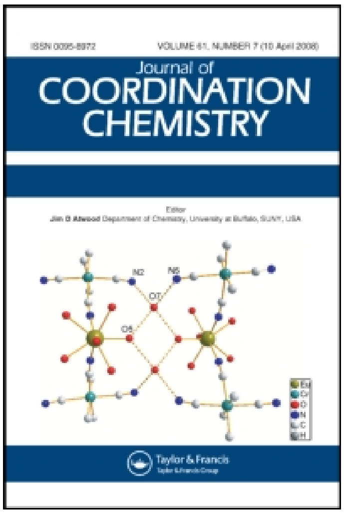

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Synthesis, structural, photophysical and thermal properties of some praseodymium(III) complexes

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Some carboxylato-bridged praseodymium(III) complexes (**1**–**5**) having tp [hydrotris(pyrazol-1-yl)borate] and sodium *p*-X-benzoate (where X = H, F, Cl, NO_2) have been synthesized and characterized by different techniques including X-ray crystallography. The X-ray studies demonstrated that **1**, **3** and **5** crystallized in triclinic space group $P\bar{1}$ with cell dimensions $a = 11.761(13)$ Å, $b = 12.536(13)$ Å, $c = 17.726(19)$ Å for **1**, $a = 9.309(8)$ Å, $b = 12.667(11)$ Å, $c = 14.421(12)$ Å for **3**, $a = 11.5688(9)$ Å, $b = 12.0055(9)$ Å, $c = 12.3005(10)$ Å for **5**. In **1**–**4** the coordination number of praseodymium is seven, whereas in **5** it is eight. IR suggested that the benzoate groups in **1**–**5** are bidentate bridging. The photophysical properties of these complexes have been studied in solution at room temperature. Thermogravimetric analysis showed that these complexes undergo complete decomposition with formation of praseodymium oxide.

Keywords: Praseodymium(III); Carboxylate ligands; X-ray studies; Photophysical; Thermal properties

1. Introduction

Luminescent properties of lanthanide coordination compounds with different organic ligands proceed through intramolecular energy transfer from excited triplet states of ligand to the coordinated ion. The efficiency of this process depends on the absorption by organic ligand and the ligand-to-lanthanide energy transfer. Emission from lanthanides plays a very important role in biological systems.

For praseodymium(III), there are three possible emitting f–f states: $^3P_0$, $^1D_2$ and $^1G_4$. However, the energy gap for $^1D_2$ is twice as large as for the other two levels and it could be expected that Pr(III) would emit from $^1D_2$-state only (assuming similar values of radiative transition probabilities for all states). However, Pr(III) emits luminescence with comparable efficiency from two excited states ($^3P_0$ and $^1D_2$) in solutions [1] and from three excited states ($^3P_0$, $^1D_2$ and $^1G_4$) in solids [2, 3]. The *f*–*f* emission of Pr(III) in solvents containing O–H/C–H bonds is inefficient due to low energy gaps ($<7000\,\mathrm{cm}^{-1}$). Pr(III) also emits efficient ultraviolet 5d–4f-luminescence used for the fluorimetric

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determination of Pr(III) in solutions [4]. In general, lanthanide complexes of aromatic carboxylates have higher thermal or fluorescent stabilities than other lanthanide systems because they readily form polymeric structures [5–10]. Pr(III) complexes with different ligands [11–17] show photophysical properties [18–24]. Pr(III) complexes with only trispyrazolylborate ligands are available [25, 26] but not with trispyrazolylborate and benzoate together. This study is to see the effect of different ligands on the structure and photophysical properties of Pr(III) complexes, as studies suggest variation of ligand plays an important role in photophysical properties of lanthanide complexes. In this work, both pyrazolylborate and carboxylates are used because pyrazolylborates have few CH oscillators close to the metal centers compared to carboxylates and these mixed-ligand complexes will have relatively little luminescence quenching from CH oscillators. Also, the carboxylate ligands have a much longer wavelength absorption for their π–π^* transitions than do the pyrazolylborates and will sensitize luminescence from lanthanides at relatively long wavelengths. We report the synthesis, crystal structure, luminescence and thermal properties of some carboxylato bridged praseodymium(III) complexes with nitrogen and oxygen donor ligands.

2. Experimental

2.1. *Materials*

All solvents were predried by the literature methods [27]. Benzoic acid and its derivatives were commercially available and their sodium salts were prepared by reacting sodium hydroxide in water. Praseodymium chloride of the highest grade was purchased from Indian Rare Earths Ltd., India. The potassium salt of hydrotris (pyrazol-1-yl)borate [K(tp)] was prepared by published procedure [28].

2.2. *Synthesis of complexes*

2.2.1. Synthesis of [(tp)Pr(μ-OBz)$_4$Pr(tp)] (1). A mixture of sodium benzoate (0.144 g, 1.0 mmol) and [K(tp)] (0.125 g, 0.5 mmol) in 15.0 mL methanol was added to methanolic solution of $PrCl_3 \cdot 6H_2O$ (0.186 g, 0.5 mmol). The suspension was stirred at room temperature for 4 h. After removal of solvent under vacuum, the residue was extracted with dichloromethane and the solution filtered to eliminate the salt. The filtrate was dried under vacuum to afford a powder in 84% yield. Recrystallization of the resultant solid from dichloromethane at 4°C gave crystals suitable for X-ray measurements. The elemental analysis was performed on a completely dried sample for several hours. Anal. Calcd (%) for $C_{46}H_{40}N_{12}O_8B_2Pr_2$: C, 46.33; H, 3.38; N, 14.09. Found: C, 46.15; H, 3.26; N, 14.17. MS (ESI+, CH_3CN): m/z 1070 (5%) $[(tp)_2Pr_2(O_2CPh)_3]^+$; 686 (10%) $[(tp)_2Pr(O_2CPh)]^+$; 565 (100%) $[(tp)_2Pr]^+$. IR (KBr, cm^{-1}): 2457 (νB–H), 1607 (ν_{as} COO), 1506 (ν_s COO). Magnetic moment μ_{eff} (290 K): 3.42 B.M.

2.2.2. Synthesis of [(tp)Pr(μ-*p*-F–OBz)$_4$Pr(tp)] (2). This complex was prepared in 82% yield as outlined above for **1**. Anal. Calcd (%) for $C_{46}H_{36}N_{12}O_8B_2F_4Pr_2$: C, 43.70;

H, 2.86; N, 13.29. Found: C, 43.95; H, 2.95; N, 13.10. MS (ESI+, CH_3CN): *m*/*z* 1122 (8%) $[(tp)_2Pr_2(p\text{-}F\text{–}O_2CPh)_3]^+$; 727 (10%) $[(tp)_2Pr(p\text{-}F\text{–}O_2CPh) + Na]^+$; 565 (100%) $[(tp)_2Pr]^+$. IR (KBr, cm^{-1}): 2458 (νB–H), 1605 (ν_{as} COO), 1509 (ν_s COO). Magnetic moment μ_{eff} (290 K): 3.49 B.M.

2.2.3. Synthesis of $[(tp)Pr(\mu\text{-}p\text{-}Cl\text{–}OBz)_4Pr(tp)]$ (3). This complex was prepared in 81% yield as outlined above for **1**. Recrystallization of complex from dichloromethane at 4°C gave crystals suitable for X-ray measurements. Anal. Calcd (%) for $C_{46}H_{36}N_{12}O_8B_2Cl_4Pr_2$: C, 41.53; H, 2.72; N, 12.63. Found: C, 41.88; H, 2.54; N, 12.25. MS (ESI+, CH_3CN): *m*/*z* 1172 (8%) $[(tp)_2Pr_2(p\text{-}Cl\text{–}O_2CPh)_3]^+$; 721 (5%) $[(tp)_2Pr(p\text{-}Cl\text{–}O_2CPh]^+$; 565 (100%) $[(tp)_2Pr]^+$. IR (KBr, cm^{-1}): 2455 (νB–H), 1606 (ν_{as} COO), 1508 (ν_s COO). Magnetic moment μ_{eff} (290 K): 3.54 B.M.

2.2.4. Synthesis of $[(tp)Pr(\mu\text{-}p\text{-}NO_2\text{–}OBz)_4Pr(tp)]$ (4). This complex was prepared in 82% yield as outlined above for **1**. Anal. Calcd (%) for $C_{46}H_{36}N_{16}O_{16}B_2Pr_2$: C, 40.26; H, 2.64; N, 16.33. Found: C, 40.84; H, 2.35; N, 16.38. MS (ESI+, CH_3CN): *m*/*z* 1205 (10%) $[(tp)_2Pr_2(p\text{-}NO_2\text{–}O_2CPh)_3]^+$; 731 (9%) $[(tp)_2Pr(p\text{-}NO_2\text{–}O_2CPh)]^+$; 565 (100%) $[(tp)_2Pr]^+$. IR (KBr, cm^{-1}): 2454 (νB–H), 1608 (ν_{as} COO), 1510 (ν_s COO). Magnetic moment μ_{eff} (290 K): 3.47 B.M.

2.2.5. Synthesis of $[(tp)(pz)Pr(\mu\text{-}p\text{-}F\text{–}OBz)_4Pr(pz)(tp)] \cdot 2CH_2Cl_2$ (5). A mixture of sodium fluorobenzoate (0.162 g, 1.0 mmol), [K(tp)] (0.125 g, 0.5 mmol) and pyrazole (0.034 g, 0.5 mmol) in 15.0 mL methanol was added to methanolic solution of $PrCl_3 \cdot 6H_2O$ (0.186 g, 0.5 mmol). The suspension was stirred at room temperature for 5 h, the solvent removed under vacuum, the residue extracted with dichloromethane (three times) and the solution filtered on celite. The filtrate was dried under vacuum and light green powder was obtained in 83% yield. Recrystallization from dichloromethane at 4°C gave crystals suitable for X-ray measurements. Elemental analysis was performed on a dried sample for several hours. Anal. Calcd (%) for $C_{52}H_{44}N_{16}O_8F_4B_2Pr_2$: C, 46.60; H, 3.29; N, 16.76. Found: C, 46.88; H, 3.25; N, 16.51. IR (KBr, cm^{-1}): 2458 (νB–H), 1603 (ν_{as} COO), 1506 (ν_s COO). Magnetic moment μ_{eff} (290 K): 3.51 B.M.

2.3. *Physical measurements*

Elemental analyses (C, H, N) were determined on a Vario EL elemental analyzer. Infrared spectra were obtained on a Thermo Nikolet Nexus spectrometer in KBr. Electro Spray Ionization mass spectra (ESI-MS) for **1**–**4** in positive mode were recorded on a Micromass Quattro II triple quadrupole mass spectrometer. The intensity and possible composition in parentheses of the peaks are given. The room temperature magnetic susceptibility measurements were done on a Princeton applied research vibrating sample magnetometer Model 155. Ultraviolet absorption spectra were recorded on a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer and emission spectra were measured on a Fluorolog spectrophotometer (Jobin Yvon Inc., Horiba Group). TG-DTG experiments were

Table 1. Crystal data and structure refinement details for **1**, **3** and **5**.

Complex	**1**	**3** $\cdot 2(CH_2Cl_2)$	**5** $\cdot 2(CH_2Cl_2)$
Formula	$C_{46}H_{40}N_{12}B_2O_8Pr_2$	$C_{46}H_{36}N_{12}B_2Cl_8O_8Pr_2$	$C_{52}H_{44}N_{16}B_2F_4O_8Pr_2$
Molecular weight	1192.34	1531.96	1602.32
Temperature (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Radiation	Mo-Kα	Mo-Kα	Mo-Kα
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit dimensions (Å, °)			
a	11.761(13)	9.3095(8)	11.5688(9)
b	12.536(13)	12.6676(11)	12.0055(9)
c	17.726(19)	14.4210(12)	12.3005(10)
α	75.565(6)	72.978(4)	73.614(4)
β	74.449(6)	75.498(4)	83.366(4)
γ	77.966(5)	77.623(4)	80.119(4)
Volume (Å^3)	2410.2(4)	1556.0(2)	1610.6(2)
Z	2	1	1
Density (D_c) (Mg m^{-3})	1.643	1.631	1.651
Diffractometer used	Bruker Kappa Apex	Bruker Kappa Apex	Bruker Kappa Apex
θ range (°)	1.22–31.63	1.51–27.15	1.73–38.03
Goodness-of-fit on F^2	1.666	1.108	1.404
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0971$	0.0654	$R_1 = 0.0602$

performed using Perkin-Elmer's (Pyris Diamond) thermogravimetry analyzer under air.

2.4. *X-ray crystallographic studies*

Single crystals suitable for X-ray data collection were mounted on cryoloop using fomblin (mounting glue). Diffraction data were collected on a Bruker Kappa Apex-CCD diffractometer by use of graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$) at room temperature. The structures were solved by direct methods and in anisotropic approximation refined using the SHELXTL package [29, 30]. Hydrogen atoms were constrained by rigid model. A summary of crystallographic data and refined parameters for **1**, **3** and **5** are given in table 1.

3. Results and discussion

Complexes [(tp)Pr(μ-p-X–OBz)$_4$Pr(tp)] (X = H, F, Cl, NO_2) (**1**–**4**) were synthesized by reaction of $PrCl_3 \cdot 6H_2O$, [K(tp)] and sodium p-X-benzoate (X = H, F, Cl, NO_2); reaction of $PrCl_3 \cdot 6H_2O$, [K(tp)], sodium p-fluoro-benzoate and free pyrazole (pz) gave [(tp)(pz)Pr(μ-p-F–OBz)$_4$Pr(pz)(tp)]. In **1**–**4**, one tp ligand and four benzoate groups coordinate to one praseodymium giving seven coordination. In **5**, one tp ligand, four p-fluorobenzoate groups and one pyrazole give eight coordination. All complexes were characterized by elemental analysis, IR, thermo gravimetric, ESI mass spectroscopy (**1**–**4**) and **1**, **3** and **5**, X-ray crystallography. The spectroscopic studies suggest that the structure of **2** and **4** are same as **1** and **3**.

Table 2. Bond lengths (Å) and angles (°) for **1**.

Pr1–O1	2.380(6)	Pr2–O6	2.394(6)
Pr1–O4	2.383(6)	Pr2–O7	2.396(6)
Pr1–O3	2.418(6)	Pr2–O5	2.431(6)
Pr1–O2	2.440(6)	Pr2–O8	2.466(7)
Pr1–N1	2.601(7)	Pr2–N9	2.548(7)
Pr1–N4	2.621(7)	Pr2–N7	2.578(7)
Pr1–N5	2.586(7)	Pr2–N11	2.628(7)
Pr1–Pr1′	3.982(8)	Pr2–Pr2′	3.953(9)
O1–Pr1–O4	77.8(2)	O5–Pr2–N11	138.0(2)
O1–Pr1–O3	77.2(2)	O5–Pr2–N9	120.3(2)
O1–Pr1–O2	128.4(2)	O5–Pr2–N7	74.9(2)
O1–Pr1–N5	95.3(2)	O5–Pr2–O8	87.9(2)
O1–Pr1–N1	158.0(2)	O5–Pr2–O7	70.82(19)
O2–Pr1–N5	126.2(2)	O6–Pr2–O7	77.6(2)
O2–Pr1–N4	130.7(2)	O6–Pr2–O5	135.5(2)
O2–Pr1–N1	72.5(2)	O6–Pr2–N7	144.4(2)
O3–Pr1–N1	114.6(2)	O6–Pr2–O8	78.4(2)
O3–Pr1–N5	72.5(2)	O6–Pr2–N9	96.6(2)
O3–Pr1–O2	86.8(2)	O7–Pr2–O8	128.8(2)
O3–Pr1–N4	139.4(2)	O6–Pr2–N11	73.3(2)
O4–Pr1–N1	102.0(2)	O7–Pr2–O5	79.0(2)
O4–Pr1–O2	80.4(2)	O7–Pr2–N9	152.6(2)
O4–Pr1–O3	135.25(19)	O7–Pr2–N7	95.4(2)
O4–Pr1–N5	146.4(2)	O7–Pr2–N11	80.3(2)
O8–Pr2–N7	128.6(2)	O8–Pr2–N9	74.6(2)
O8–Pr2–N11	133.0(2)	O8–Pr2–O7	49.57(19)

3.1. *Description of crystal structures*

3.1.1. Molecular structure of [(tp)Pr(μ-OBz)$_4$Pr(tp)] (1). The structure of **1** has been determined by X-ray crystallography; bond lengths and angles are listed in table 2. The unit cell consists of two crystallographically independent molecules, each lying on a center of inversion. Thus, the crystal of **1** has two binuclear molecules as shown in figure 1(a) and (b). In both molecules, praseodymium is seven-coordinate, with four oxygens from four benzoate groups and three nitrogen atoms from a tris(pyrazolyl) borate ligand. Pr–Pr separations are different in the molecules, i.e. 3.928 Å (figure 1a) and 3.953 Å (figure 1b). The same is true for praseodymium-oxygen bond distances which are between 2.380(6)–2.440(6) Å (figure 1a) and 2.394(6)–2.466(6) Å (figure 1b) in the range of reported values for carboxylate-bridged praseodymium [31]. Carboxylate groups may coordinate in three modes, chelating, bridging and chelating bridging. In **1**, all four carboxylate ligands are bridging within the dimeric unit (table 2). The Pr–O bond distances [Pr1–O1, 2.380(6); Pr1–O4, 2.383(6); Pr1–O3, 2.418(6); Pr1–O2, 2.440(6) Å] in figure 1a and [Pr2–O6, 2.394(6); Pr2–O7, 2.396(6); Pr2–O5, 2.431(6); Pr2–O8, 2.466(6) Å] in figure 1b differ. The average Pr–O bond distance [2.413 Å] in **1** is longer than average Ln–O bond distances [2.369 Å, 2.344 Å and 2.328 Å] in isostructural lanthanide complexes [32, 33] and shorter than average Pr–O bond distances in other binuclear praseodymium complexes having different numbers of carboxylate groups [12, 34]. The praseodymium-nitrogen bond distances of the coordinated pyrazolylborate ligands are in the range 2.586(7)–2.621(7) Å in figure 1a and 2.548(7)–2.662(7) Å in figure 1(b). Pr1–N4 [2.621(7) Å] is longer than Pr1–N5

[2.586(7) Å] and Pr1–N1 [2.601(7) Å] (figure 1a) and Pr2–N11 [2.628(7) Å] is longer than Pr2–N7 [2.578(7) Å] and Pr2–N9 [2.547(7) Å] (figure 1b). The average Pr–N bond distance [2.593 Å] in **1** is longer than the average Ln–N bond distances [2.556 Å, 2.511 Å and 2.497 Å] in isostructural lanthanide complexes, and shorter than average Pr–N bond distance [2.696 Å] in [Pr(tp)$_3$] [35]. The average C–C bond distance in the aromatic ring of the benzoate group is 1.390 Å. Crystal packing views of **1** are shown in figure 2(a) and (b). Two symmetrically-independent molecules in the asymmetric unit are linearly arranged in the crystal lattice to form AB-AB type arrangement. The individual layers are made of symmetry-dependent molecules with different types of interactions. One layer is held together by CH-π interactions (2.653 Å) formed between benzoate and the pyrazole (figure 2a). The other one is stabilized by π–π interactions (3.421 Å) between the benzoates in adjacent molecules (figure 2b). The symmetry-independent molecules interact through C–H–O (2.767 Å) hydrogen bond between hydrogen on the benzoate ring and oxygen of the other benzoate.

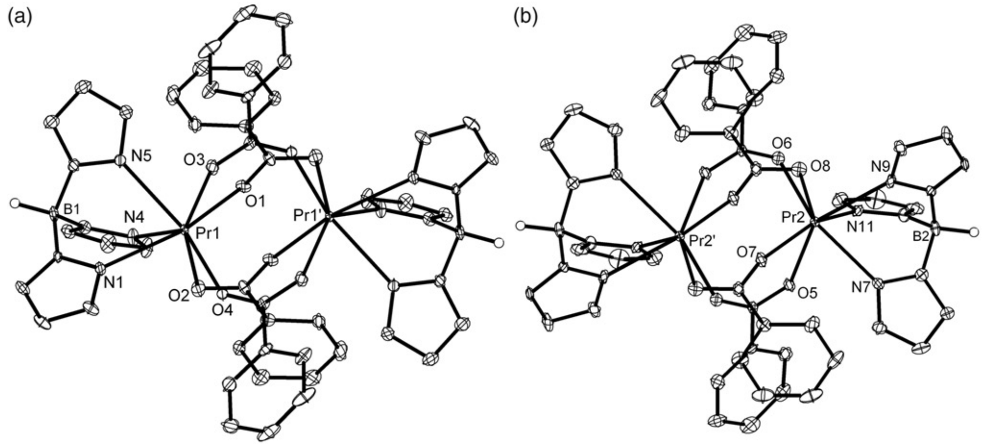

Figure 1. Thermal ellipsoidal representation for [(tp)Pr(μ-OBz)$_4$Pr(tp)] at 50% probability level (H atoms are omitted for clarity).

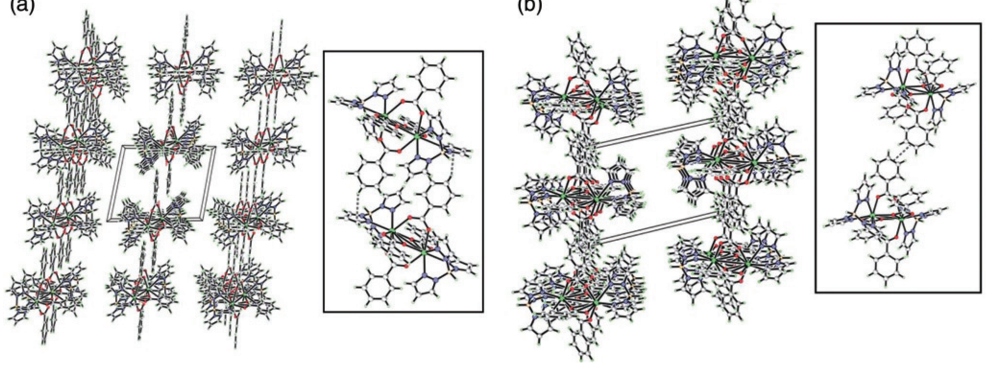

Figure 2. Crystal packing views for [(tp)Pr(μ-OBz)$_4$Pr(tp)].

3.1.2. Molecular structure of [(tp)Pr(μ-*p*-Cl–OBz)$_4$Pr(tp)]•2(CH$_2$Cl$_2$) (3). The molecular structure and atomic numbering of **3** is shown in figure 3. The bond lengths and angles are listed in table 3. This complex crystallizes in the triclinic system with space group $P\bar{1}$ ($Z = 1$) and contains a binuclear metal center. Each praseodymium coordinates three nitrogen atoms from a tris(pyrazolyl)borate ligand and four oxygen atoms from four bridged chlorobenzoates. The Pr–Pr distance is 4.025 Å, longer than in **1**. The Pr–O bond distances are in the range 2.377(5)–2.425(5) Å with average

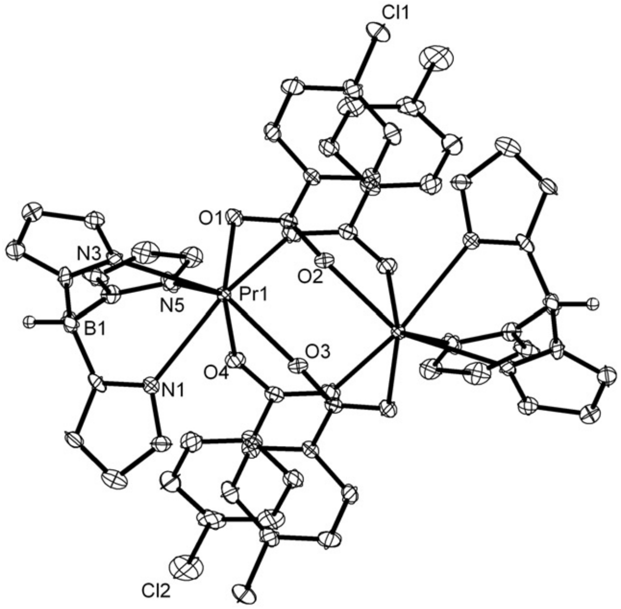

Figure 3. Thermal ellipsoidal representation for [(tp)Pr(μ-*p*-Cl–OBz)$_4$Pr(tp)] at 50% probability level (H atoms are omitted for clarity).

Table 3. Bond lengths (Å) and angles (°) for **3**.

Pr1–O4	2.377(5)	Pr1–N3	2.571(6)
Pr1–O3	2.393(5)	Pr1–N1	2.599(6)
Pr1–O2	2.401(5)	Pr1–N5	2.611(7)
Pr1–O1	2.425(5)	Pr1–Pr1′	4.025(7)
O4–Pr1–O3	76.87(18)	O4–Pr1–N3	98.1(2)
O4–Pr1–O2	134.68(18)	O3–Pr1–N3	153.34(19)
O3–Pr1–O2	76.73(18)	O2–Pr1–N3	121.0(2)
O4–Pr1–O1	81.67(19)	O1–Pr1–N3	75.66(18)
O3–Pr1–O1	128.22(17)	O4–Pr1–N1	72.11(19)
O2–Pr1–O1	86.60(19)	O3–Pr1–N1	82.76(19)
O2–Pr1–N1	138.7(2)	O1–Pr1–N1	133.4(2)
O4–Pr1–N5	143.75(19)	O3–Pr1–N5	95.3(2)
O2–Pr1–N5	74.86(19)	O1–Pr1–N5	127.2(2)
N3–Pr1–N1	70.9(2)	N3–Pr1–N5	73.1(2)
N1–Pr1–N5	71.8(2)	N3–Pr1–O3	123.60(17)
N1–Pr1–O3	139.61(18)	N5–Pr1–O3	145.53(18)

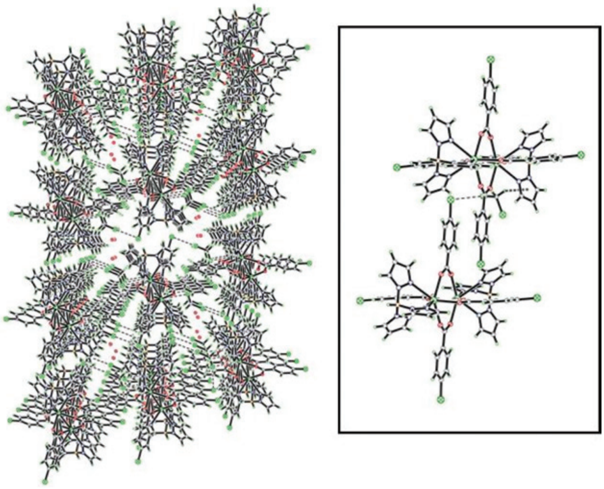

Figure 4. Crystal packing views for [(tp)Pr(μ-*p*-Cl–OBz)$_4$Pr(tp)].

of 2.399 Å, longer than average Ln–O bond distances in other chlorobenzoate-bridged complexes [32, 33], but shorter than the average Pr–O bond distance of 2.413 Å in **1**, suggesting that the interaction between praseodymium and oxygen of carboxylate groups in **3** is stronger than in **1**, due to the presence of an electron-donating group (–Cl) at the para position. The praseodymium-nitrogen bond distances are in the range 2.571(6)–2.611(6) Å. The Pr1–N5 bond distance [2.611 Å] is slightly longer than the Pr1–N3 [2.571(6) Å] and Pr1–N1 [2.599(6) Å]. The average Pr–N distance in **3** is 2.593 Å, longer than the average Ln–N bond distances reported in isostructural lanthanide complexes and equal to the average Pr–N in **1**. The average C–C distance in the aromatic ring of the benzoate group is 1.378 Å. From crystal packing of **3** (figure 4), it is clear that molecules interact with each other through different interactions. A Cl–Cl interaction (3.428 Å) occurs between the para chlorine on benzoate of one molecule and chlorine of solvent; a CH-π (2.650 Å) interaction occurs between dichloromethane and a pyrazole ring of another molecule.

3.1.3. Molecular structure of [(tp)(pz)Pr(μ-*p*-F–OBz)$_4$Pr(pz)(tp)]•2CH$_2$Cl$_2$ (5).

The praseodymium(III) complex, **5**, crystallizes in triclinic space group $P\bar{1}$. The molecular structure is shown in figure 5 with thermal ellipsoidal representation at 50% probability. The selected bond lengths and angles are listed in table 4. The praseodymium is eight coordinate with three nitrogens from one tris (pyrazolyl) borate, one nitrogen from free pyrazole and four oxygens from four bridging fluorobenzoates; Pr–Pr distance is 4.0866 Å, longer compared to Pr–Pr distances in **1** and **3**. Like **1** and **3**, the coordinated fluorobenzoates have Pr–O bond distances in the range 2.415–2.473 Å and are of bridge type II. The average Pr–O bond distance [2.440 Å] in **5** is longer than the average Pr–O bond distances [2.413 Å and 2.399 Å] in **1** and **3**. This average bond distance is also longer than average Nd–O bond distances [2.418 Å] in an isostructural neodymium(III) complex [36]. The praseodymium–nitrogen bond distances of coordinated pyrazolylborate are in the range 2.575–2.656 Å and the average

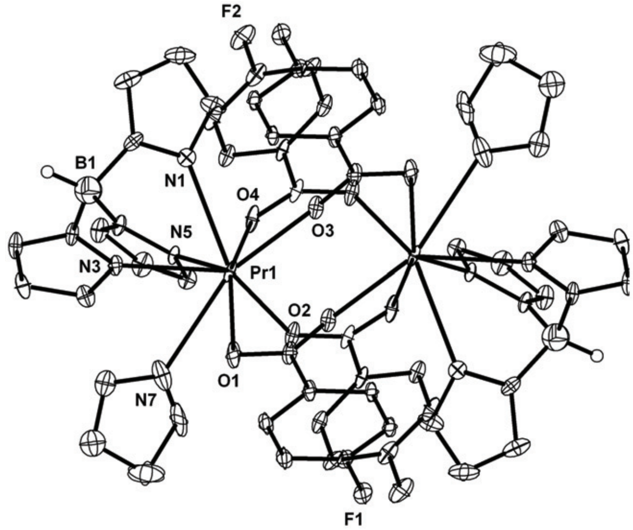

Figure 5. Thermal ellipsoidal representation for $[(tp)(pz)Pr(\mu\text{-}p\text{-}F\text{–}OBz)_4Pr(pz)(tp)]\cdot 2CH_2Cl_2$ at 50% probability level (H atoms are omitted for clarity).

Table 4. Bond lengths (Å) and angles (°) for **5**.

Pr1–N1	2.656(3)	Pr1–N3	2.575(3)
Pr1–N5	2.601(2)	Pr1–N7	2.823(5)
Pr1–O1	2.473(3)	Pr1–O2	2.433(3)
Pr1–O3	2.415(3)	Pr1–O4	2.441(3)
Pr1–Pr1′	4.086(4)		
O3–Pr1–O1	125.44(9)	O3–Pr1–O2	74.66(10)
O3–Pr1–O4	78.90(10)	O3–Pr1–N3	141.65(9)
O1–Pr1–N3	84.74(9)	O2–Pr1–N3	135.32(10)
O4–Pr1–N3	88.19(9)	O3–Pr1–N5	93.28(8)
O1–Pr1–N5	134.57(9)	O2–Pr1–N5	79.18(9)
O4–Pr1–N5	141.56(9)	O1–Pr1–N1	136.32(11)
O2–Pr1–N1	134.99(10)	O3–Pr1–N1	74.32(9)
O4–Pr1–N1	70.72(10)	O3–Pr1–O3	75.97(9)
O2–Pr1–O3	69.85(9)	O4–Pr1–O3	65.80(9)
O1–Pr1–O3	49.62(8)	O1–Pr1–N7	66.97(12)
O2–Pr1–N7	70.85(13)	O3–Pr1–N7	143.01(12)
O4–Pr1–N7	135.61(11)	N3–Pr1–N7	65.87(13)
N5–Pr1–N7	67.68(11)	N1–Pr1–N7	123.43(13)
N3–Pr1–O3	130.69(8)	N5–Pr1–O3	148.88(8)

Pr–N bond distance [2.610 Å] in **5** is longer than the average Pr–N bond distances in **1** and **3**.

3.2. *Photophysical properties*

Lanthanide complexes are known for bright emission under UV irradiation because of the effective energy transfer from ligands to central ions called the "antenna effect." Pr(III) complexes are only weakly emissive because of the small energy gap between the

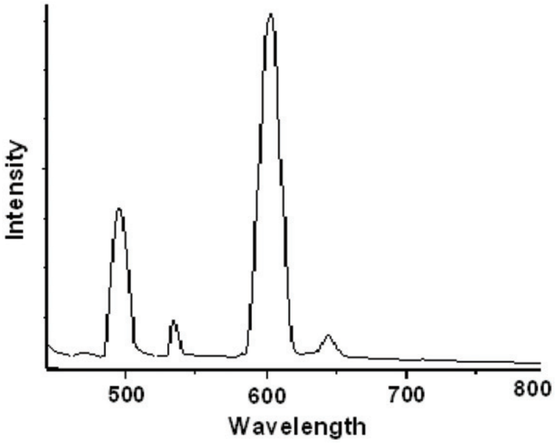

Figure 6. Emission spectrum of [(tp)Pr(μ-OBz)$_4$Pr(tp)].

ground state and emissive state which causes non-radiative decay, an important factor in the luminescence intensities for Pr(III) complexes. The ultraviolet absorption spectra show bands at 233.0 and 280.0 nm for **1**, 238.0 and 285.0 nm for **2**, 243.0 and 287.0 nm for **3**, 286.0 nm for **4**, 241.0 and 288.0 nm for **5**. Figure 6 shows a representative emission spectrum ($\lambda_{exc} = 280.0$ nm) of **1** in dichloromethane. The main emission features of **1** centered at 603 nm arise from overlap of both $^3P_0 \rightarrow {}^3H_6$ and $^1D_2 \rightarrow {}^3H_4$ transitions. Other sharp bands at 490 nm ($^3P_0 \rightarrow {}^3H_4$), 530 nm ($^3P_0 \rightarrow {}^3H_5$) and 649 nm ($^3P_0 \rightarrow {}^3F_2$) are also present. The intensity sequence of the peaks is $I^3P_0 \rightarrow {}^3H_6$ and $^1D_2 \rightarrow {}^3H_4 > I^3P_0 \rightarrow {}^3H_4 > I^3P_0 \rightarrow {}^3H_5 > I^3P_0 \rightarrow {}^3F_2$. All the complexes show the same emission features with different luminescent intensities.

3.3. *Thermal properties*

Thermograms for all complexes were recorded in the temperature range 25.0–900.0°C with heating rate of 10.0°C min^{-1} under air. The thermal decomposition data for **1**–**4** are listed in table 5. TGA curve of **1** exhibits two well-separated weight loss stages. The first weight loss (observed 34.98%, calculated 35.56% between 98.0–335.0°C) corresponds to loss of tp. The second weight loss (observed 35.15%, calculated 35.66% between 365.0–900.0°C) is due to the loss of $C_{28}H_{20}O_{4.33}$. The remaining weight of 29.15% is due to praseodymium oxide. TGA curve of **2**, **3** and **4** also show two well-separated analogous weight loss stages. Thermogravimetric analysis indicated that **5** was stable to 100.0°C but at higher temperatures showed an irregular pattern until plateau was reached at 800–900°C, due to formation of praseodymium oxide.

4. Conclusion

In summary, four seven- and one eight-coordinate complexes of praseodymium(III) have been prepared by reaction of praseodymium(III) chloride, sodium *p*-X-benzoate

Table 5. Thermal decomposition data for **1**–**4**.

Stage	DTG peak (Temp. °C)	Mass loss (%) Obs.	Mass loss (%) Calcd	Constituents lost
1				
I	299.0	34.98	35.56	$C_{18}H_{20}N_{12}B_2$
II	486.0	35.15	35.66	$C_{28}H_{20}O_{4.33}$
2				
I	284.0	33.04	33.54	$C_{18}H_{20}N_{12}B_2$
II	472.0	39.08	39.34	$C_{28}H_{16}F_4O_{4.33}$
3				
I	287.0	31.25	31.87	$C_{18}H_{20}N_{12}B_2$
II	442.0	41.98	42.38	$C_{28}H_{16}Cl_4O_{4.33}$
4				
I	295.0	31.05	30.90	$C_{18}H_{20}N_{12}B_2$
II	465.0	44.28	44.11	$C_{28}H_{16}N_4O_{12.33}$

and a tp ligand. Their structures have been determined showing bridging bidentate of bridge type II benzoate ligands. The crystal packing of **1** suggested that two symmetrically independent molecules in the asymmetric unit linearly arranged in the form of AB-AB type arrangement, whereas in **2**, the molecules in unit cell interact with each other through different interactions. All these complexes show the emission properties.

Supplementary material

CCDC numbers 634576, 634577 and 645627 contain the supplementary crystallographic data (CIF) for this article. These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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