Russian Chemical Bulletin, International Edition, Vol. 54, No. 11, pp. 2519—2534, November, 2005

Coordination chemistry of 2,6-bis(diphenylphosphorylmethyl)-4-methylphenol*

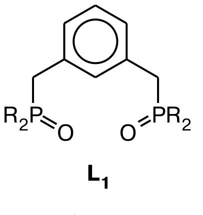
*A. G. Matveeva,** *E. I. Matrosov, Z. A. Starikova, G. V. Bodrin,*
S. V. Matveev, P. V. Petrovskii, and E. E. Nifant´ev

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (495) 135 6549. E-mail: phoc@ineos.ac.ru

The trifunctional ligand, 2,6-bis(diphenylphosphorylmethyl)-4-methylphenol (**L$_2$**), forms complexes with cerium(III) nitrate having a ligand to metal ratio of 1 : 1, 2 : 1, and 3 : 1. The structures of these complexes in the solid state and in solution were studied by X-ray diffraction, IR and NMR (^{1}H and ^{31}P) spectroscopy, and conformational analysis (molecular mechanics). The 2 : 1 complexes of **L$_2$** with lanthanum(III) and neodymium(III) nitrates were synthesized and characterized. In all complexes, the neutral ligand is coordinated through both phosphoryl oxygen atoms. The hydroxy oxygen atom is coordinated only in some complexes, and the hydrogen atom of the hydroxy group is involved in hydrogen bonding. The compositions and structures of the resulting complexes depend on the method of synthesis and the nature of solvent. The ligand was found to undergo easy inner-sphere oxidation. The structure of one of the transformation products was established by X-ray diffraction. Unlike the coordinated ligand, the free ligand is very stable to oxidation.

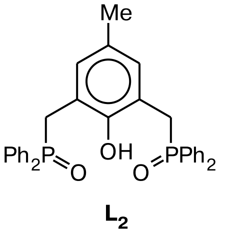
Key words: 2,6-bis(diphenylphosphorylmethyl)-4-methylphenol, complexes, lanthanides, structure, hydrogen bonds, solutions.

Bis- and polyphosphoryl compounds containing an aromatic moiety and the phosphorylmethyl groups in the *ortho* and *meta* positions of the benzene ring are convenient extractants for separation of transuranium and rare-earth metals from aqueous solutions of nitric acid.[1—6] In particular, reagents **L$_1$** containing substituents in the *meta* positions exhibit high separation factors (*f*) with respect to the Eu^{III}/Am^{III} pair. However, the absolute partition coefficients $D = [M]_{org}/[M]_{aq}$ are small.



L$_1$

R = Ar, Alk, AlkO



L$_2$

Modified ligand **L$_2$** containing an additional coordinating center in the second position of the benzene ring would be expected to exhibit the coordination and extraction properties analogous to those of **L$_1$**, because the main ligand contour remains unchanged. At the same time, additional coordination of the phenolic OH group should increase stability of the extracted complexes and, consequently, increase the extraction coefficients with retention of the selectivity level typical of **L$_1$**, because the phosphoryl groups will remain the main coordinating centers. Actually, already our first experiments on extraction of U^{VI}, Am^{III}, and Eu^{III} from aqueous solutions of nitric acid with solutions of **L$_2$** in dichloroethane have showed[7] that the efficiency of extraction (*D*) increases by an order of magnitude compared to that of the prototype, *viz.*, dioxide **L$_1$** (R = Ph), the separation factor of the metals (*f*) remaining the same (more detailed data will be published elsewhere).

Coordination chemistry of ligand **L$_2$** is poorly known. Only two 1 : 1 complexes with erbium[8] and cerium[9] nitrates were characterized.

In the present study, the coordination ability of **L$_2$** was studied using complexation with cerium(III) nitrate as an example. The 2 : 1 complexes with neodymium(III) and lanthanum(III) nitrates were examined in less detail. Here, we report only data necessary for comparison. Since the resulting complexes are unstable during storage, we studied also the properties and structures of the phenol and its potassium salt in solution and in the solid state and exam-

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* Dedicated to Corresponding Member of the Russian Academy of Sciences T. A. Mastryukova.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2440—2454, November, 2005.

ined the ability of the ligand and its complexes to be oxidized.

Experiments

All operations, unless otherwise stated, were carried out under argon. Solvents were saturated with argon, purified, and dried according to known procedures.[10] Potassium metal of reagent grade (in glass ampoules) was used. The salts $La(NO_3)_3 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, and $Nd(NO_3)_3 \cdot 6H_2O$ (Fisher Scientific Company) were used without additional purification. The NMR spectra were recorded in deuterated solvents, *viz.*, $CDCl_3$, CD_2Cl_2, acetone-d_6, and DMSO-d_6 (Aldrich), which were also saturated with argon.

The IR spectra were measured in KBr pellets, Nujol or hexachlorobutadiene mulls, and solutions in $CHCl_3$ and CH_2Cl_2 at concentrations of 0.02—0.2 mol L^{-1} on a UR-20 spectrophotometer (in the 400—3700 cm^{-1} region) with the use of 0.07—0.1 mm cells; the resolution was 5 cm^{-1}. In some cases, the IR spectra of solid samples and highly dilute solutions were recorded on a Nicolet Magna IR-750 Fourier-transform spectrometer; the resolution was 2 cm^{-1}.

The ^1H NMR spectra were measured on a Bruker AMX-400 spectrometer operating at 400.13 MHz at 298 K using residual protons of the deuterated solvent as the internal standard. Standard ampoules with a diameter of 5 mm were used. The concentrations of the solutions were 0.05 and 0.15 mol L^{-1}.

The $^{31}P—\{^1H\}$ NMR spectra were recorded on a Bruker AMX-400 spectrometer operating at 161.98 MHz at 298 K using 85% H_3PO_4 as the external standard. Standard ampoules with a diameter of 5 mm were used. The concentration of solutions was 0.05 mol L^{-1}.

The ESR spectra were measured on a Bruker EMX-10/12 spectrometer; samples were irradiated in a resonator using a high-pressure mercury lamp (1000 W). Saturated solutions in anhydrous benzene or a benzene—*tert*-butyl peroxide mixture (4 : 1 v/v) were evacuated before measurements.

2,6-Bis(diphenylphosphorylmethyl)-4-methylphenol (L_2) was prepared by the Arbuzov reaction of 2,6-bis(chloromethyl)-4-methylphenol[11] with methyl diphenylphosphinite in refluxing xylene in 91.0% yield, m.p. 185—186 °C (from benzene), 186—187 (from methyl ethyl ketone) (*cf.* lit. data[8]: m.p. 176—178 °C (from ethyl acetate)). $^{31}P—\{^1H\}$ NMR ($CDCl_3$): δ_P 35.72 (*cf.* lit. data[8]: δ_P 38.11). Ligand L_2 is soluble in benzene (moderately), chloroform, dichloroethane, DMSO, acetone, and acetonitrile (moderately on heating) and insoluble in water. The ^1H and ^{31}P NMR spectroscopic parameters are given in Table 1.

Potassium 2,6-bis(diphenylphosphorylmethyl)-4-methylphenoxide (1). A solution of ligand L_2 (1.37 g, 0.00256 mol) in ethanol (15 mL) was added to a solution of potassium ethoxide, which was prepared by dissolving potassium metal (0.1 g, 0.00256 g-at) in ethanol (15 mL) under argon. The solution turned lemon-yellow. Then anhydrous benzene was added, and the solution was concentrated to ~10 mL. Hexane was added to the resulting benzene solution until the solution turned opaque. Then the reaction mixture was kept in the cold. The yellow crystalline precipitate that formed was separated, washed with a 1 : 4 benzene—hexane mixture, and dried at 140 °C *in vacuo* (1—2 Torr) over P_2O_5 for 3 h. Salt **1** was obtained as dihydrate in a yield of 1.42 g (97.0%) as a pale-yellow fine-crystalline precipitate, t.decomp. >190 °C. Found (%): C, 65.54; H, 5.29; P, 9.99. $C_{33}H_{29}KO_3P_2 \cdot 2H_2O$. Calculated (%): C, 64.91; H, 5.45; P, 10.14. The salt is soluble in benzene, THF, chloroform, dichloromethane, acetone, and water. The ^1H and ^{31}P NMR and IR spectroscopic parameters are given in Tables 1 and 2.

Synthesis of lanthanide complexes 2a, 3a—c, and 4a (general procedure). A solution of a stoichiometric amount of $Ln(NO_3)_3 \cdot 6H_2O$ (0.0003, 0.00015, or 0.0001 mol) in acetonitrile (2 mL) was slowly added dropwise to a solution of ligand L_2 (0.0003 mol) in chloroform (1—2 mL) at ~25 °C. The solution was concentrated to ~1.5 mL *in vacuo* (~5 Torr). The precipitate that formed was filtered off and dried at room temperature *in vacuo* (1 Torr).

[2,6-Bis(diphenylphosphorylmethyl)-4-methylphenol-*O*,*O*,*O*]tri(nitrato-*O*,*O*)aquacerium(III) dihydrate, $[Ce(L_2)(NO_3)_3 \cdot (H_2O)] \cdot 2H_2O$ (2a). The yield was 62%. White powder. Found (%): C, 43.00; H, 3.75; N, 4.71; P, 6.68. $C_{33}H_{36}CeN_3O_{15}P_2$. Calculated (%): C, 43.24; H, 3.96; N, 4.58; P, 6.76. The IR spectroscopic data are given in Table 2.

[2,6-Bis(diphenylphosphorylmethyl)-4-methylphenol-*O*,*O*,*O*]tri(nitrato-*O*,*O*)acetonecerium(III), $[Ce(L_2)(NO_3)_3 \cdot (Me_2CO)]$ (2b) was prepared by the reaction of equimolar amounts of ligand L_2 and the salt $Ce(NO_3)_3 \cdot 6H_2O$ according to a procedure described earlier.[9] The characteristics of **2b** corre-

Table 1. ^1H and ^{31}P NMR spectroscopic data for phenol L_2, its salt **1**, and complexes **2b** and **3a,c** (δ, *J*/Hz)

Compound	Solvent	^1H					^{31}P
		OH (s, 1 H)	Ph (m, 20 H)	m-C_6H_2 (s, 2 H)	CH_2P (4 H)	Me (s, 3 H)	
L_2	CD_2Cl_2	9.90	7.40—7.75	6.74	3.68 (d, $^2J_{P,H}$ = 13.67)	1.82	34.56, s
	$CDCl_3$	9.76	7.35—7.71	6.76	3.67 (d, $^2J_{P,H}$ = 13.60)	2.01	35.72, s
1	CD_2Cl_2	—	7.31—7.73	6.11	3.72 (d, $^2J_{P,H}$ = 12.75)	1.68	33.50, s
	$CDCl_3$	—	7.30—7.66	6.03	3.75 (d, $^2J_{P,H}$ = 12.70)	1.65	34.30, s
2b	CD_2Cl_2	—[a]	7.70—9.20[b]	5.78 (0.08)[c]	4.20, br (0.2)[c]	1.23 (0.002)[c]	64.4, br.s (4)[c]
3a	CD_2Cl_2	—[a]	7.50—9.50[b]	5.78 (0.07)[c]	4.10, br (0.24)[c]	1.22 (0.003)[c]	62.8, br.s (4)[c]
3c	$CDCl_3$	—[a]	7.24—7.62	6.20 (0.03)[c]	3.70, br (0.26)[c]	1.68 (0.0008)[c]	37.72, br.s (0.26)[c]

[a] The signal was not recorded.

[b] A very broad unresolved multiplet.

[c] The half-width of the line $\Delta_{1/2}$ (ppm).

Table 2. Main frequencies in the IR spectra (ν/cm^{-1}) of compounds $\mathbf{L_2}$ and **1—4a**

Compound	Conditions of spectrum measurements[a]	ν(P=O)	ν(C—O(H))	ν((C)O—H)	ν(N=O)	$\nu_{as}(NO_2)$	$\nu(H_2O)$
$\mathbf{L_2}$	KBr	1195, 1150	1250	3000	—	—	—
	$CHCl_3$	1185, 1160	1250	3000	—	—	—
	CH_2Cl_2	1195, 1155	1250	3000	—	—	—
1	KBr	1195	1470[b]	—	—	—	3600—2900
	$CHCl_3$	1190, 1175	1470[b]	—	—	—	
2a	KBr	1151	1218	3200—2600	1480	1315	3240[c]
2b	KBr	1151	1219	3200—2600	1481	1314	—
	$CHCl_3$	1152 (br)	1223	~3000	1484	1304	—
3a	KBr	1155	1225	3200—2600	1490	1300	3500—3400
	$CHCl_3$	1160, 1150	1220	3000	1490	1305	—
3b	KBr	1160	1223	3200—2600	1480	1310	3500—3400
	$CHCl_3$	1170, 1155	1220	3000	1480	1320	—
3c	KBr	1160	1230	3200—2600	1480	1310	3500—3400
3d	KBr	1155	1235, 1218	3200—2600, 3380[d]	1490	1300	3240[c]
4a[e]	KBr	1155	1235	3600—2200	1485	1305	—
	CH_2Cl_2	1195, 1150, 1140	1255, 1218	3000	1470	1305	—

[a] The spectra of solid samples were recorded also as Nujol and hexachlorobutadiene mulls.

[b] ν(C—O—).

[c] Coordination water.

[d] (Et)O—H.

[e] $\nu^E(NO_3)$ = 1350 cm^{-1}.

spond to the published data. Complex **2b** is poorly soluble in chloroform, dichloromethane, and acetonitrile. The ^{1}H and ^{31}P NMR and IR spectroscopic parameters are given in Tables 1 and 2.

Bis{2,6-bis(diphenylphosphorylmethyl)-4-methylphenol-*O,O,O*}tri(nitrato-*O,O*)cerium(III) trihydrate, $\mathbf{[Ce(L_2)_2(NO_3)_3] \cdot 3H_2O}$ (3a). M.p. (with decomp.) 105—107 °C. The yield was 65%. White powder. Found (%): C, 54.15; H, 4.22; N, 2.91; P, 8.33. $C_{66}H_{66}CeN_3O_{18}P_4$. Calculated (%): C, 54.54; H, 4.58; N, 2.89; P, 8.52. Complex **3a** is soluble in chloroform (readily), dichloromethane, acetone, and DMSO (with decomposition) and is poorly soluble in acetonitrile and ethanol (on heating). The ^{1}H and ^{31}P NMR and IR spectroscopic parameters are given in Tables 1 and 2.

Bis{2,6-bis(diphenylphosphorylmethyl)-4-methylphenol-*O,O,O*}tri(nitrato-*O,O*)neodymium(III) trihydrate, $\mathbf{[Nd(L_2)_2(NO_3)_3] \cdot 3H_2O}$ (3b). M.p. (with decomp.) 115—117 °C. The yield was 66%. A weakly colored almost white powder with a pale-lilac tint. Found (%): C, 54.09; H, 4.36; N, 2.86; P, 8.38. $C_{66}H_{66}N_3NdO_{18}P_4$. Calculated (%): C, 54.39; H, 4.56; N, 2.88; P, 8.50. Complex **3b** is soluble in chloroform, dichloromethane, acetone, and DMSO (with decomposition) and poorly soluble in acetonitrile and ethanol. The IR spectroscopic data are given in Table 2.

Bis{2,6-bis(diphenylphosphorylmethyl)-4-methylphenol-*O,O,O*}tri(nitrato-*O,O*)lanthanum(III) trihydrate, $\mathbf{[La(L_2)_2(NO_3)_3] \cdot 3H_2O}$ (3c). The yield was 65%. White powder. Found (%): C, 54.39; H, 4.46; N, 3.11; P, 8.33. $C_{66}H_{66}LaN_3O_{18}P_4$. Calculated (%): C, 54.59; H, 4.58; N, 2.90; P, 8.53. Complex **3c** is soluble in chloroform, acetone, and DMSO (with decomposition). The ^{1}H and ^{31}P NMR and IR spectroscopic parameters are given in Tables 1 and 2.

[2,6-Bis(diphenylphosphorylmethyl)-4-methylphenol-*O,O,O*][2,6-bis(diphenylphosphorylmethyl)-4-methylphenol-*O,O*](nitrato-*O,O*)aquacerium(III) dinitrate ethanol solvate, $\mathbf{[Ce(L_2)_2(H_2O)(NO_3)]^{2+} \cdot (2NO_3^-) \cdot EtOH}$ (3d). A weighed sample of complex **3a** (0.0700 g) was dissolved with heating in ethanol. Colorless crystals that precipitated during storage of the ethanolic solution were filtered off and dried at room temperature *in vacuo* (1—2 Torr), m.p. (with decomp.) 130—135 °C. The yield was 75%. Virtually colorless transparent crystals suitable for X-ray diffraction study were obtained. Found (%): C, 55.61; H, 4.69; N, 2.85. $C_{68}H_{68}CeN_3O_{17}P_4$. Calculated (%): C, 55.81; H, 4.68; N, 2.87. Complex **3d** is insoluble in chloroform, acetone, and acetonitrile and is poorly soluble in ethanol. The IR spectroscopic data are given in Table 2.

Tris{2,6-bis(diphenylphosphorylmethyl)-4-methylphenol-*O,O*}(nitrato-*O,O*)aquacerium(III) dinitrate, $\mathbf{[Ce(L_2)_3(NO_3)(H_2O)]^{2+}(NO_3)_2}$ (4a). T.decomp. >95 °C. The yield was 65%. White powder. Found (%): C, 60.66; H, 4.74; N, 2.32; P, 9.47. $C_{99}H_{92}CeN_3O_{19}P_6$. Calculated (%): C, 60.86; H, 4.75; N, 2.15; P, 9.51. Complex **4a** is soluble in chloroform, dichloromethane, acetone, DMSO (with decomposition), methanol, and ethanol. The IR spectroscopic data are given in Table 2. ^{31}P—{^{1}H} NMR (CD_2Cl_2), δ: 64 ($\Delta_{1/2}$ = 10 ppm).

Bis{2,6-bis(diphenylphosphorylmethyl)-4-formylphenolato-*O,O,O*}(nitrato-*O,O*)cerium(III) hemihydrate diacetonitrile solvate, $\mathbf{[Ce(L_3)_2(NO_3)] \cdot 2MeCN \cdot 0.5H_2O}$ (5a) ($\mathbf{L_3}$ = 4-CHO-2,6-$[Ph_2P(O)CH_2]_2C_6H_2O^-$) is one of decomposition products. Operations were carried out without protection from air. A weighed sample of phenol $\mathbf{L_2}$ (0.1610 g, 0.3 mmol) was dissolved in CH_2Cl_2 (3 mL), and a solution of $Ce(NO_3)_3 \cdot 6H_2O$ (0.0651 g, 0.15 mmol) in acetonitrile (3 mL) was slowly added dropwise at ~25 °C. Then anhydrous diethyl ether was added.

The white precipitate that formed was filtered off, washed with anhydrous diethyl ether, and dried at room temperature *in vacuo* (1 Torr). Complex **3a** was obtained in a yield of 0.1416 g (65%). The transparent filtrate was kept without protection from air for several hours, after which it turned pale-blue and then gradually turned intense black-blue. After storage overnight, a black inhomogeneous precipitate was obtained, from which dark crystals were manually separated. The crystals were purified from the dark powdered precipitate in a mineral oil under a microscope. Transparent slightly lilac crystals of complex **5a** were obtained and characterized by X-ray diffraction analysis.

Oxidation of complexes 3a—c in solution (general procedure). A weighed sample of complex **3** (0.1 mmol) was dissolved in $CHCl_3$ (2 mL) without protection from air. After 1 h, the solution turned blue. After several hours, the solution turned intense black-blue. After storage overnight, the solution yielded a black precipitate as a mixture of products (~60% yield; m.p. (with decomp.) 170—174 °C in the case of **3a** or 168—172 °C in the case of **3b**). The IR spectra of the precipitates (Ce and Nd products) were identical. The spectra were compared with the spectra of the starting nonoxidized complexes **3a,b**. The spectra of the precipitates (oxidation products) show a band of coordinated P=O groups at 1145 cm^{-1} and bands of bidentate NO_3 groups at 1480 and 1300 cm^{-1}. The band of the C—O(H) group is less intense and is observed at 1233 cm^{-1}, and the intensity of the C=C band at 1600 cm^{-1} becomes substantially higher. Absorption of coordinated (C_{arom})O—H groups is observed at 3420 cm^{-1}, an absorption band of quinoid-type carbonyl[12] appears at 1685 cm^{-1}, and a band of aldehyde carbonyl is observed as a shoulder at 1700 cm^{-1}. The spectra show also medium- and low-intensity bands at 1060 (absorption of the C—O(C) group) and 1350 cm^{-1} (absorption of the coordinated (C_{arom})C—O^- group). One of oxidation products, *viz.*, complex **5a**, was isolated from the mixture (14% by weight) and characterized by X-ray diffraction.

During storage without protection from air, complex **5a**, like a mixture of decomposition products, undergoes further transformations both in the solid state and in solution.

X-ray diffraction study. Crystals of **3d** and **5a** suitable for X-ray diffraction study were obtained as described above.

Experimental X-ray data sets were collected on a Bruker SMART diffractometer equipped with a CCD area detector at 110 (**3d**) and 120 K (**5a**). The X-ray data were processed using the SAINT [13] and SADABS [14] program packages. The structures were solved by direct methods. The nonhydrogen atoms were located from difference electron density maps and refined anisotropically by the least-squares method against F^2_{hkl}. The coordinates of the hydrogen atoms (except for the hydrogen atoms of the water molecules and OH groups) were calculated geometrically and refined isotropically using a riding model with $U(H) = 1.2U(C)$ (for the atoms of the Ph groups) and $U(H) = 1.5U(C)$ (for the atoms of the CH_2 groups and the EtOH molecules), where $U(C)$ are the equivalent thermal parameters of the pivot carbon atoms. The hydrogen atoms of the water molecules and the hydroxy groups were determined from difference maps and refined isotropically using a riding model with $U(H) = 1.5U(O)$, where $U(O)$ is the equivalent thermal parameter of the pivot oxygen atom.

All calculations were carried out with the use of the SHELXTL PLUS 5 program package.[15]

The unit cell parameters, details of X-ray diffraction study, and parameters of structure refinement are given in Table 3. The atomic coordinates and displacement parameters were deposited with the Cambridge Structural Database.

Conformational analysis The energy of the complex-forming conformation of the ligand was calculated by the molecular mechanics method (PC Model, Serena Soft Ware, the MM2 (QCPE 395) and MMP1 (QCPE 318) force fields) with speci-

Table 3. Principal crystallographic data for the complexes $[Ce(\mathbf{L_2})_2(NO_3)(H_2O)]^{2+}(NO_3)_2 \cdot EtOH$ (**3d**) and $[Ce(\mathbf{L_3})_2(NO_3)] \cdot 2MeCN \cdot 0.5H_2O$ (**5a**)

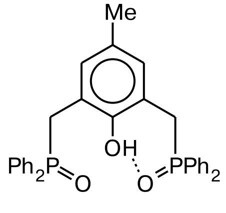
Parameter	**3d**	**5a**
Molecular formula	$C_{68}H_{68}N_3CeO_{17}P_4$	$C_{70}H_{61}N_3CeO_{11.5}P_4$
Molecular weight	1463.25	1392.22
Space group	$P2_1/c$	$C2/c$
T/K	110(2)	120(2)
a/Å	13.862(2)	22.7234(4)
b/Å	21.323(2)	15.686(4)
c/Å	22.488(3)	18.626(4)
α/deg	—	—
β/deg	91.696(4)	96.989(5)
γ/deg	—	—
V/Å^3	6644(2)	6590(2)
Z	4	4
d_{calc}/g cm^{-3}	1.463	1.403
Color and habit of crystals	Pale-blue prismatic	Pale-gray platelet-like
Crystal dimensions/mm	0.50×0.30×0.20	0.45×0.35×0.25
Diffractometer	«Bruker SMART»	
Radiation	Mo-Kα (λ = 0.71073 Å)	
μ/mm^{-1}	0.853	0.851
Absorption correction	Sadabs	
T_{min}/T_{max}	0.645/0.802	0.665/0.802
Scan mode	φ/ω	
2θ$_{max}$/deg	48.00	55.10
Total number of reflections	43871	27641
Number of independent reflections (R_{int})	9901 (0.0470)	6226 (0.0388)
R_1 (against F for reflections with $I > 2\sigma(I)$)	0.0472 (6831 отр.)	0.0444 (5068 отр.)
wR_2 (against F^2 for all reflections)	0.0987	0.1050
Number of parameters in refinement	838	418
Weighting scheme:	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = 1/3(F_o^2 + 2F_c^2)$	
a	0.0236	0.0398
b	20.2500	23.106
GOOF	0.986	1.020
Electron density (max/min), e Å^{-3}	1.305/−0.469	0.822/−0.337
F(000)	3004	2848

fied distances between the atoms involved in coordination. Models of Ce^{III} complexes were constructed with the use of the corresponding polyhedra and the Ce...O(C) and Ce...O(P) coordination bond lengths (2.66 Å and 2.41 Å, respectively), which were calculated by averaging the bond lengths determined by X-ray diffraction analysis in the present study and those published earlier.[9] The strain energy of the conformation (ΔE) was estimated as the difference between the calculated energies of this conformer and the conformer corresponding to the global minimum.

Results and Discussion

Ligand $\mathbf{L_2}$ was synthesized by the Arbuzov reaction of 2,6-bis(chloromethyl)-4-methylphenol with ethyl (or methyl) diphenylphosphinite in refluxing xylene in 91.0% yield. Earlier,[8] this ligand has been prepared in higher yield (94.5%) by an analogous reaction with the use of other solvents for the reaction (triglyme) and recrystallization (ethyl acetate). The melting point of the latter reaction product is lower (by 10 °C) and the ^{31}P NMR data (solution in $CDCl_3$) are somewhat different from our data, although the structure of the resulting phenol was beyond doubt. The structure of $\mathbf{L_2}$ in the solid state and in solution was not investigated.

The molecule of ligand $\mathbf{L_2}$ contains three donor oxygen atoms, which can potentially be involved in complexation. At the same time, the structure of $\mathbf{L_2}$ is favorable for hydrogen bonding due to the presence of two phosphoryl groups, which are strong proton acceptors, along with the hydroxy group. In the solid state, related (to ligand $\mathbf{L_2}$) phosphorylated phenols, *viz.*, 2-(diphenylphosphorylmethyl)phenol and 2-[bis(diphenylphosphoryl)methyl]phenol, are associated *via* intermolecular hydrogen bonds.[16,17] Unlike these compounds, molecules $\mathbf{L_2}$ in the crystalline state contain a strong intramolecular O—H...O=P hydrogen bond (X-ray diffraction data), which is retained in solution (IR spectroscopic data).[9]



The ^{31}P and ^{1}H NMR spectroscopic data (see Table 1), which remain virtually unchanged upon dilution (solutions in dichloromethane, chloroform, acetone, and DMSO), are also consistent with the proposed structure.

Therefore, a strong intramolecular P=O...H—O hydrogen bond in molecules $\mathbf{L_2}$ is retained both in the solid state and in solution.

It is known[18—20] that the intramolecular hydrogen bonds in *ortho*-substituted phenols, along with the steric accessibility of the OH group, are among factors responsible for stability of these compounds to oxidation by a radical mechanism.

It appeared that compound $\mathbf{L_2}$ is extremely stable to oxidation under homolytic conditions. Attempts to oxidize $\mathbf{L_2}$ with PbO_2 and 30% H_2O_2 in organic media failed. The signal of phenoxide radicals was completely absent when PbO_2 or the *tert*-butoxide radical, which was generated by photolysis of *tert*-butyl peroxide in a resonator of an ESR spectrometer, was used as an oxidizing agent. Under analogous conditions, the alkyl analog of compound $\mathbf{L_2}$, *viz.*, 2,6-di-*tert*-butyl-4-methylphenol, gave an intense spectrum of the corresponding radical. Presumably, resistance of $\mathbf{L_2}$ to radical oxidation is associated not only with an increase in steric shielding of the phenoxide radical but also with strong binding of the proton of the OH group to the phosphoryl group.

Potassium salt **1**, which was prepared by the reaction of $\mathbf{L_2}$ with potassium ethoxide in an ethanolic solution, was isolated as dihydrate because we failed to remove the water molecules by vacuum drying over P_2O_5 at 140 °C for 4 h. The IR spectra of solid salt **1** show a single band of free P=O groups at 1195 cm^{-1}. The band of the C—O$^-$ groups[12] of the phenoxide ion is observed at 1470 cm^{-1}. The 3660—3680 cm^{-1} region shows absorption of the water solvate molecules. In the spectra of solutions of salt **1** in chloroform, absorption of the phosphoryl groups appears at 1190 and 1175 cm^{-1}, which is indicative of coordination of one P=O group to the potassium cation, another P=O group remaining free. The position of the band of the C—O$^-$ group of the phenoxide ion remains unchanged, and absorption of water of solvation is absent.

In the solid state, dihydrate of potassium salt **1** exists, apparently, as the solvated ion pair, in which the potassium cation is coordinated by the oxygen atoms of the water molecules and the phenoxide group, whereas both phosphoryl groups remain uncoordinated. In a chloroform solution, salt **1** exists as a tight ion pair. The potassium cation is coordinated by two oxygen atoms of the C—O$^-$ and P=O groups resulting in the closure of the six-membered chelate ring, and another phosphoryl group remains free.

In the ^{1}H NMR spectra of solutions of salt **1** in $CDCl_3$ and CD_2Cl_2, the signals for the protons of the phenoxide ion are present in the expected region and are shifted relative to the signals of the free ligand (see Table 1). The ^{31}P NMR spectra of salt **1** in the same solvents (see Table 1) show one narrow signal due, apparently, to fast exchange processes. This signal is shifted downfield by ~1 ppm with respect to the signal of the free ligand.

Unlike the starting compound $\mathbf{L_2}$, its salt **1** is less stable to atmospheric oxygen. The color changes both in solid samples upon storage under ambient conditions and, more rapidly, in solution (color of the solution gradually changes from pale-yellow to brown-orange; new signals appear in the NMR spectra).

Complexation

In studies of the coordination properties of phenol $\mathbf{L_2}$ with respect to lanthanide cations, it was of interest to determine the compositions of chelate complexes, which can be formed at different metal : ligand ratios and establish their structures in the solid state and in solution.

Coordination of ligand $\mathbf{L_2}$ was studied in the reaction with cerium(III) nitrate in CH_2Cl_2 at room temperature for the molar metal : ligand ratios of 1 : 1, 1 : 2, 1 : 3, and 1 : 4. At the molar ratios L : M = 1, 2, or 3, complexes of the general formula $[Ln(\mathbf{L_2})_n(NO_3)_3]\cdot xH_2O$ (n = 1—3) were obtained. The ^{31}P NMR spectra of solutions show one broadened signal belonging to the coordinated ligand in the expected region[21] at δ ~60 (in the ^{31}P NMR spectrum, free ligand is characterized by a singlet at δ 34.56). In the IR spectra of these solutions, absorption of the P=O groups of the free ligand is absent.

When the metal : ligand ratio of 1 : 4 was used, one mole of the ligand remained unconsumed. The ^{31}P NMR spectra show one broadened signal at δ 47 ($\Delta_{1/2}$ = ~15 ppm), which is indicative of fast exchange between the free ligand and the complex. The IR spectrum of this solution contains, along with a band of coordinated P=O groups at 1158 cm^{-1}, a band of free P=O groups at 1195 cm^{-1} with an intensity ratio of ~(3 : 1) (second expected band of the free ligand at 1175 cm^{-1} is not observed because of overlap with a wing of the band at 1158 cm^{-1}).

Analogous spectral changes were observed in the study of coordination of the ligand $\mathbf{L_2}$ in methanol.

Conformational analysis by the molecular mechanics method demonstrated that mono-,[9] bis-, and tris-ligand complexes with the tridentate *O,O,O*-coordinated ligands can be formed. In the bis-ligand complex, the energy of complex-forming conformations differs from that of the global maximum by 4.8 kcal mol^{-1}. Coordination of three ligand molecules to one cerium(III) cation is less favorable (but is probable). The strain energies of the complex-forming conformations for the complex of this composition is ~4, 5, and 8 kcal mol^{-1}. As in the earlier publication,[9] the arrangement of the atoms and the interatomic distances in all the complexes under consideration are such that the intramolecular P=O...H—O hydrogen bonds can exist.

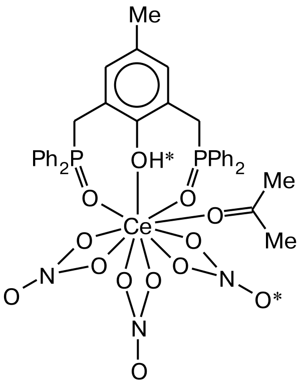
The 1 : 1, 1 : 2, and 1 : 3 complexes of $\mathbf{L_2}$ with cerium(III) nitrate and the 1 : 2 complexes of $\mathbf{L_2}$ with neodymium(III) and lanthanum(III) nitrates were isolated in the individual state and studied in the solid state and in solution. The structures of the 1 : 1 and 1 : 2 cerium complexes were established by X-ray diffraction analysis (see Ref. 9 and the results of the present study). The IR and NMR (^1H and ^{31}P) spectroscopic data for complexes **2a,b**, **3a—d**, and **4a** are given in Tables 1 and 2, where the spectroscopic data for ligand $\mathbf{L_2}$ and its K salt **1** are presented for comparison.

The complexes with $\mathbf{L_2}$ are stable in standard organic media in the absence of oxygen. This is evident from the fact that the ^{31}P NMR spectra of freshly prepared solutions of these complexes are identical to the spectra measured after prolonged storage of the solutions under an inert atmosphere. However, the complexes decompose in coordinatively active media. After dissolution of these complexes in DMSO, a single signal of the free ligand was found.

It should be noted that the signals in the ^1H and ^{31}P NMR spectra of the cerium(III) and neodymium(III) complexes are broadened due apparently to the paramagnetic properties of the cation. The spectra of lanthanum(III) complex **3c**, which was synthesized for comparison, only signals of the CH_2 groups are broadened (see Table 1). The cerium(III) coordination complexes of different compositions are characterized by virtually the same chemical shift (δ_P ~60), the signal being most broadened in the spectrum of the tris-ligand complex. Probably, this led the authors of the study[8] to conclude that complexation of phenol $\mathbf{L_2}$ with Ln^{III} affords exclusively monoligand complexes.

In investigations of coordination of the ligand, not only its dentation but also coordination of the phenol oxygen atom is of considerable interest. The question is whether the proton is displaced upon coordination and, if not, whether the intramolecular hydrogen bond that is present in the free ligand molecule is retained upon coordination.

Complexes of composition 1 : 1. Complexes with $\mathbf{L_2}$ of composition $Ln(\mathbf{L_2})(NO_3)_3\cdot n$Solv, where Solv is the solvent molecule (water or acetone), are readily formed in solvents of different polarity with the use of the reagents in a ratio of 1 : 1. Earlier,[9] we have studied and structurally characterized the $[Ce(\mathbf{L_2})(NO_3)_3\cdot Me_2CO]$ complex (**2b**). In this complex, the neutral phenol molecule is tridentately coordinated. The inner coordination sphere contains also three bidentate NO_3 groups and one acetone molecule. The coordination number of the cerium atom is 10.



2b (solid)

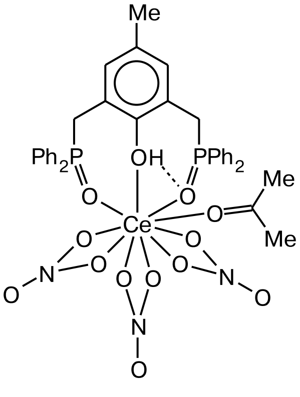
Note. Hereinafter, the structure in the solid state is referred to as "solid;" in solution, as "solv." The atoms involved in the intermolecular hydrogen bond are marked with asterisks.

The proton of the phenolic hydroxy group is involved in an intermolecular hydrogen bond with the oxygen atom of one NO_3 group of another molecule of the complex. In the crystals, the molecules of the complex are linked into dimers by two such hydrogen bonds.

The IR spectrum of solid complex **2a** is virtually identical to the spectrum[9] of crystalline complex **2b** except for absorption bands of the solvent molecules. Instead of absorption of coordinated acetone, the spectrum shows absorption of water solvate molecules (3500—3400 cm^{-1}) and coordinated water molecules (3240 cm^{-1}).

The complex of phenol $\mathbf{L_2}$ with erbium nitrate $[Er(\mathbf{L_2})(NO_3)_3]Me_2CO$ and the neodymium complex $[Nd(\mathbf{L_4})(NO_3)_3Me_2CO]Me_2CO$, where $\mathbf{L_4}$ is the homolog of $\mathbf{L_2}$, *viz*., 2,6-bis(diphenylphosphorylmethyl)-4-*tert*-butylphenol, have structurally been characterized earlier.[8] In both complexes, the neutral phenol ligand exhibits the *O*,*O*,*O*-coordination mode, and three nitrate ions are bidentate. In both structures, the protons of the phenolic hydroxy groups are involved in intermolecular hydrogen bonds. In the structure of the Er^{III} complex, this intermolecular hydrogen bond is formed between the phenolic hydroxy group and the outer-sphere acetone molecule. In the structure of the Nd^{III} complex, the intermolecular hydrogen bonds, analogous to those in the structure of complex **2b**, link the molecules into centrosymmetric dimers.

In chloroform and dichloromethane, the structures of complexes **2a,b** are virtually identical to those in the solid state,[9] with the only exception that the intramolecular O—H...O=P hydrogen bond exists in solutions instead of the intermolecular O—H...O—NO_2 hydrogen bond that is present in the solid state.



2b (solv)

The IR spectroscopic data, the ^1H and ^{31}P NMR spectra (see Tables 1 and 2 and the published data[9]) complexes **2a,b**, and the results of conformational analysis (molecular mechanics)[9] are consistent with the proposed structures. In the IR spectra of solutions of **2b** in chloroform and dichloromethane (see Table 2), the band of coordinated P=O groups is observed at 1152 cm^{-1} and is broadened due to the additional involvement of one P=O group in the intramolecular hydrogen bond. The band of the C—O(H) groups of phenol at 1223 cm^{-1} is indicative of coordination of the oxygen atom and the involvement of the proton in hydrogen bonding. A broad absorption band at about 3000 cm^{-1} characterizes the involvement of the proton of the OH group of phenol in hydrogen bonding. An analogous bifurcate coordination of P=O groups has been documented earlier (see, for example, the study[22] and references therein), in particular, in the Cu^{II} complex with *cis*,*cis*-1,3,5-tris[2-(diphenylphosphoryl)ethylamino]cyclohexane in aprotic solvents. The bands of bidentate NO_3 groups are observed at 1484 and 1304 cm^{-1} (separation is 180 cm^{-1}).[23] The band of the C=O groups of the coordinated acetone ligand, like that in the spectrum of the crystalline complex, appears at 1700 cm^{-1}.

In the ^1H NMR spectra of solutions of complex **2b** in CD_2Cl_2, the signal for the phenolic proton is absent due, apparently, to both paramagnetic broadening and fast exchange processes. The signals for the other protons are shifted relative to those of the free ligand and are differently broadened. The signals for the protons of four Ph groups are most broadened, whereas the signals for the methyl protons are characterized by the smallest broadening (see Table 1).

The ^{31}P NMR spectrum of complex **2b** (see Table 1) shows one broadened signal shifted upfield with respect to the signal of the free ligand by ~27 ppm, which is evidence for coordination of one or both P=O groups. The ^{31}P and ^1H NMR spectroscopic data, as opposed to the IR spectroscopic data, did not allow us to make a conclusion about coordination of the phenolic OH group in monoligand complexes **2a,b**.

Therefore, coordination of phenol $\mathbf{L_2}$ with Ln^{III} nitrates in solutions, where M : L = 1 : 1, gives rise to mononuclear chelate complexes, in which the neutral ligand is tridentate, and three NO_3 groups are bidentate. The complexes are stabilized by the intramolecular P=O...H—O hydrogen bond.

Complexes of composition 1 : 2. The reactions of phenol $\mathbf{L_2}$ with lanthanide nitrates $Ln(NO_3)_3$ (Ln = La, Ce, or Nd) at a metal : ligand ratio of 1 : 2 in low-polarity aprotic media gave complexes **3a—c** of the general formula $Ln(\mathbf{L_2})_2(NO_3)_3 \cdot 3H_2O$. Unlike monoligand complexes **2a,b**, complexes **3a—c** are readily soluble in chloroform, dichloromethane, acetone, and, on heating, in ethanol.

Crystallization of complex **3a** from ethanol afforded crystalline complex **3d** of composition $Ce(\mathbf{L_2})_2(NO_3)_3 \cdot H_2O \cdot EtOH$. The structure of **3d** was established by X-ray diffraction. The structure of complex **3d** contains the complex cations $[Ce(\mathbf{L_2})_2(NO_3)(H_2O)]^{2+}$, the NO_3^- anions and the EtOH solvate molecules linked by hydrogen bonds (Figs 1 and 2).

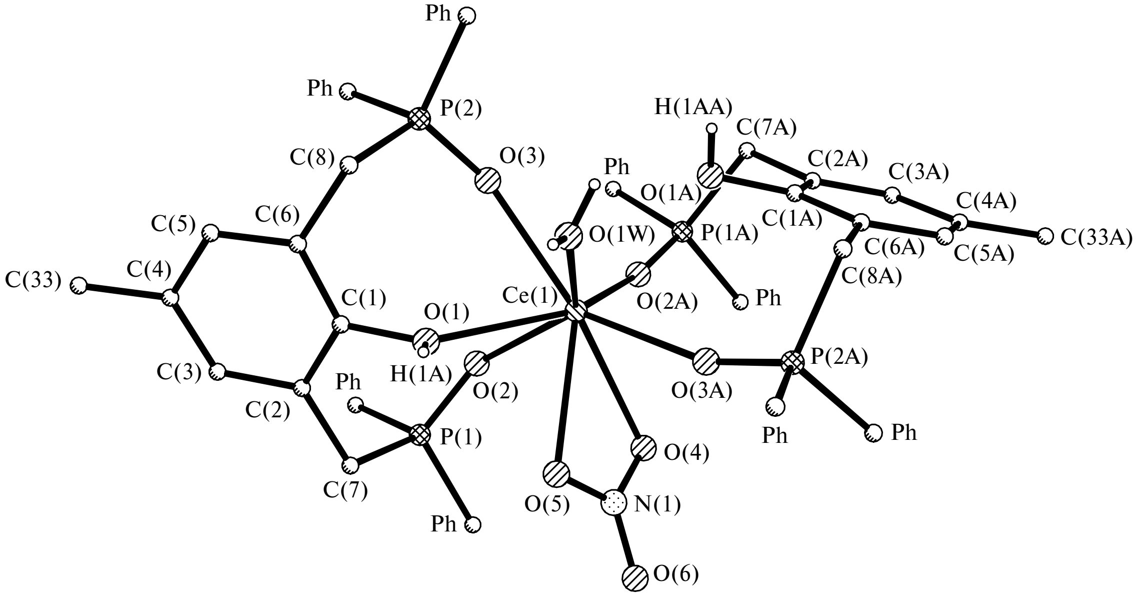


Fig. 1. Structure of the $[Ce(\mathbf{L_2})_2(NO_3)(H_2O)]^{2+}$ cation in complex **3d**. The phenyl rings in the $P(O)Ph_2$ groups are denoted as Ph.

The coordination polyhedron $\{CeO_8\}$ is formed by eight oxygen atoms, five of which belong to two independent molecules of ligand $\mathbf{L_2}$, two atoms belong to the bidentate nitrate ion, and one oxygen atom belongs to the water molecule. Assuming that the bidentate NO_3^- anion occupies one coordination site (X), the coordination polyhedron of the cerium atom in the $[Ce(\mathbf{L_2})_2(NO_3)(H_2O)]^{2+}$ cation can be represented as a distorted octahedron, whose upper faces are formed by the O(1), O(3), and O(3A) atoms and O(2), O(2A), and X (X is the midpoint of the distance between the O(4) and O(5) atoms of the NO_3^- anion). These faces are noncoplanar, the dihedral angle

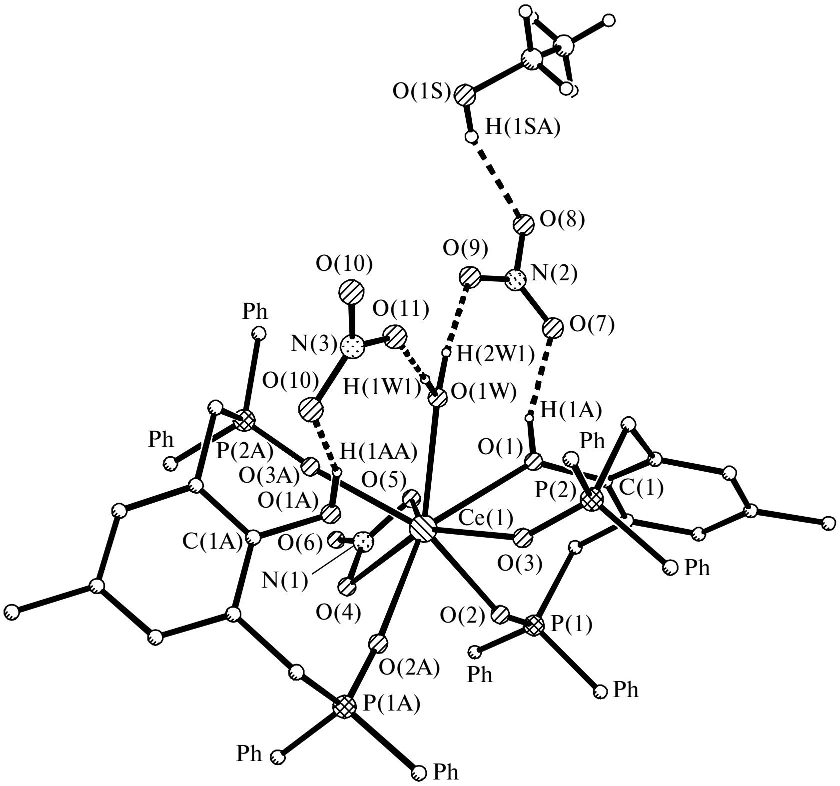


Fig. 2. Structure of complex **3d**. The phenyl rings in the $P(O)Ph_2$ groups are denoted as Ph.

between the faces is 12.8°, and the Ce atom is at different distances from two faces (0.74 and 1.52 Å). The former face is centered by the water molecule, which is located at a distance of 1.80 Å from this plane.

The bonds between the cerium atom and the oxygen atoms of two ligand molecules in the cation differ in length. The distances between the cerium atom and the phosphoryl oxygen atoms, Ce—O(P), in one ligand molecule (**A**) are rather similar to each other (Ce(1)—O(2), 2.437(3) Å; Ce(1)—O(3), 2.461(3) Å; Δd = 0.24 Å), whereas these distances in another ligand molecule (**B**) are substantially different (Ce(1)—O(2A), 2.363(3) Å and Ce(1)—O(3A) 2.413(3) Å; Δd = 0.50 Å). The bond between the Ce atom and the phenol oxygen atom of one ligand molecule (Ce(1)—O(1), 2.590(3) Å) is substantially shorter than the Ce(1)...O(1A) distance (2.937(3) Å), although the HO—C(Ar) bonds are equal in length (aver., 1.393 Å) and are elongated compared to the standard[24] uncoordinated Ar—OH bonds (1.367 Å). The Ce(1)...O(1A) distance is so large that it cannot be considered as a bond. Therefore, one molecule $\mathbf{L_2}$ in the complex cation is tridentate, and another molecule is only bidentate.

In both ligand molecules, the phenol fragments 4-Me-2,6-$(CH_2)_2$-C_6H_2O are planar (average deviations of the atoms from the plane are ±0.069 and ±0.032 Å for the molecules containing the O(1) and O(1A) atoms, respectively) and are almost orthogonal to each other (dihedral angle between the planes is 79.0°).

The uncoordinated NO_3^- anions are held near the cation by hydrogen bonds with the coordinated water molecule and the OH groups of both ligand molecules (Fig. 2). These hydrogen bonds, O—H...O(NO_2) and O_w—H...O(NO_2), belong to strong O—H...O and O_w—H...O bonds (particularly, the O(1)—H(1A)...O(7) bond; the O(1)...O(7) distance (2.631(4) Å) is much shorter than the other O...O distances (O(1A)...O(10), 2.708(4) Å; O(1W)...O(11), 2.731(4) Å; O(1W)...O(9), 2.746(4) Å); the H...O distances are 1.80—1.96 Å). The hydrogen atoms of the OH groups in both ligand molecules are not involved in intramolecular shortened contacts with the oxygen atoms of the P=O groups (all H...O(P) distances are longer than 3.5 Å). Both ligand molecules have identical contacts between the oxygen atoms of the OH and P=O groups within the cations, in spite of the fact that the O(1A) atom is not coordinated to the cerium atom. The O(1)...O(2) and O(1)...O(3) distances in one ligand molecule are 2.942 and 3.020 Å, and the analogous distances in another molecule are 2.940 and 2.999 Å, respectively.

Therefore, the structure of complex **3d** is composed of isolated cation-anion pairs, in which two NO_3^- anions are held near the doubly charged cation thus compensating its charge. In addition to Coulombic interactions between the counterions, the structure is stabilized by hydrogen bonds. The ethanol solvate molecule is held in the outer coordination sphere by a hydrogen bond with the nitrate ion. The main bond lengths and bond angles are given in Table 4.

In the spectrum of crystalline complex **3d**, the band of the coordinated P=O groups is observed at 1155 cm^{-1}. Two bands at 1218 and 1235 cm^{-1} correspond to the coordinated and free C—O(H) groups, the hydrogen atoms of both groups being involved in hydrogen bonding. The spectrum shows also bands of the NO_3 groups at 1490 and 1300 cm^{-1}. These bands are attributed to absorption of two types of bidentate NO_3 ions (ions coordinated to the metal cation in a chelate fashion and bridging ions, which are involved in a tight ion pair and form two strong hydrogen bonds each) because both types of species have the same symmetry. In the OH vibration region, absorption at 3200—2600 cm^{-1} corresponds to vibrations of the phenolic hydroxy group involved in hydrogen bonding. The band at ~3240 cm^{-1} belongs to the coordinated water molecule, and the band at 3380 cm^{-1} is assigned to the OH groups of the ethanol solvate molecules. The spectra of solutions of complex **3d** were not recorded because crystals of **3d** are insoluble in chloroform, acetonitrile, and acetone and are poorly soluble in ethanol.

The spectra of the solid complexes $Ln(\mathbf{L_2})_2(NO_3)_3 \cdot 3H_2O$ (**3a—c**) are virtually identical to each other and differ only slightly from the spectrum of crystalline complex **3d**. The spectra of complexes **3a—c** show broad absorption in the OH vibration region at 3200—2600 cm^{-1}, which is indicative of the involvement of the phenolic hydroxy group in hydrogen bonding. This region contains also a weak band at 3500—3400 cm^{-1}, which can be assigned to the outer-sphere water molecules. Absorption of the P=O groups appears as one rather narrow band at 1155—1160 cm^{-1}, which is indicative of coordination and equivalence of the phosphoryl groups of both ligand molecules. The bands of the C—O(H) groups at 1223—1230 cm^{-1} are also shifted to lower frequencies with respect to the bands of the free ligand (see Table 2), which is evidence that these groups are involved in complexation. Intense bands of the coordinated NO_3 groups are observed at 1480—1490 and 1300—1310 cm^{-1} (see Table 2). The separation between the bands is ~190 cm^{-1}, which is consistent with the bidentate coordination.[23] The NO_3 groups are most probably coordinated to the Ln^{III} cation in a chelate fashion.*

Analysis of the IR spectra shows that both ligand molecules in solid bis-ligand complexes **3a—c** exhibit the maximum *O*,*O*,*O*-coordination due to the involvement of

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* Complexes **3a—c** lose solubility in aprotic solvents upon storage. In the IR spectra, a weak band of coordinated water appears in the region of OH vibrations at 3300—3200 cm^{-1}; the positions of other bands remain unchanged. Presumably, the structures of complexes **3a—c** change with time and become similar to the structure of crystalline complex **3d**.

Table 4. Selected bond lengths, interatomic distances (*d*), and bond angles (ω) in the $[Ce(\mathbf{L_2})_2(NO_3)(H_2O)]^{2+}$ cation (complex **3d**) and the $[Ce(\mathbf{L_3})_2(NO_3)]$ molecule (complex **5a**)

Parameter	Value		
	3d		**5a**
Bond, distance	*d*/Å		
	A	B	
Ce(1)—O(1)	2.590(3)	2.937(3)	2.374(3)
Ce(1)—O(2)	2.437(3)	2.363(3)	2.497(3)
Ce(1)—O(3)	2.461(3)	2.413(3)	2.433(2)
Ce(1)—O(4)	2.636(3)		2.605(3)
Ce(1)—O(5)	2.575(3)		—
Ce(1)—O(1W)	2.565(3)		—
P(1)—O(2)	1.517(3)	1.502(3)	1.485(3)
P(2)—O(3)	1.506(3)	1.496(3)	1.508(3)
P(1)—C(7)	1.838(5)	1.811(4)	1.812(4)
P(1)—C(9)	1.803(5)	1.802(5)	1.815(4)
P(1)—C(15)	1.800(5)	1.809(5)	1.797(4)
P(2)—C(8)	1.830(5)	1.815(5)	1.814(4)
P(2)—C(21)	1.804(5)	1.811(5)	1.795(4)
P(2)—C(27)	1.806(5)	1.806(5)	1.803(4)
O(1)—C(1)	1.394(5)	1.392(5)	1.302(4)
C(1)—C(6)	1.385(7)	1.412(6)	1.437(5)
C(1)—C(2)	1.408(6)	1.407(6)	1.413(5)
C(2)—C(3)	1.406(6)	1.383(6)	1.379(5)
C(2)—C(7)	1.492(7)	1.503(6)	1.506(5)
C(3)—C(4)	1.393(7)	1.395(7)	1.396(5)
C(4)—C(5)	1.376(7)	1.389(7)	1.374(6)
C(4)—C(33)	1.506(7)	1.504(7)	1.445(5)
C(5)—C(6)	1.402(6)	1.390(6)	1.368(5)
C(6)—C(8)	1.523(6)	1.516(6)	1.507(5)
N(1)—O(4)	1.265(5)		1.254(3)
N(1)—O(5)	1.303(5)		—
N(1)—O(6)	1.207(5)		1.238(6)
O(1)...O(7)	2.627(5)		—
O(1A)...O(10)	2.707(5)		—

Parameter	Value		
	3d		**5a**
Angle	ω/deg		
	A	B	
O(1)—Ce(1)—O(1A)	134.19(9)		76.2(1)
O(1)—Ce(1)—O(2)	71.4(1)		71.96(9)
O(1)—Ce(1)—O(3)	73.35(9)		76.83(8)
O(1)—Ce(1)—O(4)	112.6(1)		132.71(8)
O(1)—Ce(1)—O(5)	67.1(1)		—
O(1)—Ce(1)—O(1W)	67.36(9)		—
O(1A)—Ce(1)—O(2A)	66.07(9)		71.96(9)
O(1A)—Ce(1)—O(3A)	67.36(9)		76.83(8)
O(1A)—Ce(1)—O(4)	109.40(9)		132.71(8)
O(1A)—Ce(1)—O(5)	137.80(9)		—
O(1A)—Ce(1)—O(1W)	70.04(9)		—
O(2)—Ce(1)—O(2A)	77.7(1)		140.6(1)
O(3)—Ce(1)—O(3A)	139.4(1)		153.7(1)
P(1)—O(2)—Ce(1)	141.6(2)	162.9(2)	146.1(2)
P(2)—O(3)—Ce(1)	146.6(2)	161.2(2)	133.4(1)
C(1)—O(1)—Ce(1)	130.7(2)	121.1(2)	138.0(2)
C(1)—C(2)—C(7)	121.2(4)	119.8(4)	118.2(3)
C(1)—C(6)—C(8)	120.1(4)	121.4(4)	118.0(3)
C(2)—C(7)—P(1)	108.6(3)	111.0(3)	114.6(3)
C(6)—C(8)—P(2)	108.7(3)	108.2(3)	109.7(3)
C(7)—P(1)—O(2)	111.6(2)	112.0(2)	114.8(2)
C(8)—P(2)—O(3)	113.6(2)	111.3(2)	113.2(2)

Note: A is the tridentate molecule, and B is a bidentate molecule.

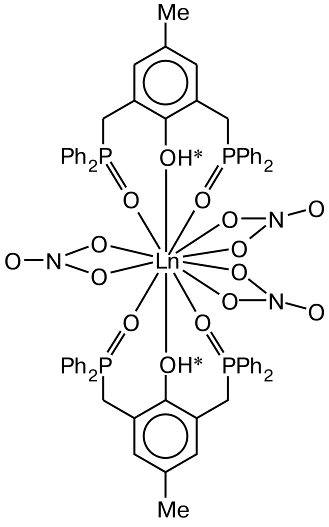
two P=O groups and one C—O(H) group giving rise to two seven-membered rings. The protons of the phenolic hydroxy groups are involved in intermolecular hydrogen bonds. It is highly probable that three NO_3 groups are coordinated to the central cation in a chelate fashion. If this is the case, the coordination number of the lanthanide(III) cation is 12, and the structures of the neutral complexes $[Ln(\mathbf{L_2})_2(NO_3)_3] \cdot 3H_2O$ can be represented as follows.

In solutions, the structures of the complexes are, on the whole, retained. In the IR spectra of solutions of the bis-ligand complexes in chloroform, only slight changes are observed in the bands of the functional C—O(H) and NO_3 groups. A new broad band with a maximum at 3000 cm^{-1} appears in the spectrum, which corresponds to vibrations of the phenolic OH groups involved in hydrogen bonding. The band of the outer-sphere water molecules disappears. The band of the coordinated P=O groups appears as a doublet (see Table 2). These spectral changes can be attributed to the fact that one P=O group (at 1140—1155 cm^{-1}) is involved not only in coordination to metal but also in additional intramolecular hydrogen bonding with the phenolic hydroxy group.

The coordination number of the lanthanide cation in complexes **3a—c** is 12.

The ^1H and ^{31}P NMR spectroscopic parameters of solutions of bis-ligand complex **3a** are similar to those of monoligand complex **2b** (see Table 1), do not contradict the proposed structure, and suggest that the ligand in these complexes exhibits a similar coordination mode. A fine structure is absent from the spectra. The observed broadening of the signals is associated primarily with the paramagnetic properties of the cations in the complexes.

As in the case of the monoligand complexes, the structures of bis-ligand complexes **3a—c** in the solid state differ from those in solution primarily in that the intramo-



3a—c (solid)

Ln = Ce (**a**), Nd (**b**), La (**c**)

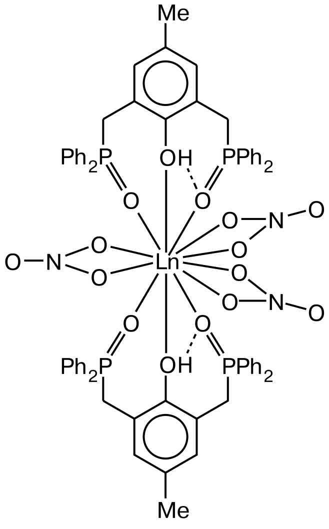
lecular P=O...H—O hydrogen bonds are present in solution instead of intermolecular hydrogen bonds involving the same HO groups found in the crystals.

Complexes of composition 1 : 3. As mentioned above, the reaction of cerium nitrate with the ligand in dichloromethane or methanol in a ratio of 1 : 3 and 1 : 4 affords the tris-ligand complex. The $Ce(\mathbf{L_2})_3(NO_3)_3 \cdot 2H_2O$ complex (**4a**) was isolated in the solid state. It is soluble in chloroform, dichloromethane, and methanol.

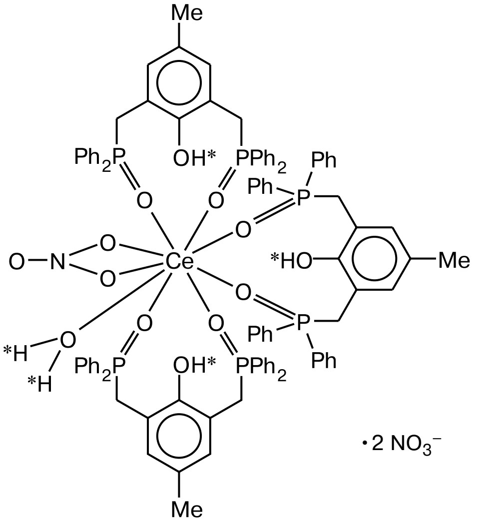
Attempts to isolate the crystalline 1 : 3 complex suitable for X-ray diffraction study failed. The 1 : 2 complex crystallized from methanol even when the metal : ligand ratio of 1 : 4 was used. According to the preliminary X-ray diffraction data, monoclinic crystals of this complex, $[Ce(\mathbf{L_2})_2(NO_3)(H_2O)](NO_3)_2 \cdot MeOH$ (**3e**), are isotypic with complex **3d**. The unit cell parameters of **3e** are virtually identical to those of complex **3d**, which was prepared from an ethanolic solution with the use of the metal : ligand ratio of 1 : 2 and was characterized in the present study.

In the IR spectrum of solid complex **4a**, the band of free P=O groups is absent, and a single band of the P=O groups is observed at 1155 cm^{-1}, which indicates that all coordinated P=O groups in this complex are equivalent and are not involved in additional interactions. The C—O(H) group is characterized by one band at 1235 cm^{-1}, which (based on analysis of the data for structurally characterized complex **3d**) can be assigned to vibrations of the uncoordinated phenol group, whose hydrogen atom is involved in hydrogen bonding. Therefore, all three ligand molecules are coordinated in a bidentate fashion. The bands of the NO_3 groups are observed at 1485 and 1305 cm^{-1}, which is evidence that they are bidentate.[23] Very broad absorption at 3600—2200 cm^{-1} in the OH vibration region includes, apparently, vibrations of the phenolic OH groups and the OH groups of water molecules involved in hydrogen bonding.

The elemental analysis data and the IR spectra for compound **4a** suggest that this compound, most probably, has the structure of the cationic complex $[Ce(\mathbf{L_2})_3(NO_3)(H_2O)]^{2+} \cdot 2NO_3^-$, in which the ligand is bidentate due to the involvement of both P=O groups in coordination. The inner sphere of the cation contains one water molecule and one chelate NO_3 group. The protons of the OH groups of the coordinated ligand and water molecules form hydrogen bonds with the oxygen atoms of two outer-sphere NO_3 groups due to which these bridging groups manifest themselves in the spectra like the inner-sphere chelate NO_3 group. The coordination number of cerium in this complex is 9.



3a—c (solv)



4a (solid)

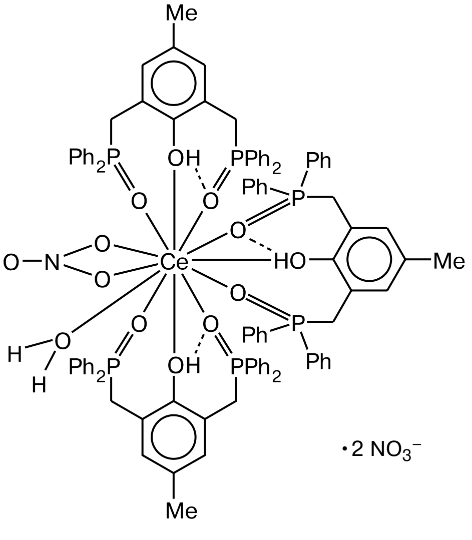
In the IR spectrum of a solution of complex **4a** in dichloromethane, changes in the bands of the functional groups are observed. Vibrations of the phosphoryl groups appear as a narrow band at 1195 cm^{-1} and a poorly resolved broadened doublet at 1150 and 1140 cm^{-1} with an intensity ratio is ~1 : ~4 : ~4. Vibrations of C—O(H) groups are observed as two bands at 1255 and 1218 cm^{-1} with an intensity ratio of ~1 : ~4. In addition to the bands of the bidentate NO_3 groups at 1470 and 1305 cm^{-1}, a band of free NO_3 groups appears at 1350 cm^{-1}. The spectrum also shows a broad pronounced band with a maximum at 3000 cm^{-1} corresponding to vibrations of the OH groups of the phenol and water molecules involved in hydrogen bonding.

These spectral changes can be attributed to partial dissociation of the tris-ligand complex giving rise to the free ligand and the bis-ligand complex:

$$[\mathrm{Ce}(\mathbf{L}_2)_3(\mathrm{NO}_3)(\mathrm{H_2O})] + 2\ \mathrm{NO}_3 \longleftrightarrow$$

$$\longleftrightarrow [\mathrm{Ce}(\mathbf{L}_2)_2(\mathrm{NO}_3)_3] + \mathbf{L}_2. \qquad (1)$$

According to the equilibrium (1), the observed spectral pattern is a superposition of the spectra of three species, *viz.*, the tris-ligand complex with outer-sphere (free) NO_3 groups, the bis-ligand complex, and the free ligand. The tris-ligand complex is characterized by two absorption bands of the P=O groups at 1150 and 1140 cm^{-1}, which (as in the above-considered cases) can be interpreted as absorption of the coordinated P=O groups, one of which is involved in an intramolecular hydrogen bond with the OH group of the ligand. The phosphoryl groups of the free ligand are characterized by bands at 1195 and 1155 cm^{-1}, and absorption of the P=O groups of the bis-ligand complex in dichloromethane appears at 1155 and 1145 cm^{-1}. In both complexes, the band of the coordinated C—O(H) group involved in the hydrogen bond is observed at 1218 cm^{-1}, whereas the band of this group in the free ligand appears at 1255 cm^{-1}. The observed intensities of the bands of the free and bidentate NO_3 groups suggest that one NO_3 group in the tris-ligand complex, as opposed to the bis-ligand complex, is coordinated to the cation in a chelate fashion, whereas two other NO_3 groups (which are observed in the spectra as free groups) are held in the outer sphere of the complex by nonspecific Coulombic interactions. Therefore, the structure of complex **4a** in the solid state differs from that in an aprotic solvent, although the composition of the complex cation $[\mathrm{Ce}(\mathbf{L}_2)_3(\mathrm{NO}_3)(\mathrm{H_2O})]^{2+}$ remains unchanged. In solutions, the ligand molecules are tridentate and the phenolic OH groups are involved in intramolecular hydrogen bonds, as opposed to the complex in the solid state, where the ligand molecules are bidentate and the phenolic OH groups are involved in intermolecular hydrogen bonds. The coordination number of cerium is 12.

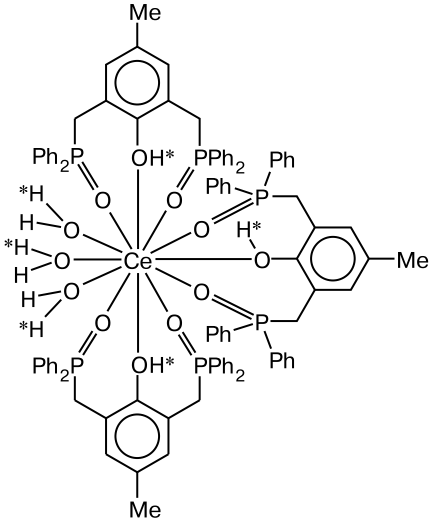


4a (solv)

In solution, this complex is unstable and exists in equilibrium with the corresponding bis-ligand cerium complex and the free ligand.

Unlike complex **4a**, the tris-ligand complex, which was prepared without isolation in a solution by the reaction of 1 mole of $\mathrm{Ce(NO_3)_3 \cdot 6H_2O}$ with 3 moles of ligand $\mathbf{L}_2$ and, as a consequence, in a solvent containing ~0.2 *M* H_2O, is stable. The IR and NMR spectra show no evidence for the free ligand. Bands of the free ligand appear only after the addition of the fourth mole of phenol $\mathbf{L}_2$.

The ^{31}P NMR spectrum of a solution of 1 mole of $\mathrm{Ce(NO_3)_3 \cdot 6H_2O}$ and 3 moles of ligand $\mathbf{L}_2$ in dichloromethane shows one broadened signal at δ 64 ($\Delta_{1/2}$ = 10 ppm). In the IR spectrum of this solution, the band of the coordinated P=O groups is observed at 1155 cm^{-1}, and the C—O(H) groups are characterized by one band at 1125 cm^{-1}. According to the above analysis, the latter band should be assigned to vibrations of the coordinated C—O(H) group, whose proton is involved simultaneously in a hydrogen bond. A broad clear band with a maximum at 3000 cm^{-1} corresponds to vibrations of the phenolic hydroxy group involved in hydrogen bonding. The band of coordinated water is observed at 3400 cm^{-1}, and the bands at 3680 and 3660 cm^{-1} correspond to free water (introduced into the solution together with $\mathrm{Ce(NO_3)_3 \cdot 6H_2O}$). Intense bands of the NO_3 groups appear at 1480 and 1305 cm^{-1}, which indicates that these groups are bidentate (groups coordinated to the cation in a chelate fashion and/or bridging groups, each being involved in two hydrogen bonds with the OH groups of the coordinated ligand and water molecules). Apparently, the complex has the composition $\mathrm{Ce}(\mathbf{L}_2)_3(\mathrm{NO}_3)_3(\mathrm{H_2O})_n$, where n = 2 or 3, in solution. Assuming that the coordination number of the cerium(III) atom in this complex is 12 (many lanthanide complexes, including cerium complexes, with this coordination number were documented[25]), the structure of the complex can be represented by the formula $[Ce(\mathbf{L_2})_3(H_2O)_3]^{3+} \cdot 3NO_3^-$.



$[Ce(\mathbf{L_2})_3(H_2O)_3]^{3+}$ (solv)

Three outer-sphere NO_3 ions in low polarity solvents, which cannot be involved in solvation through hydrogen bonds (in the case under consideration, dichloromethane), form a tight ion pair with the complex cation. In this pair, the counterions can be held together not only by Coulombic forces but also by hydrogen bonds with the inner-sphere coordinated groups; the latter bonds can be very strong (see, for example, X-ray diffraction data for complex **3d**). Six P=O groups are coordinated to the cation. All three neutral ligands $\mathbf{L_2}$ are tridentate. The protons of the phenolic hydroxy groups and the coordinated water molecules are involved in intermolecular hydrogen bonds with the outer-sphere NO_3 groups. The spectroscopic characteristics of these NO_3 groups (two oxygen atoms of each group are involved in hydrogen bonding) are analogous to those of the groups coordinated to the metal cation in a bidentate fashion.[26]

Conformational analysis (molecular mechanics) showed that the formation of complexes of composition L : M = 3 : 1 is quite probable.

The formation of complexes with transition metal cations (Co^{II} and Cu^{II}), in which L : M = 3 : 1, in solution was documented[27] also for compound $\mathbf{L_1}$ (R = Ph), which is a prototype of phenol $\mathbf{L_2}$ having the same ligand contour (1 : 1 and 2 : 1 complexes are formed at other L : M ratios).

Therefore, the reaction of $\mathbf{L_2}$ with cerium(III) nitrate in nonpolar aprotic solvents gives complexes containing the ligand and metal in a ratio of 1 : 1, 2 : 1, or 3 : 1 depending on the ratio of the starting components. In the complexes, the neutral ligand exhibits variable dentation. Unlike the phosphoryl oxygen atoms, the oxygen atom of the hydroxy group is not always involved in coordination. The proton of the phenolic hydroxy group is involved in intra- or intermolecular hydrogen bonding.

Stability to oxidation with atmospheric oxygen

We demonstrated that phenol $\mathbf{L_2}$ is very stable to radical oxidation compared to other sterically hindered phenols due in part to stabilization of the molecule by a strong intramolecular hydrogen bond.

However, the ligand is readily oxidized with atmospheric oxygen upon coordination with lanthanide nitrates. In the complexes under study, easy inner-sphere oxidation of the ligand with atmospheric oxygen occurs. The structure of one of the oxidation products (complex **5a**) was established by X-ray diffraction. According to the results of IR spectroscopy, quinoid-like compounds are present, along with salt **5a** (~14%), as the main components in a nonseparable mixture.

The structure of complex (chelate salt) **5a** consists of the neutral $[Ce(\mathbf{L_3})_2(NO_3)]$ molecules containing two deprotonated ligands (phenoxide anions) ($\mathbf{L_3}$ = 4-CHO-2,6-$[Ph_2P(O)CH_2]_2C_6H_2O^-$) and one NO_3^- ion. The crystal structure contains also acetonitrile and water solvate molecules. The oxygen atom of the CHO substituent is disordered over two positions (O(6) and O(6A)) with equal occupancies, which corresponds to the twist of the substituent relative to the ring by 180°. The molecular structure of the $[Ce(\mathbf{L_3})_2(NO_3)]$ complex **5a** is shown in Fig. 3.

The $[Ce(\mathbf{L_3})_2(NO_3)]$ molecule in the structure of **5a** lies on a twofold axis. The coordination polyhedron $\{CeO_8\}$ is formed by the oxygen atoms of the P=O groups, the atoms of the deprotonated hydroxy groups of two ligands $\mathbf{L_3}$, and the bidentate NO_3 group. The polyhedron can be described as a distorted pentagonal bipyramid whose base is formed by the O(1), O(2), O(1A), and O(2A) atoms and the point X (X is the midpoint between the O(4) and O(4A) atoms of the coordinated NO_3 group); the apices of the bipyramid are occupied by the O(3) and O(3A) atoms. The O(3A)—Ce(1)—O(3A) angle is 153.7°, and the NO_3 group is orthogonal to the base of the bipyramid.

The Ce—O(Ar) bond lengths in the $[Ce(\mathbf{L_3})_2(NO_3)]$ molecule are substantially shorter than the Ce—O(H)(Ar) bonds in the $[Ce(\mathbf{L_2})_2(NO_3)(H_2O)]^{2+}$ cation (see Table 4), which is reasonable because ligand $\mathbf{L_3}$ in compound **5a** is an anion, whereas ligand $\mathbf{L_2}$ in **3d** is a neutral molecule. The Ce—O(P) bonds in **5a** are longer than those in **3d,** but they also differ substantially from each other (Δd = 0.64 Å).

The central phenol ring C(1)—C(6) in the $[Ce(\mathbf{L_3})_2(NO_3)]$ molecule is characterized by a certain contribution of the quinoid form, unlike the ring in the $[Ce(\mathbf{L_2})_2(NO_3)(H_2O)]^{2+}$ cation. In the structure of **5a**, the C(2)—C(3) and C(5)—C(6) bonds in the central

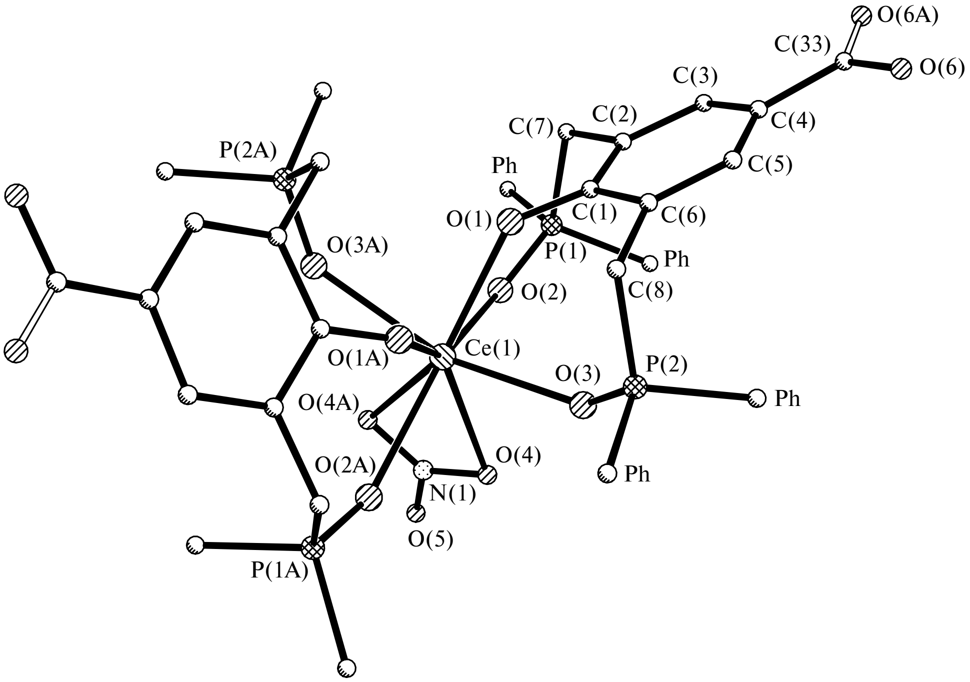


Fig. 3. Structure of the [Ce($\mathbf{L_3}$)$_2$(NO$_3$)] molecule. The phenyl rings in the P(O)Ph$_2$ groups are denoted as Ph.

ring are shorter (aver., 1.373 Å) than the other bonds (aver., 1.405 Å). The C(4)—C(33) and C(1)—O(1) bonds are also shorter than the analogous bonds in the [Ce($\mathbf{L_2}$)$_2$(NO$_3$)(H$_2$O)]$^{2+}$ cation, where the ring has a standard benzoid structure, and than the standard C—O and C(Ph)—C(sp^2) bonds in enols (1.333 and 1.483 Å, respectively[24]). Apparently, this difference is due to deprotonation of the hydroxy group and the mesomeric effect of the formyl substituent in ligand $\mathbf{L_3}$. Since phenol H$\mathbf{L_3}$ should be a much stronger acid than phenol $\mathbf{L_2}$, its coordination to the lanthanide cation can be accompanied by the displacement of the proton to form chelate salt **5a**. For example, the acidity of the analog of 2,6-di-*tert*-butyl-4-methylphenol containing the CHO group instead of the methyl group in the *para* position of the phenol ring increases by more than four orders of magnitude.[28]

The phenol fragments 4-Me-2,6-(CH$_2$)$_2$C$_6$H$_2$O, like those in complex **3d**, are planar (average deviation of the atoms is ±(0.032—0.069) Å) and are almost orthogonal with respect to each other (dihedral angle between the planes is 85°).

A comparison of the structures of **3d** and **5a** shows that the molecules differ in the twist of the Ph$_2$P=O groups with respect to the P—CH$_2$ bond, although the geometric parameters of the O=P—CH$_2$—C$_6$H$_2$(O)—CH$_2$—P=O moieties of ligands $\mathbf{L_2}$ in complex **3d** are similar to those of ligands $\mathbf{L_3}$ in complex **5a** (C(Ar)—CH$_2$, P—CH$_2$, and P=O bond lengths and the corresponding bond angles, see Table 4). For example, the deviations of the O(2) and O(3) atoms in complex **3d** from the plane of the C$_6$H$_2$O(CH$_2$)$_2$ fragment in both molecules of coordinated neutral ligand $\mathbf{L_2}$ are nearly equal (2.235(5) and 2.247(5) Å in one molecule and 2.190(5) and 2.309(5) Å in another molecule). In chelate salt **5a**, these deviations are substantially different (1.730(5) and 2.284(4) Å, respectively). Presumably, this difference in the conformation of the coordinated ligands is associated with steric factors caused by "contraction" of the coordination polyhedron of the cerium atom in the [Ce($\mathbf{L_3}$)$_2$(NO$_3$)] molecule due to formation of the stronger Ce—O(1) bonds and the absence of coordinated water molecules. The molecular packing in the structure of **5a**, unlike that in **3d**, is determined only by van der Waals interatomic interactions.

The formation of salt **5a** as one of oxidation products agrees well with the known data on catalytic oxidation of sterically hindered phenols with atmospheric oxygen.[28] For example, oxidation of 4-methyl-2,6-di-*tert*-butylphenol in the presence of amines and copper salts affords a complex mixture of compounds, from which several quinoid-like compounds (main component was obtained in ~50% yield) and 4-hydroxy-3,5-di-*tert*-butylbenzaldehyde (~12%) were isolated.[29] The fact that oxidation products of phenols $\mathbf{L_2}$ are structurally similar to oxidation products of the alkyl analog of $\mathbf{L_2}$ suggests that inner-sphere oxidation of the coordinated phenol occurs in both cases.

Oxidation of sterically hindered phenols with atmospheric oxygen, which is a typical radical reaction, has been studied in-depth.[28] In the absence of catalysts, extensive oxidation of sterically hindered phenols with oxygen is possible in an alkaline medium only. In this case, the reaction involves the phenoxide ion, the electron transfer from which to an oxidizing agent occurs more easily than from the neutral phenol molecule.[28] Potassium salt **1** is less resistant to atmospheric oxygen than the starting phenol $\mathbf{L_2}$.

Apparently, oxidation of both phenols proceeds by the same mechanism. Although it is impossible to study the reactions of cerium compounds by ESR,[30] analysis of the IR spectra of a mixture of oxidation products and the structure of one of this product established by X-ray diffraction provide support for this assumption.

Therefore, unlike free phenol $\mathbf{L_2}$ stable to oxidation, its K salt **1** is much readily oxidized with atmospheric oxygen. In the complexes with lanthanide nitrates, inner-sphere oxidation of coordinated phenol readily occurs already at room temperature. Taking into account the structure of one of oxidation products and based on analysis of the IR spectra of a mixture of products, it can be concluded that oxidation of phenol $\mathbf{L_2}$ in lanthanide complexes and its alkyl analogs catalyzed by copper salts occurs presumably by the same (radical) mechanism.

In conclusion, it should be noted that phenol $\mathbf{L_2}$, like its prototype, *viz.*, bis(diphenylphosphorylmethyl)benzene $\mathbf{L_1}$ (R = Ph) containing no OH groups in the central benzene ring, is coordinated to metal salts to form polyligand complexes with M : L = 1 : 1, 1 : 2, or 1 : 3. In solutions, additional coordination of the oxygen atom of the OH group was observed in all complexes of phenol $\mathbf{L_2}$ with rare-earth nitrates. In the solid phase, additional coordination is observed only in some cases. Coordination of both phosphoryl oxygen atoms in the pendant groups plays the major role and retains the necessary ligand contour, which is apparently responsible for selectivity of extraction.

We thank B. L. Tumanskii for help in performing ESR experiments and helpful discussion.

This study was financially supported by the Council on Grants of the President of the Russian Federation (Federal Program for the Support of Leading Scientific Schools, Grants NSh-1100-2003-3 and NSh-1060-2003-3) and the Russian Academy of Sciences (State Contract No. 0002-251/P-09/118-125.100603-589).

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Received July 6, 2005