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Coordination number 12 in praseodymium and 11 in neodymium complexes with organofluorotitanate ligands

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Abstract

The complexes of $[Pr\{(C_5Me_5)_2Ti_2F_7\}_3]$ **2** and $[Nd\{(C_5Me_5)_2Ti_2F_7\}_3]$ **3** were obtained by the reaction of $[Hdmpy]^+[(C_5Me_5)_2Ti_2F_7]^-$ **1** (dmpy = 2,6–dimethylpyridine, $C_5H_3NMe_2$), with praseodymium(III) and neodymium(III) trifluoromethanesulfonate. The X–ray crystal structures of **2** and **3** exhibit a fluorine environment of 12 at the praseodymium and of 11 at the neodymium with $[(C_5Me_5)_2Ti_2F_7]^-$ acting as well as a tetra- and as a three-fluorodentate ligand. Both complexes retained their structures in solution. Complex **2** is the first molecular compound containing Pr–F bonds.

Keywords: Fluoride; Praseodymium; Neodymium; X-ray structure; Titanium

1. Introduction

Lanthanide (Ln) contraction, a decrease of bond distances (d(Ln–X)) with an increase of the lanthanide atom number, was observed in ionic (a shrinking of the ionic radii), covalent, and coordination compounds [1]. Moreover, lanthanide contraction affects the coordination number at the central atom and the geometry of the complexes [2], the mechanism and consequently the rate of ligand exchange [3]. This property was used for the optimization of the catalytic behavior of lanthanide catalysts [4]. The coordination number 12 in lanthanide complexes was achieved with small atoms, such as oxygen and in a few cases with nitrogen [2,5]. Recently we prepared the complex $[La\{(C_5Me_4Et)_2Ti_2F_7\}_3]$ with the coordination number of 12 at the lanthanum atom surrounded exclusively by fluorine atoms [6]. Praseodymium(III) and neodymium(III) compounds are considered as twins due to their very similar structures and reactivity [7]. In this paper we report on praseodymium(III) and neodymium(III) complexes with the fluorodentate ligand $[(C_5Me_5)_2Ti_2F_7]^-$ to prove if the lanthanide contraction (from lanthanum(III) to neodymium(III)) causes changes in the structure and coordination number of the complexes containing a crowded coordination sphere of fluorine atoms around the lanthanide ion.

2. Results and discussion

The complex $[Ln\{(C_5Me_5)_2Ti_2F_7\}_3]$ (Ln = Pr **2**, Nd **3**) is formed from a solution of $[Hdmpy]^+[(C_5Me_5)_2Ti_2F_7]^-$ and lanthanide trifluoromethanesulfonate, according to Scheme 1. The reactions of Sm(III), Gd(III), Eu(III) and Lu(III) trifluoromethanesulfonates with **1** in toluene did not result in crystalline products. Single crystals of **2** are obtained from THF and for **3** from toluene. Both complexes contain one molecule of solvent in the crystal. Attempts to isolate **3** from the reaction carried out in THF solution resulted in a red oily product. A broad resonance for the methyl (C_5Me_5) hydrogen atoms was observed in the ^1H NMR spec-

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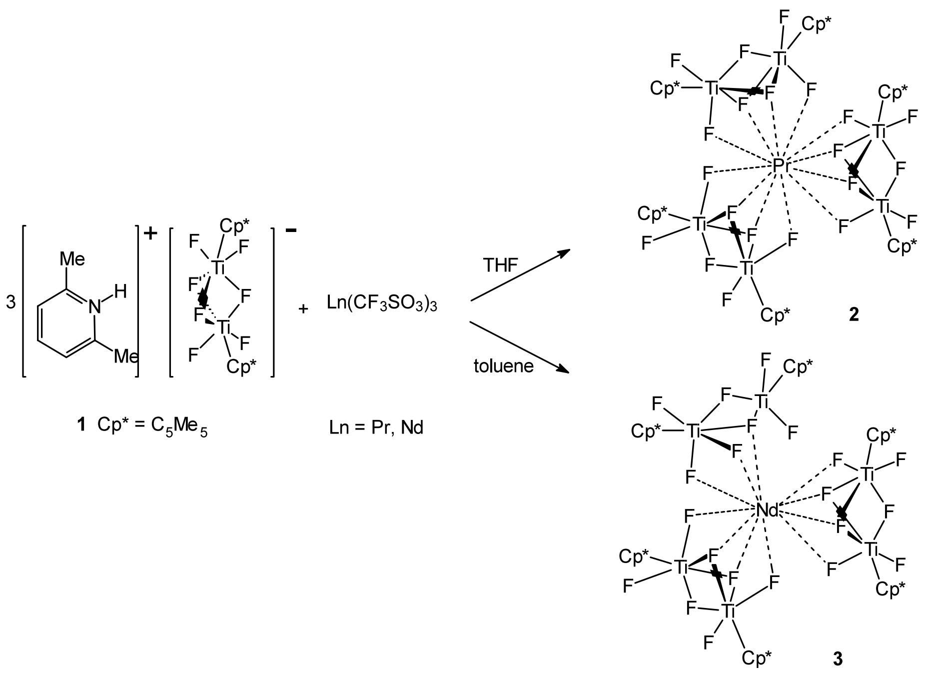

Scheme 1.

trum, while the ^{19}F NMR resonances give a broadened baseline.

2.1. Crystal and solution structure of (**2**) and (**3**)

The central metal ion in **2** and **3** is coordinated to fluorine atoms of the dititanate $[(C_5Me_5)_2Ti_2F_7]^-$ groups (Figs. 1 and 2). Selected bond lengths and angles are given in Table 2 and Table 3. In both complexes the inorganic core is surrounded by a hydrocarbon envelope of six C_5Me_5 groups. There is a twofold rotation axis in **2** that passes through the Pr and F6 atoms, while the molecule of **3** has no symmetry. Four fluorine donating atoms of the dititanate ligand arranged on a part of a sphere with an approximate radius of 2.2 Å [8] fit the corners of a distorted icosahedron and prefer the coordination number 12 of lanthanides in $[La\{(C_5Me_4Et)_2Ti_2F_7\}_3]$ and **2** (Fig. 3(a)). In contrast, the coordination number of lanthanides in tysonite LnF_3 structures (Ln = La, Pr) is 11 [2a]. Two fluorine atoms are in terminal and two in bridging positions to the titanium atoms. The decrease of the ionic radius from

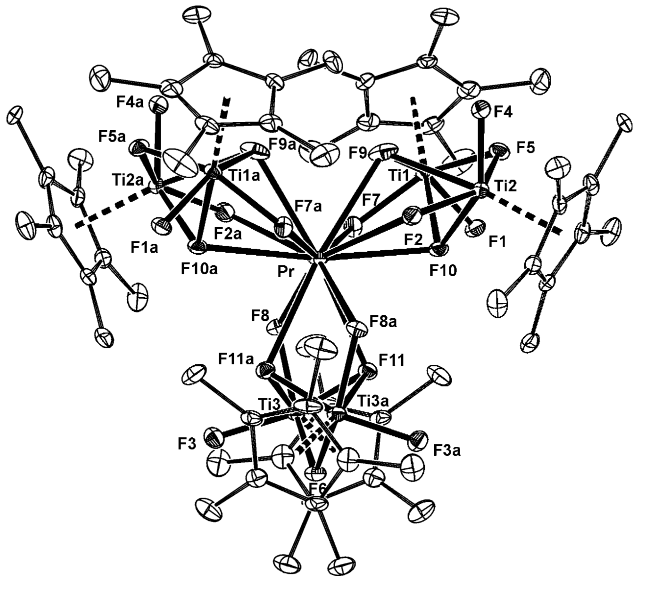

Fig. 1. Molecular structure of $[Pr\{(C_5Me_5)_2Ti_2F_7\}_3]$ **2**.

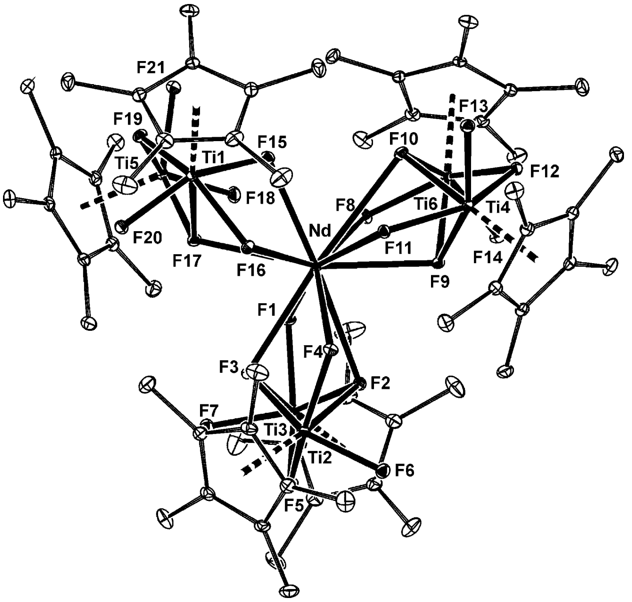

Fig. 2. Molecular structure of $[Nd\{(C_5Me_5)_2Ti_2F_7\}_3]$ **3**.

Table 1
Crystallographic data, data collection and structure refinement data for compounds **2** and **3**

	2	3
Chemical formula	$C_{60}H_{90}F_{21}PrTi_6 \cdot C_4H_8O$	$C_{60}H_{90}F_{21}NdTi_6 \cdot C_7H_8$
Molecular weight	1710.7	1734.09
Crystal system	orthorombic	monoclinic
Space group	*Pccn* (no. 56)	$P2_1/c$ (no. 14)
a (Å)	14.588(2)	14.40410(10)
b (Å)	17.322(3)	17.28290(10)
c (Å)	29.068(5)	29.1874(2)
β (°)	90.0	91.5659(3)
V (Å^3)	7445(2)	7263.33(8)
Z	4	4
D_{calc} (g cm^{-3})	1.547	1.586
μ (cm^{-1})	1.351	1.419
Crystal size (mm)	0.32 × 0.23 × 0.15	0.15 × 0.15 × 0.15
θ Range (°)	1.4–24.94	1.37–27.00
Tot. no. coll. data	21426	28904
No. of unique data	6430	15681
R (int)	0.056	0.0272
No. of obs. data	2259	12905
Threshold	$[I > 2.5\sigma(I)]$	$[I > 2\sigma(I)]$
Numbers of par.	410	856
R^a (observed)	0.052	0.0413
$R_w{}^b$ or $wR_2{}^c$ (obs.)	0.062^b	0.1043^c
S	1.143	1.134
Largest difference peak and hole (e Å^{-3})	0.83, −1.07	1.270, −0.969

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$.
[b] $R_w = \Sigma(w(|F_o| - |F_c|))/\Sigma(w|F_o|)$.
[c] $wR_2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(wF_o^2)^2)^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) for **2**

Bond lengths			
Pr–F2	2.848(9)	Ti1–F7	1.897(8)
Pr–F7	2.452(7)	Ti1–F9	1.951(9)
Pr–F8	2.506(6)	Ti1–F10	2.296(7)
Pr–F9	2.658(7)	Ti2–F2	1.851(8)
Pr–F10	2.596(7)	Ti2–F4	1.819(7)
Pr–F11	2.649(6)	Ti2–F5	2.009(7)
Ti1–F1	1.811(8)	Ti2–F9	2.524(9)
Ti1–F5	1.985(7)	Ti2–F10	2.014(7)
Bond angles			
F2–Pr–F7	107.0(2)	F2–Ti2–F5	140.0(4)
F2–Pr–F9	58.5(3)	F2–Ti2–F10	80.7(3)
F2–Pr–F10	54.5(2)	Pr–F2–Ti2	106.1(4)
F2–Pr–F11	97.6(2)	Pr–F10–Ti2	110.5(3)
F2–Pr–F8	153.9(2)	Pr–F10–Ti1	93.9(2)
F2–Ti2–F4	94.0(4)	Pr–F7–Ti1	110.1(3)

Table 3
Selected bond lengths (Å) and angles (°) for **3**

Bond lengths			
Nd–F1	2.460(2)	Nd–F17	2.588(2)
Nd–F2	2.627(2)	Ti1–F15	1.966(2)
Nd–F3	2.586(2)	Ti1–F16	1.919(2)
Nd–F4	2.482(2)	Ti1–F17	2.355(2)
Nd–F8	2.434(2)	Ti1–F19	1.972(2)
Nd–F9	2.509(2)	Ti1–F20	1.831(2)
Nd–F10	2.896(2)	Ti5–F17	2.000(2)
Nd–F11	2.539(2)	Ti5–F18	1.810(2)
Nd–F15	2.453(2)	Ti5–F19	2.016(2)
Nd–F16	2.402(2)	Ti5–F21	1.829(2)
Bond angles			
F11–Nd–F8	106.76(7)	F11–Nd–F15	82.33(7)
F11–Nd–F9	59.76(7)	F11–Ti4–F9	79.20(9)
F11–Nd–F10	54.82(6)	F11–Ti4–F10	75.93(9)
F11–Nd–F2	103.81(7)	F11–Ti4–F12	142.79(10)
F11–Nd–F4	64.03(7)	F11–Ti4–F13	95.52(10)
F11–Nd–F1	158.82(7)	Nd–F11–Ti4	109.09(10)
F11–Nd–F3	122.40(7)	Nd–F9–Ti4	105.38(9)
F11–Nd–F16	69.03(7)	Nd–F9–Ti6	98.29(8)
F11–Nd–F17	127.83(7)	Nd–F8–Ti6	113.40(10)

La^{3+} to Nd^{3+} results in a distortion of the icosahedron with 12 coordinated fluorine atoms (Fig. 3). The coordination behavior of the dititanate ligand is comparable to that of the lanthanum complex but different both in terms of distance (La–F ranges from 2.543(2) to 2.724(2) Å [6]) and the coordination site. Therefore the change of the coordination number of 12 in the lanthanum complex to 11 in the neodymium complex **3** is apparent also in the physical properties of the praseodymium complex **2**. The Pr–F distance for one of the coordinated fluorine (F2) is elongated to 2.848(9) Å, while the remaining Pr–F ones are in the range from 2.452(7) to 2.658(7) Å. The decrease of the ionic radii from Pr^{3+} to Nd^{3+} (we estimate the decrease of 0.015(2) Å [1] for coordination number 12) results in the non-bonding Nd–F(18) distance (3.535 Å). There are ten coordinated fluorines with Nd–F distances of 2.402(2)–2.627(2) Å and one (F10) with 2.896(2) Å. The coordination number of 11 is reminiscent of that in the tysonite structure of NdF_3 which could be considered as nine plus two [2a]. The averages of 12 Pr–F bonds in **2** (2.618 Å) and 11 Nd–F bonds in **3** (2.543 Å) differ by 0.075 Å. This difference is in agreement with the smaller ionic radius of lanthanide ion in **3** than in **2** due to the lanthanide contraction (decrease for 0.015 Å) and due to the lower coordination number 11 (decrease for 0.04–0.05 Å) [1a]. The Pr–F and Nd–F distances in **2** and **3** are longer than those in known complexes with Ln–F bonds (2.324(9)–2.349(7) Å for La–F and 2.335(2)–2.337(2) Å for Nd–F in $[\{(Me_3Si)_2C_5H_3\}_2Ln(\mu\text{–}F)]_2$ [9]). Similar Ln–F distances (2.000–2.502 Å) were also found by quantum chemical calculations [10]. To the best of our knowledge no structural characterized molecular complex with a Pr–F bond was found in the literature. The geometry and bond lengths of the dititanate $[(C_5Me_5)_2Ti_2F_7]^-$ in **2** are similar to those in known lanthanum and calcium complexes [6,8]. The tridentate dititanate in **3** has a severely distorted geometry. In the latter there are only two fluorine-bridges between both titanium atoms. One titanium

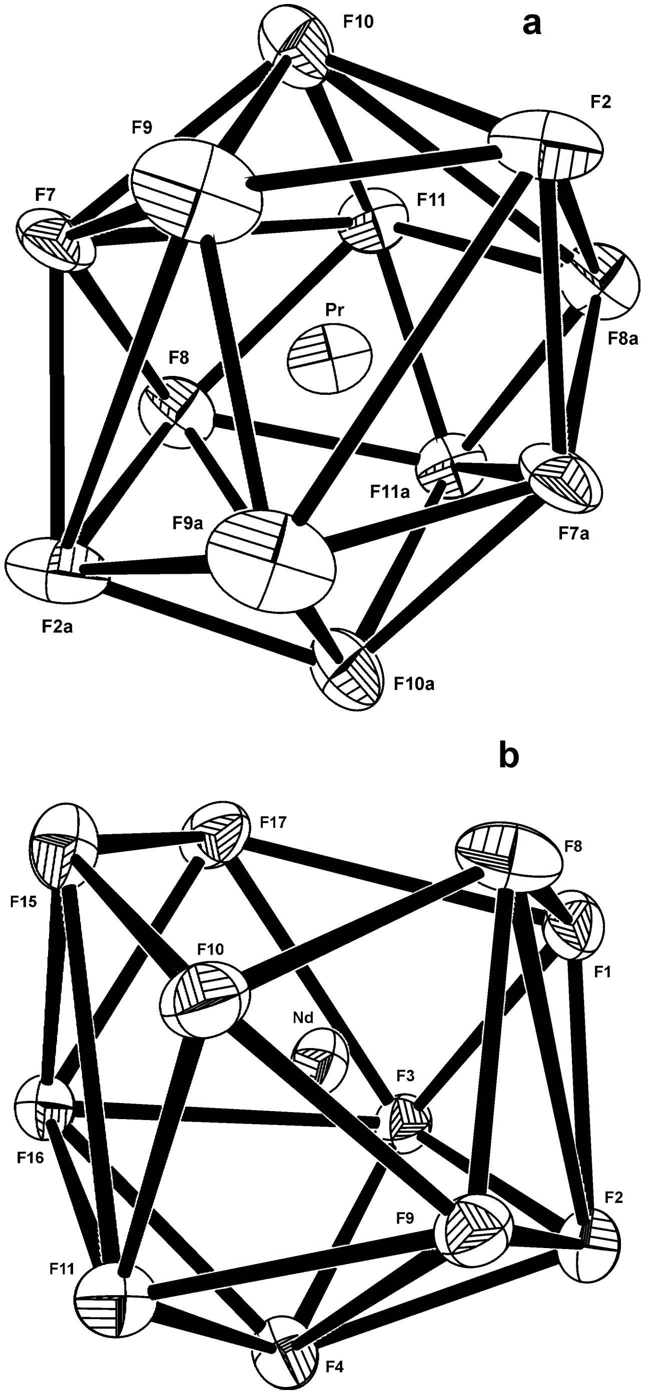

Fig. 3. Coordination polyhedra in (a) $[Pr\{(C_5Me_5)_2Ti_2F_7\}_3]$ **2** and (b) $[Nd\{(C_5Me_5)_2Ti_2F_7\}_3]$ **3**.

atom in the dititanate is coordinated to two and the other to three terminal fluorine atoms. Furthermore the dititanate is coordinated to the neodymium ion by a bridging and by two terminal fluorine atoms.

The ^1H NMR spectra of **2**·THF and **3** in $CDCl_3$ respectively with additional added THF to the latter show resonances of THF without a paramagnetic shift or broadening [11]. Consequently we propose that the solid state structure of **2** and **3** with the ligands-wrapped lanthanide ion remains stable without dissociation in solution. Obviously, three dititanate ligands effectively prevent the interaction of THF with the lanthanide ion. The coordination of THF to the calcium ion was observed in toluene-THF solution of the corresponding calcium complex $[Ca\{(C_5Me_4Et)_2Ti_2F_7\}_2]$ [12].

3. Conclusion

Pr^{3+} and Nd^{3+} form complexes of composition $[Ln\{(C_5Me_5)_2Ti_2F_7\}_3]$ with 12 (Pr^{3+}) and 11 (Nd^{3+}) coordination sites with fluorines as well in the solid as in $CDCl_3$ solution.

4. Experimental

4.1. General

NMR spectra were recorded on a Bruker DPX 300 spectrometer operating at 300 and 282 MHz for ^1H and ^{19}F NMR, respectively. IR spectra (Nujol) were recorded on a Perkin-Elmer FT-1720X spectrometer. Elemental analyses were carried out on a Perkin-Elmer 2400 CHN analyzer at the University of Ljubljana (Department of Organic Chemistry). Melting points were measured using Büchi 535 apparatus and are reported uncorrected. Reactions were performed under a protective argon or nitrogen atmosphere using standard Schlenk techniques and a drybox.

4.2. Chemicals

All solvents were dried over Na/K alloy and distilled prior to use. $[Hdmpy]^+[(C_5Me_5)_2Ti_2F_7]^-$ was prepared according to Ref. [6]. $Pr(CF_3SO_3)_3$ and $Nd(CF_3SO_3)_3$ were purchased from Aldrich.

*4.3. Preparation of $[Pr\{(C_5Me_5)_2Ti_2F_7\}_3]$ (**2**)*

To a mixture of **1** (0.607 g, 1.0 mmol) and $Pr(CF_3SO_3)_3$ (0.194 g, 0.33 mmol) was added THF (40 ml) at room temperature. The resulting orange solution was stirred overnight and then filtered. From the filtrate compound **2** crystallized in the form of orange crystals by slow evaporation of the solvent at reduced pressure. Yield 0.29 g, 52%. M.p. 206 °C. ^1H NMR ($CDCl_3$, 300 MHz, 302 K): 3.74(m, 4H, THF), 2.65 (bs, 90H, C_5Me_5), 1.85 (m, 4H, THF). *Anal.* Calc. for $C_{60}H_{90}F_{21}PrTi_6$: C 43.98; H 5.54. Found: C 43.76; H 5.75%. IR spectrum (cm^{-1}, Nujol) 632, 617, 555, 477, 433.

*4.4. Preparation of [Nd{(C_5Me_5)$_2$$Ti_2F_7$}$_3$] (**3**)*

To a mixture of **1** (0.607 g, 1.0 mmol) and Nd(CF_3SO_3)$_3$ (0.195 g, 0.33 mmol) was added toluene (40 ml) at room temperature. The resulting orange solution was stirred overnight and filtered. The filtrate was then placed at 4 °C for 24 h to give orange crystals, identified as **2**·C_7H_8. Yield 0.38 g, 66%. M.p. 190 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 302 K):7.26 (m, 2H, C_7H_8), 7.18 (m, 3H, C_7H_8), 2.35 (s, 3H, C_7H_8),2.30 (bs, 60H, C_5Me_5). *Anal.* Calc. for $C_{67}H_{98}F_{21}NdTi_6$: C 46.41; H 5.70. Found: C 45.81; H 5.66%. IR spectrum (cm^{-1}, Nujol) 632, 617, 559, 478, 418.

*4.5. X-ray crystal structural analysis of (**2**) and (**3**)*

The details of crystal data collection and refinement parameters for **2** and **3** are listed in Table 1. An orange octaeder of compound **2** was glued, and an orange prism of compound **3** was greased on a glass thread. Diffraction data for **2** were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature and those for **3** on a Nonius Kappa CCD diffractometer with CCD area detector at 200(2) K. A Cryostream Cooler (Oxford Cryosystems) was used for cooling the sample. A graphite monochromated Mo Kα radiation (λ = 0.71073 Å) was employed in both measurements. Structure **2** was solved by direct methods and refined using Xtal 3.2 by a full-matrix least-squares procedure based on F [13]. Structure **3** was solved by direct methods implemented in SHELXS-97 [14] and refined by a full-matrix least-squares procedure based on F^2 (SHELXL-97) [15]. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were included in the model at geometrically calculated positions and refined using a rigid model.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 185497 for compound **2** and CCDC no. 185496 for compound **3**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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