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Inorganica Chimica Acta 358 (2005) 4172-4176

Inorganica Chimica Acta

www.elsevier.com/locate/ica

New homoleptic tris(diphosphanylamido) complexes of the lanthanides – synthesis and structure

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Received 4 January 2005; accepted 6 February 2005 Available online 14 March 2005

Dedicated to Professor Hubert Schmidtbaur on the occasion of his 70th birthday.

Abstract

New homoleptic diphosphanylamido compounds of the lanthanides, $[Ln{N(PPh_2)_2}_3]$ (Ln = Sm, Gd, Dy), were synthesized and characterized by single crystal X-ray diffraction in the solid state and partly by NMR in solution. In the solid state the complexes solely show a η^2 -coordination of the {(Ph_2P)_2N}⁻ ligand. The dependence of the Ln–N and the Ln–P bond distance on the ion radius of the center metal was investigated.

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Keywords: Chelates; Coordination chemistry; Lanthanides; N,P ligands

1. Introduction

Recently, there has been a significant research effort in *d*- and *f*-transition metal chemistry to find as an alternative to the well established cyclopentadienyl ligand [1] new ancillary ligands for stabilizing high reactive metal centers. In these regards one approach among others is the use of phosphines with P–N bonds [2]. Recently, we have introduced the well known monophosphanylamide, $(Ph_2PNPh)^-$ [3] and diphosphanylamide, $\{(Ph_2P)_2N\}^-$ [4–6], as ligands in lanthanide chemistry. In dependence of the steric demand of the ligand either metallate complexes of composition $[Li(THF)_4][(Ph_2PNPh)_4Ln]$ (Ln = Y, Yb, Lu) [3] or the homoleptic compounds $[Ln\{N(PPh_2)_2\}_3]$ (Ln = Y, La, Nd, Er) [4] can be obtained. The later complexes were used as catalysts for the polymerization of ε -caprolactone. Significant differ-

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ences in terms of correlation of theoretical and experimental molecular weights as well as polydispersities were observed depending on the nature of Ln. The single crystal X-ray structures of these complexes solely show a η^2 -coordination of the ligand via the nitrogen and one phosphorous atom. In solution a dynamic behavior of the ligand is observed, which is caused by the rapid exchange of the two different phosphorous atoms. Thus, the coordination of phosphorous atom to the metal center is weak and the corresponding bond length is rather long. So far, we have studied only a limited number of homoleptic compounds $[Ln{N(PPh_2)_2}_3]$. As a result, we are now interested to see if the Ln-P bond length linearly decreases with decreasing ion radius of the lanthanide atom as it is observed in normal σ -bonds or if the influence of the crystal packing is superior. Therefore, we wanted to establish more than the previous reported four data points. Herein, we report the synthesis and structure of some new homoleptic diphosphanylamide complexes of the lanthanides and establish the relation of the Ln-P bond length to the ion radius of the center metal.

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2. Results and discussion

Reaction of the previously described potassium compound $[K(THF)_n N(PPh_2)_2][4](1)$ with anhydrous lanthanide trichlorides in a 3:1 molar ratio in THF or reaction of the homoleptic bis(trimethylsilyl)amides of the lanthanides, $([Ln{N(SiMe_3)_2}_3])$ [7], with three equivalents of (Ph₂P)₂NH in boiling toluene followed by crystallization from toluene afforded the homoleptic diphosphinoamide complexes $[Ln{N(PPh_2)_2}]$ (Ln = Sm (2a), Gd (2b), Dy (2c)) as large crystals in good yields (Scheme 1). The samarium compound 2a was characterized by ¹H, ³¹P{¹H} NMR spectroscopy and elemental analysis, whereas for all other new compounds IR spectra and elemental analysis were obtained. The solid-state structures of all new compounds were established by single crystal X-ray diffraction. The NMR spectra of the weekly paramagnetic samarium complex 2a were investigated. In the ¹H spectrum three well resolved sets of signals for the phenyl protons are observed at δ 6.87, 7.07, and 7.45 ppm. Very characteristic is also the ${}^{31}P{}^{1}H{}$ NMR spectrum. Only one signal for all phosphorous atoms is observed, showing that the phosphorous atoms in each case are chemically equivalent in solution. In contrast to the diamagnetic compounds $[Y{N(PPh_2)_2}_3]$ (δ 42.0 ppm) and $[La{N(PPh_2)_2}_3]$ (δ 44.6 ppm) the ${}^{31}P{}^{1}H$ } NMR signal of compound 2a is strongly shifted upfield $(\delta - 62.7 \text{ ppm}).$

Due to the similar ion radii of the lanthanides used, the single crystal X-ray structures of **2a–2c** are isostructural to each other and to the previously reported compounds [Ln{N(PPh₂)₂}₃] (Ln = Y, La, Nd, Er). As a representative example, the structure of **2a** is shown in Fig. 1. **2a–2c** crystallize in the trigonal space group $P\overline{1}$ having two molecules of **2** and two molecules of toluene in the unit cell. Three symmetrically chelating (η^2) {(Ph₂P)₂N}⁻ ligands are coordinated to the lanthanide atom with the six coordinate LnN₃P₃ geometry closely trigonal prismatic (Fig. 1). As observed for other lantha-



Fig. 1. Perspective ORTEP view of the molecular structure of 2a. Thermal ellipsoids are drawn to encompass 30% probability. Selected bond lengths [pm] or angles [°] (also given for isostructural 2b-2c): N1-P1 168.3(3), N1-P2 171.4(2), N2-P3 166.3(3), N2-P4 172.3(3), N3-P5 167.4(3), N3-P6 172.3(2), N1-Sm 234.3(2), N2-Sm 232.7(2), N3-Sm 236.1(2), P1-Sm 286.48(8), P3-Sm 286.41(7), P5-Sm 285.51(8); P1-N1-P2 121.00(14), P3-N2-P4 124.43(14), P5-N3-P6 118.18(14), P1-N1-Sm 89.16(10), P2-N1-Sm 149.75(14), P4-N2-Sm 145.24(13), P5-N3-Sm 88.37(9), P6-N3-Sm 151.67(14), N1-Sm-P1 35.98(6), N2-Sm-P3 35.50(6), N3-Sm-P5 35.89(6). 2b: N1-P1 167.7(2), N1-P2 171.4(2), N2-P3 166.5(2), N2-P4 171.2(2), N3-P5 167.7(2), N3-P6 172.1(2), N1-Gd 231.4(2), N2-Gd 230.7(2), N3-Gd 232.8(2), P1-Gd 282.12(7), P3-Gd 282.56(7), P5-Gd 281.61(7); P1-N1-P2 120.85(14), P3-N2-P(4) 124.79(14), P5-N3-P6 117.35(13), P1-N1-Gd 88.48(9), P2-N1-Gd 150.53(13), P3-N2-Gd 89.19(10), P4-N2-Gd 145.92(13), P5-N3-Gd 87.77(9), P6-N3-Gd 153.00(13), N1-Gd-P1 36.45(6), N2-Gd-P3 36.10(6), P5-Gd-P3 98.62(2). 2c: N1-P1 168.3(2), N1-P2 171.3(2), N2-P3 167.1(2), N2-P4 171.3(2), N3-P5 168.1(2), N3-P6 172.5(2), N1-Dy 228.3(2), N2-Dy 227.3(2), N3-Dy 229.0(2), P1-Dy 279.48(6), P3-Dy 279.75(6), P5-Dy 279.01(6); P1-N1-P2 120.19(12), P3-N2-P4 124.02(12), P5-N3-P6 116.61(11), P1-N1-Dy 88.27(8), P2-N1-Dy 151.44(11), P3-N2-Dy 89.01(8), P4-N2-Dy 146.86(10), P5-N3-Dy 87.87(8), P6-N3-Dy 153.70(10), N1-Dy-P1 37.01(5), N2-Dy-P3 36.67(5), N3-Dy-P5 37.02(5).



Scheme 1.

nide complexes having the $\{(Ph_2P)_2N\}^-$ ligand in the coordination sphere such as [{(Ph₂P)₂N}LnCl₂(THF)₃] [6] and $[{(Ph_2P)_2N}_2Yb(C_5Me_5)]$ [8] the diphosphanylamide ligand in **2a–2c** is η^2 -coordinated via the nitrogen and one phosphorous atom. Thus, one of the phosphorous atoms of the ligand binds to the lanthanide center whereas the other phosphorous atom is bent away. The average Ln-N1 and Ln-P1 bond lengths are 234.4(2)and 286.13(8) pm (2a), 231.6(2) and 282.10(7) pm (2b), and 228.2(2) and 279.41 pm (2c). The free electron pair of the nonbonded phosphorous atom points away from the lanthanide center. In Fig. 2 a chart of the average Ln–N and Ln–P1 bond distances versus the effective ionic radii after Shannon [9] for coordination number six is shown. The average Ln-N distances increases as expected with increasing ion radius of the center metal in a linear fashion. A similar dependency is observed for the average Ln–P1 bond distance. Even though the Ln-P interactions are weak and a dynamic rearrangement is observed in solution (see above), the Ln-P bond distances do not deviate from the normal behavior observed.

The average P–N–P angles within the η^2 -{ $(Ph_2P)_2N$ }⁻ ligand are 121.20(14)° (**2a**), 121.00(14)° (**2b**), and 120.27(12)° (**2c**). The deviation from this average value is significant. For example in compound **2a** the angle P3–N2–P4 (124.43(14)°) is 6.25° larger than the angle P5–N3–P6 (118.18(14)°). Within the ligand the P–N bond distance vary. The phosphorous atom, which binds to the lanthanide metal is slightly closer located to the nitrogen atom (av. N–P_{bonding} 167.3(3) pm (**2a**), 167.33(3) pm (**2b**), 167.83 pm (**2c**) and av. N–P_{nonbonding} 172.0(2) pm (**2a**), 171.57(2) pm (**2b**).

3. Summary

In summary, we have synthesized a number of new homoleptic diphosphanylamido lanthanide compounds of the general composition $[Ln{N(PPh_2)_2}_3]$. The single crystal X-ray structures of these complexes solely show a η^2 -coordination of the ligand, in which only one of the phosphorus atoms coordinates to the metal center. As seen by the dynamic behavior of the complex in solution the Ln–P interaction is weak. In the solid state a long Ln–P distance is observed. However, the Ln–P bond distances and the Ln–N bond distance linearly decrease with decreasing ionic radii.

4. Experimental

4.1. General

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-4} torr) line, or in an argon-filled M. Braun glove box. THF was predried over Na wire and distilled under nitrogen from K and benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from LiAlH₄. All solvents for vacuum line manipulations were stored in vacuo over LiAlH₄ in resealable flasks. Deuterated solvents were obtained from Chemotrade Chemiehandelsgesellschaft mbH (all ≥ 99 atom% D) and were degassed, dried, and stored in vacuo over Na/K alloy in resealable flasks.



Fig. 2. Chart of the effective ionic radii after Shannon [9] (CN: 6) versus the Ln-N, Ln-P1 bond distances of [Ln{N(PPh₂)₂}] [4].

NMR spectra were recorded on JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane and 85% phosphoric acid (³¹P NMR), respectively. IR spectra were obtained on a Shimadzu FTIR-8400s. LnCl₃ [10], [Ln{N(SiMe₃)₂}₃] [7] and [K(THF)_nN(PPh₂)₂] (n = 1.25, 1.5) [4] were prepared according to literature procedures.

4.2. $[Sm\{N(PPh_2)_2\}_3]$ (2a)

20 ml of toluene was condensed at $-196 \,^{\circ}\text{C}$ onto a mixture of 270 mg (0.5 mmol) of $[\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}_3]$ and 650 mg (1.5 mmol) of $(\text{Ph}_2\text{P})_2\text{NH}$. The mixture was refluxed for 6 h, filtered and the solvent taken off in vacuo. The product was recrystallized from toluene. Yield 564 mg (81%), yellow crystals. ¹H NMR (d₈-THF, 250 MHz, 25 °C): δ 6.87 (dd, 24H, *m*-Ph, ³*J*(H,H) = 7.3 and 7.5 Hz), 7.07 (t, 12H, *p*-Ph, ³*J*(H,H) = 7.3 Hz), 7.45 (d, 24H, *o*-Ph, ³*J*(H,H) = 7.5 Hz). ³¹P{¹H} NMR (d₈-THF, 101.3 MHz, 25 °C): δ -62.7 (br). *Anal.* Calc. for C₇₉H₆₈N₃P₆Sm (**2a** · toluene, 1395.63): C, 67.99; H, 4.91; N, 3.01. Found: C, 67.63; H, 4.92; N, 3.04%.

4.3. $[Ln \{N(PPh_2)_2\}_3]$ (Ln = Gd (2b), Dy (2c))

4.3.1. General procedure

20 ml of THF was condensed at $-196 \,^{\circ}\text{C}$ onto a mixture of 750 mg (1.5 mmol) of **1** and 0.5 mmol of LnCl₃ and the mixture was stirred for 24 h at room temperature. The solvent was then evaporated in vacuo and toluene condensed onto the mixture. The mixture was filtered, and the solvent taken off in vacuo. The product was recrystallized from toluene.

2b: Yield: 370 mg (79%). IR (KBr $[cm^{-1}]$): 3063 (m, vC=C-H), 2999 (w, vC-H), 1552 (w, vC=C), 1477 (m), 1431 (s), 1093 (m), 1025 (w, vPC), 997 (w), 950 (s), 919 (s), 907 (s), 738 (s), 710 (s), 693 (s). *Anal.* Calc. for $C_{79}H_{68}GdN_3P_6$ (**2b** · toluene) (1402.52): C, 67.65; H, 4.89; N 3.00. Found: C, 67.61; H, 4.92; N, 2.88%.

2c: Yield: 350 mg (75%). IR (KBr $[cm^{-1}]$): 3051 (m, vC=C-H), 2999 (w, vC-H), 1583 (w, vC=C), 1477 (m), 1431 (s), 1094 (m), 1025 (w, vPC), 996 (w), 944(s), 918 (s), 905 (s), 738 (s), 711 (s), 693 (s). *Anal.* Calc. for $C_{79}H_{68}DyN_3P_6$ (**2c** · toluene) (1407.77): C, 67.40; H, 4.87; N, 2.98. Found: C, 67.31; H, 4.78; N, 2.96%.

4.4. X-ray crystallographic studies of 2a-2c

Crystals of 2a-2c were grown from a toluene solution. A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the -73 °C cold stream of a STOE IPDS or a STOE IPDS 2T diffractometer. Subsequent computations were carried out on an Intel Pentium III or IV Personal Computer.

2a · toluene: Stoe IPDS diffractometer (Ag K α radiation); T = 200(2) K; data collection and refinement: SHELXS-97 [11], SHELXL-97 [12]; triclinic, space group $P\overline{1}$ (No. 2); lattice constants a = 1380.02(10), b = 1383. 92(9), c = 2086.69(13) pm, $\alpha = 91.085(8)^{\circ}$, $\beta = 97$. 883(8)°, $\gamma = 118.235(7)^{\circ}$, $V = 3461.8(4) \times 10^{6}$ pm³, Z = 2; μ (Ag K α) = 0.554 mm⁻¹; $\theta_{max} = 24.08$; 20744 ($R_{int} = 0.0511$) unique reflections measured, of which 16612 were considered observed with $I > 2\sigma(I)$; maximum residual electron density 1.825 and -1.076 e/A⁻³; 791 parameters (all nonhydrogen atoms except C33–C35 and C79 were calculated anisotropically; the positions of the H atoms were calculated for idealized positions) $R_1 = 0.0425$; $wR_2 = 0.1040$.

2b · toluene: Stoe IPDS 2T diffractometer (Mo Ka radiation); T = 200(2) K; data collection and refinement: SHELXS-97 [11], SHELXL-97 [12]; triclinic, space group PI (No. 2); lattice constants a = 1365.59(5), b = 1372.38(5), $c = 2078.37(7) \text{ pm}, \quad \alpha = 90.982(3)^{\circ}, \quad \beta = 98.051(3)^{\circ}, \\ \gamma = 118.236(2)^{\circ}, \quad V = 3382.2(2) \times 10^{6} \text{ pm}^{3}, \quad Z = 2; \quad \mu \text{ (Mo}$ Ka) = 1.169 mm⁻¹; $\theta_{max} = 29.26$; 18199 ($R_{int} = 0.0697$) unique reflections measured, of which 14998 were considered observed with $I > 2\sigma(I)$; maximum residual electron density 1.825 and -1.654 e/A^{-3} ; -1.386 parameters (all nonhydrogen atoms except C33-C35 and C79 were calculated anisotropically; the positions of the H atoms were idealized calculated for positions) $R_1 = 0.0391;$ $wR_2 = 0.0833.$

2c · toluene: Stoe IPDS 2T diffractometer (Mo K α radiation); T = 200(2) K; data collection and refinement: SHELXS-97 [11], SHELXL-97 [12]; triclinic, space group $P\overline{1}$ (No. 2); lattice constants a = 1365.45(6), b = 1371.44(7), c = 2081.49(10) pm, $\alpha = 90.932(4)^{\circ}$, $\beta = 98.021(4)^{\circ}$, $\gamma = 118.229(3)^{\circ}$, $V = 3385.5(3) \times 10^{6}$ pm³, Z = 2; μ (Mo K α) = 1.292 mm⁻¹; $\theta_{max} = 29.22$; 17962 ($R_{int} = 0.0381$) unique reflections measured, of which 14802 were considered observed with $I > 2\sigma(I)$; maximum residual electron density 1.825 and 1.585 e/A⁻³; -0.926 parameters (all nonhydrogen atoms except C33–C35 and C79 were calculated anisotropically; the positions of the H atoms were calculated for idealized positions) $R_1 = 0.0309$; $wR_2 = 0.0681$.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC-259352 (2a), 259286 (2b), and 259287 (2c). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +(44)1223-336-033; email: deposit@ccdc.cam. ac.uk).

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft (Graduiertenkolleg: Synthetische, mechanistische und reaktionstechnische Aspekte von Metallkatalysatoren) and the Fonds der Chemischen Industrie.

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