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Preparation and Crystal Structures of 1:1 Adducts of Lanthanide Nitrate with Tri(2-pyridyl)amine

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A series of 1:1 adducts between late-lanthanide nitrate and tri(2-pyridyl)amine (tpa), $[\mathrm{Ln(NO_3)_3(EtOH)_3}]\cdot(\mathrm{tpa})\cdot 0.5\mathrm{EtOH}$ ($\mathrm{Ln^{3+}} = \mathrm{Er^{3+}}$, $\mathrm{Yb^{3+}}$, and $\mathrm{Lu^{3+}}$) was synthesized. These 1:1 adducts possess similar crystal structures, in which the tpa molecules interact face-to-face with the triangular base of $[\mathrm{Ln(NO_3)_3(EtOH)_3}]$ through three hydrogen bonds.

The coordination chemistry of lanthanide(III) complexes with O-donor ligands has been the subject of numerous studies.[1] In the last decade, lanthanides(III) with N-donor ligands have received considerable attention due to their potential application as supramolecular light conversion devices,[2] and as agents to separate actinides(III) from lanthanides.[3] The structural and thermodynamic characterization of La(III) complexes with 1,10-phenanthroline, 2,2′-bipyridine, and 2,2′:6′,2″-terpyridine (terpy) in acetonitrile has been reported.[4] Subsequently, lanthanide complexes with tripodal tri(2-pyridyl)amine (tpa), which are different in geometry than the terpy complexes, have been synthesized and characterized.[5] The tpa ligand readily reacts with $\mathrm{Ln(hfac)_3}$ (hfac, hexafluoroacetylacetonate) in dichloromethane to form $[\mathrm{Ln(hfac)_3(tpa)}]$, in which the tpa is coordinated through two of its pyridyl groups (as a didentate ligand); the third pyridyl group is not coordinated. Herein, we report the preparation and structural characterization of 1:1 adducts of lanthanide nitrate with tpa.

The reaction of $\mathrm{Ln(NO_3)_3}\cdot n\mathrm{H_2O}$ (Ln = Er, Yb, and Lu) with tpa in ethanol afforded the crystalline 1:1 adducts $[\mathrm{Ln(NO_3)_3(EtOH)_3}]\cdot(\mathrm{tpa})\cdot 0.5\mathrm{EtOH}$. In order to investigate the structures of the 1:1 adducts in solution, ^{1}H NMR studies were carried out using $[\mathrm{Lu(NO_3)_3(EtOH)_3}]\cdot(\mathrm{tpa})\cdot 0.5\mathrm{EtOH}$ (**3**), which contains diamagnetic $\mathrm{Lu^{3+}}$ metal ions. Since the ^{1}H NMR spectrum of **3** in $\mathrm{C_2D_5OD}$ exhibited four signals, which were not different in chemical shift and peak width compared with those of free tpa, it can be reasoned that tpa molecules do not coordinate to $\mathrm{Lu^{3+}}$ metal ions in ethanol solutions, and that the interaction between solvated $\mathrm{Lu(NO_3)_3}$ and tpa is very weak. X-ray studies have shown that the crystal structures of the 1:1 adducts for $\mathrm{Er^{3+}}$ (**1**), $\mathrm{Yb^{3+}}$ (**2**), and $\mathrm{Lu^{3+}}$ (**3**) are isostructural (monoclinic, space group $P2_1$), and are very similar, with the exception of their bond parameters.[6] The crystal structure of **1**, as a representative crystal structure of the 1:1 adducts, is shown in Fig. 1. Although tpa is not coordinated to the lanthanide ion, face-to-face interactions were observed between the tpa molecule and the triangular base of the ethanol-solvated lanthanide nitrate $[\mathrm{Ln(NO_3)_3(EtOH)_3}]$ through three hydrogen bonds—the three pyridine nitrogen atoms of tpa were bound to the three hydrogen atoms of three hydroxy groups of the ethanol ligands.[7] For tpa in **1**, **2**, and **3**, the deviations of the central nitrogen atom N(7) from the central $\mathrm{NC_3}$ plane (N(7), C(7), C(12), and C(17)) were 0.04(1), 0.04(1), and 0.03(1) Å, respectively. The central nitrogen atom of tpa is coplanar with its three bound carbon atoms, with sp^2-hybridization similar to that of free tpa.[8] The three pyridyl rings of tpa exist in a propeller arrangement. The dihedral angles between the central $\mathrm{NC_3}$ plane and the pyridyl ring are 45.2(4)–48.8(4)° in **1**, 45.4(3)–48.7(3)° in **2**, and 45.3(3)–49.0(3)° in **3**, which are significantly larger than those in free tpa (35.3°).[8]

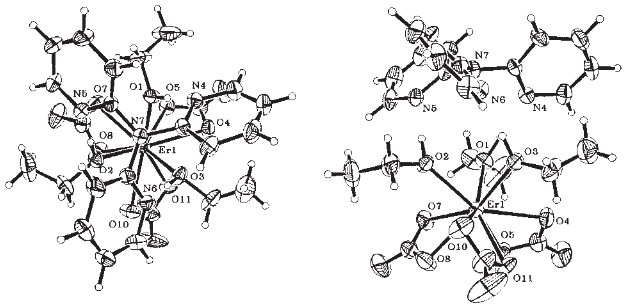

Fig. 1. Top (left) and side view (right) of $[\mathrm{Er(NO_3)_3}$-$\mathrm{(EtOH)_3}]\cdot(\mathrm{tpa})$ in **1** with 30% probability ellipsoids. The included solvent molecule is omitted for clarity.

For each lanthanide ion $[\mathrm{Ln(NO_3)_3(EtOH)_3}]$, the coordination geometry is that of a nine-coordinate tricapped trigonal prism (TTB) consisting of nine oxygen atoms: six oxygen atoms from the three didentate nitrato ligands, and three oxygen atoms from the three coordinated ethanol molecules. Three ethanol oxygen atoms, O(1), O(2), and O(3), occupy one triangular face of the TTB geometry, whereas three nitrato oxygen atoms, O(5), O(8), and O(11), occupy the other triangular face. Each square face is capped by the opposing bound nitrato oxygen atoms, O(4), O(7), and O(10). The bond angles around the lanthanide ion among **1**, **2**, and **3** are very similar, and indicate that the geometry of the coordination polyhedron is that of a fairly regular tricapped trigonal prism. The sum of the bond angles around the central lanthanide ion in the equatorial direction, O(4)–Ln–O(7), O(7)–Ln–O(10), and O(4)–Ln–O(10), is nearly 360°—specifically, 352.3(9)° in **1**, 352.4(6)° in **2**, and 352.5(9)° in **3**. The equatorial nitrato oxygen atoms, therefore, are located on the equator.

For **1**, the bond distances around the $\mathrm{Er^{3+}}$ ion follow the sequence: Er–O(ethanol) 2.330(5)–2.336(6) < Er–O(axial oxygen of nitrato) 2.380(7)–2.430(8) < Er–O(equatorial oxygen of nitrato) 2.444(7)–2.470(6) Å. The bond distances around the lanthanide ion in **2** and **3** also follow the same order. The Ln–O(ethanol) bond distances and the Ln–O(axial oxygen of nitrato) bond distances decrease upon switching from Er to Lu by 0.05–0.04 Å and by 0.05–0.03 Å, respectively. The decrease in the Ln–O bond distances reflects the decrease in the size of the lanthanide metal ion. The variation of the Ln–O(equatorial oxygen of nitrato) bond distances, however, is different from those of other Ln–O distances. The shortest equato-

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rial Ln–O bond distances among the three equatorial Ln–O bonds, Ln–O(10) (2.444(7) in **1** > 2.423(6) in **2** > 2.397(8) Å in **3**), decrease upon switching from Er to Lu by 0.05 Å, which are similar to those of axial Ln–O bonds. On the other hand, the remaining equatorial Ln–O bond distances, Ln–O(4) and Ln–O(7), show only small decrements (0.016 and 0.006 Å, respectively), which do not follow the ionic radius change. Since a smaller lanthanide ion will cause stronger steric repulsions between the adjacent coordinated O atoms, the smaller ionic radius of an Lu^{3+} ion will result in the elongation of the equatorial bond distances.

Experimental

Synthesis of Tri(2-pyridyl)amine (tpa). Tri(2-pyridyl)amine was prepared by modifying previously reported methods.[9] A round bottom flask was charged with di(2-pyridyl)amine (4.0 g, 23 mmol), 2-bromopyridine (6.0 g, 38 mmol), mesitylene (70 mL), sodium carbonate (4.0 g), copper powder (1 g), and a trace of potassium iodide (0.1 g). The mixture was refluxed for 24 h, and then cooled in an ice bath for 1 h. The resulting solid material was treated with boiling water (400 mL) to dissolve tpa, followed by the removal of the insoluble materials (copper powder). The filtrate was concentrated to 50 mL and cooled overnight in a refrigerator. The resulting crystalline needles were collected and washed with cold water. Yield 4.3 g (74%). mp 130–131 °C.

Preparation of 1:1 Adducts of Lanthanide Nitrate with tpa. **$[Er(NO_3)_3(EtOH)_3]\cdot(tpa)\cdot0.5EtOH$ (1):** A solution of tpa (0.50 g, 2 mmol) in ethanol (20 mL) was added to a solution of $Er(NO_3)_3\cdot6H_2O$ (0.92 g, 2 mmol) in ethanol (20 mL). The mixture was refluxed for 0.5 h, concentrated to 10 mL on a hot plate, then allowed to stand overnight at ambient temperature. The resulting light pink microcrystalline solid was collected and washed with a small amount of ethanol. Yield 0.85 g (55%). Single crystals suitable for X-ray diffraction were grown from an ethanolic solution of the product (150 mg/10 mL) that was allowed to stand for 2–4 days in a refrigerator. Anal. Calcd for $C_{22}H_{33}N_7O_{12.5}Er_1$: C, 34.64; H, 4.36; N, 12.85%. Found: C, 34.60; H, 4.35; N, 12.85%.

$[Yb(NO_3)_3(EtOH)_3]\cdot(tpa)\cdot0.5EtOH$ (2): Following similar methods as described for **1**, colorless crystals were obtained using $Yb(NO_3)_3\cdot4H_2O$ (0.86 g, 2 mmol) and tpa (0.5 g, 2 mmol). Yield 0.86 g (55%). Anal. Calcd for $C_{22}H_{33}N_7O_{12.5}Yb_1$: C, 34.38; H, 4.33; N, 12.76%. Found: C, 34.49; H, 4.42; N, 12.80%.

$[Lu(NO_3)_3(EtOH)_3]\cdot(tpa)\cdot0.5EtOH$ (3): Following similar methods as described for **1**, colorless crystals were obtained using $Lu(NO_3)_3\cdot2H_2O$ (0.79 g, 2 mmol) and tpa (0.5 g, 2 mmol). Yield 1.05 g (70%). Anal. Calcd for $C_{22}H_{33}N_7O_{12.5}Lu_1$: C, 34.29; H, 4.32; N, 12.73%. Found: C, 34.16; H, 4.20; N, 12.67%.

X-ray Crystallography. Data for all crystals were collected by the ω–2θ scan technique ($2\theta < 55°$) on a Rigaku AFC-7R automated four-circle X-ray diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ radiation at 23 °C. All calculations were carried out using the teXsan crystallographic software package.[10] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and included in the structure factor calculations. The crystallographic parameters are as follows: for **1**, $Er_1C_{22}H_{33}O_{12.5}N_7$, fw = 762.80, monoclinic, space group $P2_1$(#4), $a = 9.476(3)$, $b = 17.188(4)$, $c = 10.461(3)$ Å, $\beta = 103.30(3)°$, $Z = 2$, $V = 1658.3(8)$ Å^3, $D_c = 1.528$ g cm^{-3}, 3950 unique reflections used, $R = 0.059$, Rw = 0.093, GOF = 1.261. For **2**, $Yb_1C_{22}H_{33}O_{12.5}N_7$, fw = 768.58, monoclinic, space group $P2_1$(#4), $a = 9.454(4)$, $b = 17.155(5)$, $c = 10.455(4)$ Å, $\beta = 103.23(3)°$, $Z = 2$, $V = 1650.6(10)$ Å^3, $D_c = 1.546$ g cm^{-3}, 3924 unique reflections used, $R = 0.049$, Rw = 0.080, GOF = 1.314. For **3**, $Lu_1C_{22}H_{33}O_{12.5}N_7$, fw = 770.51, monoclinic, space group $P2_1$(#4), $a = 9.444(2)$, $b = 17.146(2)$, $c = 10.449(2)$ Å, $\beta = 103.17(1)°$, $Z = 2$, $V = 1647.6(4)$ Å^3, $D_c = 1.553$ g cm^{-3}, 3910 unique reflections used, $R = 0.060$, Rw = 0.104, GOF = 1.711. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 231976–231978.

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6 Selected bond distances (Å) and angles (°): For **1**, Er(1)–O(1) 2.336(6), Er(1)–O(2) 2.330(5), Er(1)–O(3) 2.333(6), Er(1)–O(4) 2.470(6), Er(1)–O(7) 2.448(6), Er(1)–O(10) 2.444(7), Er(1)–O(5) 2.394(8), Er(1)–O(8) 2.380(7), Er(1)–O(11) 2.430(8), O(4)–Er(1)–O(7) 118.8(3), O(7)–Er(1)–O(10) 118.3(3), O(4)–Er(1)–O(10) 115.2(3). For **2**, Yb(1)–O(1) 2.308(5), Yb(1)–O(2) 2.297(4), Yb(1)–O(3) 2.300(5), Yb(1)–O(4) 2.462(5), Yb(1)–O(7) 2.434(5), Yb(1)–O(10) 2.423(6), Yb(1)–O(5) 2.376(6), Yb(1)–O(8) 2.367(5), Yb(1)–O(11) 2.391(6), O(4)–Yb(1)–O(7) 119.0(2), O(7)–Yb(1)–O(10) 118.1(2), O(4)–Yb(1)–O(10) 115.3(2). For **3**, Lu(1)–O(1) 2.300(6), Lu(1)–O(2) 2.281(6), Lu(1)–O(3) 2.299(6), Lu(1)–O(4) 2.464(6), Lu(1)–O(7) 2.432(6), Lu(1)–O(10) 2.397(8), Lu(1)–O(5) 2.359(7), Lu(1)–O(8) 2.348(7), Lu(1)–O(11) 2.374(7), O(4)–Lu(1)–O(7) 119.1(3), O(7)–Lu(1)–O(10) 117.9(3), O(4)–Lu(1)–O(10) 115.5(3).

7 Hydrogen bonding parameters: For **1**, O(1)–H(1)···N(4), 2.697(7) Å, 179.650°; O(2)–H(7)···N(5), 2.716(9) Å, 178.972°; O(3)–H(13)···N(6), 2.715(9) Å, 179.402°. For **2**, O(1)–H(1)···N(4), 2.702(6) Å, 179.120°; O(2)–H(7)···N(5), 2.712(7) Å, 179.771°; O(3)–H(13)···N(6), 2.713(7) Å, 179.467°. For **3**, O(1)–H(1)···N(4), 2.703(6) Å, 179.265°; O(2)–H(7)···N(5), 2.738(8) Å, 179.853°; O(3)–H(13)···N(6), 2.715(8) Å, 179.496°.

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