectively. Considering the coordination sphere of the lanthanide cation as being pseudooctahedral, the ligands are meridionally disposed. The selected bond lengths and angles are listed in Table 2. With decreasing ionic radius of Ln³⁺, the oxygen atoms get progressively closer to the cation, with consistent difference of about 0.2 Å in Ln–O(N) and Ln–O(P) distances.

The IR spectra are very similar to those obtained for the dppeO₂ coordination polymers [1]. Again we observe the grouping of bands at 1467–1487, 1291–1323, 1029–1031, and 816–820 cm^{−1}, which we assign to the bidentate nitrate groups, in agreement with previous data [13,14]. The band at 1384–1385 cm^{−1} is also apparent and belongs to the ionic nitrate. According to Lees et al. [14], the NO₃[−] anion is displaced from the complex by Br[−] from the KBr pellet. The most prominent bands are at 1139–1159 cm^{−1} which correspond to the P=O stretching frequency. In the present compounds, they usually appear in pairs, suggesting the chelating and bridging nature of the P=O moieties.

We studied the binuclear complexes of the dppbO₂ ligand 1–5 and the complex 6 with the shorter dppeO₂

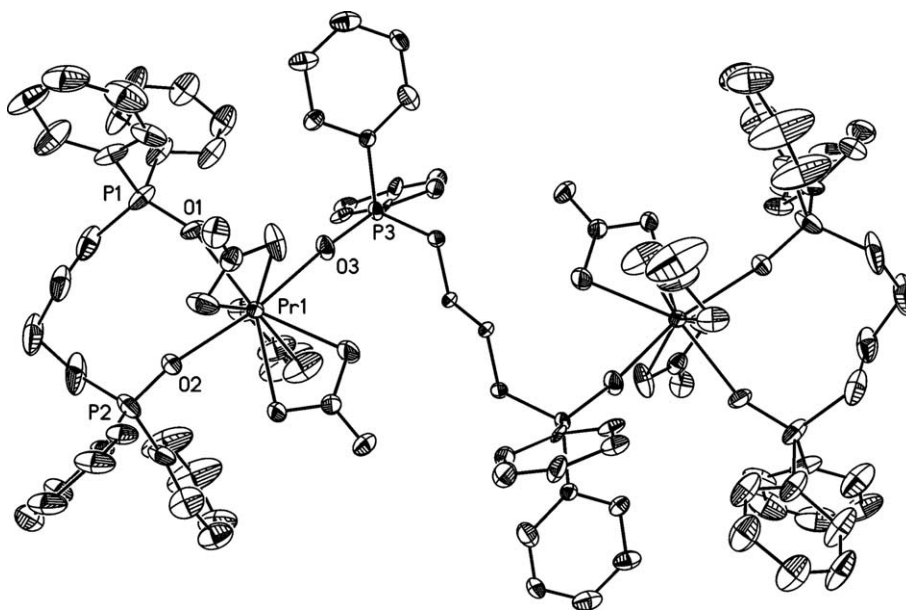


Fig. 1. The molecular structure of [(dppbO₂)Pr(NO₃)₃-(μ-dppbO₂)-Pr(NO₃)₃(dppbO₂)] (1). The thermal ellipsoids were drawn at the 50% probability level and hydrogen atoms were omitted for clarity. The compounds 2–4 are isostructural with 1.

Table 1
Crystal data and structure refinement parameters

	1	2	3	4
Empirical formula	$C_{42}H_{42}N_3O_{12}P_3Pr \cdot C_{0.75}O_{0.75}$	$C_{42}H_{42}N_3O_{12}P_3Nd \cdot C_{0.75}O_{0.75}$	$C_{42}H_{42}N_3O_{12}P_3Sm \cdot C_{0.75}O_{0.75}$	$C_{42}H_{42}N_3O_{12}P_3Dy \cdot C_{0.75}O_{0.75}$
Formula weight	1035.61	1038.94	1045.05	1057.20
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
<i>a</i> (Å)	12.577(3)	12.422(1)	12.432(1)	12.338(1)
<i>b</i> (Å)	17.035(3)	16.931(1)	16.931(1)	16.894(1)
<i>c</i> (Å)	21.789(4)	21.731(2)	21.778(1)	21.787(1)
α (°)	90	90	90	90
β (°)	90.96(3)	90.70(1)	90.89(1)	91.19(1)
γ (°)	90	90	90	90
Volume (Å ³)	4667.6(16)	4570.2(5)	4583.5(3)	4540.1(4)
<i>Z</i>	4	4	4	4
ρ (Mg/m ³)	1.474	1.510	1.514	1.547
μ (mm ⁻¹)	1.210	1.306	1.451	1.817
Reflections collected/unique	24000/8196	27059/8017	41977/8039	39406/7986
Data/parameters	8196/766	8017/771	8039/761	7986/751
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	0.0458/0.1018	0.0341/0.0798	0.0373/0.0784	0.0466/0.0884
<i>R</i> indices (all data)	0.0513/0.1038	0.0459/0.0832	0.0442/0.0807	0.0606/0.0927
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e Å ⁻³)	1.901/−1.390	0.941/−0.780	0.996/−1.111	1.025/−0.598

Table 2
Selected average bond lengths (Å) and angles (°) for prepared compounds and the parent dppbO₂ ligand

	dppbO ₂ ^b	1 (Pr)	2 (Nd)	3 (Sm)	4 (Dy)
Ln–O (to N)		2.579	2.543	2.523	2.472
Ln–O (to P)		2.385	2.354	2.334	2.281
P–O	1.482(2)	1.521	1.510	1.511	1.509
P–C ^a	1.812(2)	1.795	1.787	1.790	1.789
Ln–O–P		162.3	162.3	162.1	161.8
O–P–C ^a	114.9(1)	112.5	112.8	112.8	113.0

^a C is the carbon atom in (CH₂)₄ central moiety; the average value was calculated for both chelating and bridging ligands.

^b The values taken from [12].

ligand by ESI–MS in acetonitrile/water (1:1) solutions to ascertain their stability and ionization and fragmentation pathways (see Fig. 2). Molecular ions of all compounds were not visible in the positive mode most probably because of an easy loss of a nitrate group and a ligand to form the positively charged fragments of the highest observed mass (see Table 3). The signal for $[M - NO_3]^+$ cation was registered as a weak peak in the spectrum of **6**. In the spectra of **1–5**, the signal for $[M - NO_3]^+$ is very weak or absent but the binuclear $[(dppbO_2)_2Ln_2(NO_3)_5]^+$ fragments, formed by further loss of a neutral dppbO₂ ligand, are quite prominent in all compounds and substantiate the existence of the intact binuclear species in solution. The presence of two lanthanide atoms in these ions was clearly demonstrated by the correspondence of measured and theoretical isotope pattern for the Nd, Sm, and Dy (see Fig. 3) complexes. A subsequent loss of a neutral $Ln(NO_3)_3$

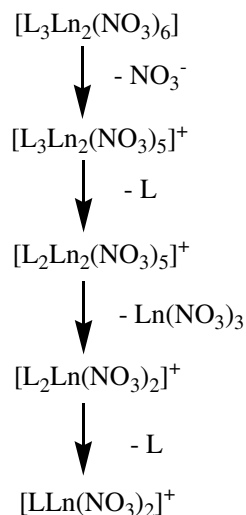


Fig. 2. The fragmentation pathway for the complexes **1–6** in ESI–MS.

Table 3
Electrospray mass spectral data for prepared compounds, m/z (rel. intensity)

Complex	1 (Pr)	2 (Nd)	3 (Sm)	4 (Dy)	5 (Lu)	6 (Lu)
Fragment						
M^+	2028 ^a	2030 ^a	2050 ^a	2074 ^a	2096 ^a	2012 ^a
$[M - NO_3]^+$	1966 ^a	1968 ^a	1988 ^a	2012 ^a	2034 ^a	1950 (1)
$[M - L - NO_3]^+$	1508 (20)	1515 (20)	1530 (10)	1551 (10)	1576 (15)	1520 (20)
$[L_2Ln(NO_3)_2]^+$	1181 (100)	1184 (100)	1194 (100)	1204 (100)	1215 (100)	1159 (100)
$[LLn(NO_3)_2]^+{}^b$	723	724	736	744	757	729
$[LLn(NO_3)_2-HNO_2]^+{}^c$	676	677	689	699	710	682

^a Not observed.

^b MS² experiments.

^c MS³ experiments.

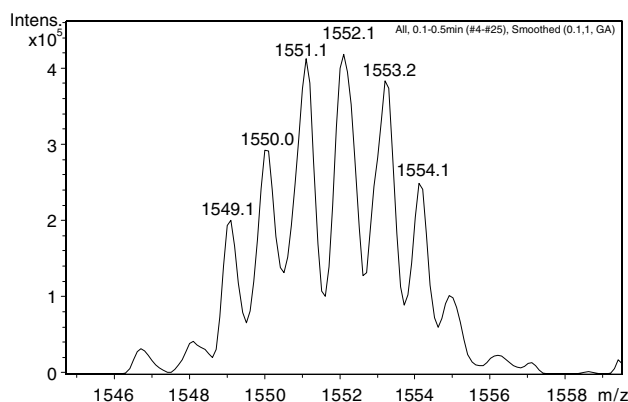


Fig. 3. The experimental isotope pattern of the binuclear $[M - L - NO_3]^+$ fragment with the composition of $C_{56}H_{56}N_5O_{19}Dy_2P_4$.

moiety provides the most intense signals $[(dppbO_2)_2Ln(NO_3)_2]^+$ in all spectra (see Table 3). Two most abundant ions $[(dppbO_2)_2Ln_2(NO_3)_5]^+$ and $[(dppbO_2)_2Ln(NO_3)_2]^+$ were mass selected and fragmented in MS² experiments. The loss of neutral $Ln(NO_3)_3$ and the sequential detachment of $dppbO_2$ was corroborated in every complex. In the next MSMS step (MS³) all fragments $[(dppbO_2)_2Ln(NO_3)_2]^+$ were found to lose 47 amu. This loss could correspond to HNO_2 . The general fragmentation pathway is summarized in Fig. 2. Addition of 0.1% of HCOOH to enhance ionization or changing the solvent to methanol/water (1:1) had no effect on the signal intensities or the appearance of the spectra. Experiments acquired in the negative ion mode displayed fragmentation patterns similar to the positive mode but with much weaker signal intensities and the spectra were dominated by the $[Ln(NO_3)_4]^-$ ions.

To conclude, we have prepared and characterized five binuclear lanthanide complexes as a continuation of our thorough study on the interaction of lanthanide cations with the ligands of diphosphine dioxide type. In the series of $Ph_2P(O)-(CH_2)_n-P(O)Ph_2$ ($n = 1, 2, 4$) ligands, the shortest one was previously found to form chelates with lanthanides [2]; we have prepared 2D coordination polymers with the medium length ligand [1]; and finally, in the present work, we observed the restoration of the

molecularity in the complexes with $dppbO_2$. It is obvious, that the lack of rigid backbone allows the aliphatic ligands to take upon chelate arrangements. Thus, for the preparation of polymeric complexes the appropriate combination of length and rigidity will be of crucial importance.

3. Experimental

The preparation of $Ph_2P(O)-(CH_2)_4-P(O)Ph_2$ ($dppbO_2$) was based on the previously described method [15]. IR spectra (KBr pellets, 4000–400 cm^{-1}) were collected on an EQUINOX 55/S/NIR FTIR spectrometer. Microanalyses were performed using a ThermoFinnigan Co. CHN Analyzer Flash EA 1112. Melting points were measured on a Boetius melting-point apparatus.

A mixture of $dppbO_2$ (250 mg, 0.545 mmol) and the lanthanide nitrate (0.273 mmol) in methanol (30 ml) was sealed in a 250-ml stainless-steel reactor Berghof HR-200 with a Teflon liner, heated for 24 h to 140 °C with a RHS-295 heater controlled by a BAR-945 unit, and then slowly cooled to room temperature. After next 24 h the autoclave was opened and a crystalline solid was collected and washed with methanol.

3.1. $(dppbO_2)Pr(NO_3)_3(\mu-dppbO_2)Pr(NO_3)_3-(dppbO_2)$ (1)

Yield: 258 mg (93.1%). M.p. >300 °C. Anal. Calc.: C, 49.72; H, 4.17; N, 4.14. Found: C, 48.70, H, 4.23, N, 4.91%. IR: 481 vw, 505 w, 542 m, 553 s, 671 vw, 694 m, 712 w, 723 m, 733 m, 744 m, 780 vw, 794 vw, 820 vw, 881 vw, 895 vw, 998 vw, 1029 w, 1072 w, 1098 s, 1124 s, 1146 vs, 1152 vs, 1171 m, 1217 vw, 1240 vw, 1291 s, 1311 s, 1355 vw, 1384 s, 1438 vs, 1468 vs, 1591 vw, 2939 vw, 3059 vw, 3419 vw.

3.2. $(dppbO_2)Nd(NO_3)_3(\mu-dppbO_2)Nd(NO_3)_3-(dppbO_2)$ (2)

Yield: 125 mg (45.0%). M.p. >300 °C. Anal. Calc.: C, 49.56; H, 4.16; N, 4.13. Found: C, 48.20; H, 4.06; N,

4.90%. IR: 480 w, 504 m, 537 m, 542 m, 552 vs, 671 w, 694 s, 711 m, 723 s, 734 m, 743 m, 780 vw, 794 vw, 820 vw, 880 vw, 895 vw, 997 w, 1029 m, 1072 w, 1099 s, 1124 s, 1138 s, 1147 vs, 1154 vs, 1173 m, 1217 vw, 1239 vw, 1291 s, 1313 vs, 1355 vw, 1385 m, 1438 vs, 1467 vs, 1591 vw, 2940 vw, 3059 vw.

3.3. $(dppbO_2)Sm(NO_3)_3(\mu-dppbO_2)Sm(NO_3)_3-(dppbO_2)$ (**3**)

Yield: 220 mg (78.6%). M.p. >300 °C. Anal. Calc.: C, 49.26; H, 4.13; N, 4.10. Found: C, 47.30, H, 4.00, N, 4.82%. IR: 481 vw, 504 w, 513 w, 537 m, 542 m, 553 s, 672 vw, 695 m, 711 w, 723 m, 737 m, 744 m, 756 w, 781 vw, 795 vw, 819 vw, 882 vw, 897 vw, 998 vw, 1030 w, 1072 w, 1100 s, 1124 s, 1139 s, 1156 vs, 1176 m, 1225 vw, 1240 vw, 1291 m, 1318 s, 1354 vw, 1384 s, 1438 vs, 1467 vs, 1591 vw, 2944 vw, 3059 vw, 3649 vw.

3.4. $(dppbO_2)Dy(NO_3)_3(\mu-dppbO_2)Dy(NO_3)_3-(dppbO_2)$ (**4**)

Yield: 198 mg (70.0%). M.p. >300 °C. Anal. Calc.: C, 48.68; H, 4.09; N, 4.06. Found: C, 46.10, H, 3.93, N, 4.73%. IR: 478 vw, 505 w, 513 w, 537 m, 542 m, 553 s, 672 vw, 695 m, 711 w, 723 m, 742 m, 756 w, 781 vw, 795 vw, 819 vw, 882 vw, 899 vw, 998 vw, 1031 w, 1073 vw, 1102 s, 1124 s, 1141 s, 1159 vs, 1180 m, 1221 vw, 1293 s, 1323 vs, 1353 vw, 1384 m, 1438 vs, 1472 vs, 1591 vw, 2941 vw, 3059 vw, 3649 vw.

3.5. $(dppbO_2)Lu(NO_3)_3(\mu-dppbO_2)Lu(NO_3)_3-(dppbO_2)$ (**5**)

Yield: 223 mg (75.5%). M.p. 241–242 °C. Anal. Calc.: C, 48.10; H, 4.04; N, 4.01. Found: C, 50.30, H, 4.29, N, 4.07%. IR: 484 vw, 508 w, 538 m, 553 s, 694 m, 710 w, 723 m, 746 m, 807 vw, 998 vw, 1030 vw, 1072 vw, 1100 m, 1124 m, 1148 vs, 1183 w, 1236 vw, 1299 m, 1384 s, 1438 m, 1480 m, 1591 vw, 2937 vw, 3058 vw, 3654 vw.

4. Mass spectrometry

The ion trap mass spectrometer Esquire 2000 (Bruker, Germany) with electrospray ionization was used for ESI–MS analyses. Solid samples were dissolved in water and diluted in acetonitrile/water (1:1). The samples were injected directly into the electrospray ion source at a flow rate of 4 $\mu\text{L min}^{-1}$. The spectra were recorded both in positive and negative mode. The capillary voltage was 4500 V. Smart Parameter Settings mode was used to optimize other parameters for MS and MSMS operation. The temperature of sampling capillary was set to 200 °C (or 250 °C).

5. Crystallography

Diffraction data were collected on a KUMA KM-4 κ -axis diffractometer equipped with a CCD detector, with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The temperature during data collection was 120(2) K. The intensity data were corrected for Lorentz and polarization effects; absorption correction was applied for all data. The structures were solved by direct methods and refined by full-matrix least-squares methods. The structures are isomorphous, the contraction in lattice parameters reflects the decreasing ionic radius in the lanthanide series. The asymmetric part is built of the $(dppbO_2)Ln(NO_3)_3(Ph_2P(O)CH_2CH_2)$ mononuclear unit, which yields the whole binuclear molecule upon inversion operation. There is a significant disorder in all structures, mainly in the bridging $dppbO_2$ ligand. Its Ph_2P moieties were refined over two sites with almost equal occupancies; the central chain was modelled over three paths in an approximately 0.5:0.25:0.25 ratio. To ensure the reasonable description of a thermal motion in disordered phenyl groups, the rigid-bond restraint was applied for the ring carbon atoms. Nevertheless, in sporadic cases some of the anisotropic displacement parameters became ‘non-positive definite’ (mainly the *ipso* carbons in phenyl groups), therefore the attempts to describe them anisotropically were abandoned. For all other non-hydrogen atoms the anisotropic thermal parameters were used. The amount of the solvent was initially refined, and later fixed to 0.75 molecules of methanol per asymmetric unit.

The software packages used were: XCALIBUR CCD system for the data collection/reduction [16], and SHELXTL for the structure solution, refinement, and drawing preparation [17]. Details of the data collection and structure refinement are listed in Table 1. Crystallographic data for structures reported in this paper are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk; www: <http://www.ccdc.cam.ac.uk>) on request, quoting the Deposition Nos. CCDC 275118–275121.

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