Supramolecular Architecture and a New Mode of Pyrazolate Coordination (η^3) in the First Homoleptic Lanthanide Pyrazolate Complexes**

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The recent preparations of the first homoleptic pyrazolate complexes [Ti(η^2-Me_2pz)$_4$] (R_2pz = 3,5-disubstituted pyrazolate)[1a,b] and [Ta(η^2-Me_2pz)$_3$(η^1-Me_2pz)$_2$][1c] for relatively small ions (ionic radii of Ti^{4+} and Ta^{5+}: 0.74 Å)[2] are in contrast to the invariable isolation of tris(η^2-pyrazolate) derivatives of the larger (ca. 1.0 Å)[2] lanthanide ions as [Ln(η^2-R_2pz)$_3$(L)$_n$] complexes (L = thf, dimethoxyethane (dme), or Ph_3PO),[3] rather than as homoleptic [Ln(R_2pz)$_3$] species. We now report the first homoleptic pyrazolatolanthanide(III) complexes **1** and the charge-separated **2**. Additional novel features are the K^+/[Er(η^2-tBu$_2$pz)$_4$]$^-$ supramolecular framework and a new pyrazolate coordination mode (η^3 to K^+) in **1**, as well as the nature of the K^+/toluene interaction in **2**. Pyrazolate ions commonly bind as μ-η^1:η^1, η^1, or η^2 ligands,[4] and μ_3-η^1:η^2:η^1 (to K^+)[5] and μ-η^2:η^2 (to Yb^{2+})[6] coordination modes were recently observed.

[K{Er(η^2-tBu$_2$pz)$_4$}$_n$] **1**

[K([18]crown-6)(dme)(PhMe)][Er(η^2-tBu$_2$pz)$_4$] **2**

Complex **1** was prepared by reaction of anhydrous erbium chloride with potassium 3,5-di-*tert*-butylpyrazolate in 1,2,4,5-tetramethylbenzene at 200 °C under vacuum [Eq. (a)] and

$$ErCl_3 + 4\,K(t\text{Bu}_2\text{pz}) \rightarrow K[Er(t\text{Bu}_2\text{pz})_4] + 3\,KCl \qquad (a)$$

obtained in good yield by crystallization from toluene, while **2** was isolated by crystallization of **1** from dme/PhMe containing [18]crown-6. Not only are these the first homoleptic pyrazolatolanthanide complexes, but they are also the first mononuclear anionic lanthanide pyrazolates. The cages [Ln_3(Me_2pz)$_6$(μ_3-O)Na_2L_2] (L = thf or Me_2pzH) can be viewed as polynuclear "ate" species.[7]

Analytical, IR, and Vis/near-IR data for **1** and **2** were consistent with the proposed compositions. Conductivity measurements in the low-polarity solvent CH_2Cl_2 suggest greater ion separation in **2**, although its conductivity is lower than that typical for a 1:1 electrolyte in this solvent.[8] X-ray crystallography[9] on **1** revealed a linear supramolecular array of [Er(η^2-tBu$_2$pz)$_4$]$^-$ anions and potassium cations. The latter are sandwiched between two of the pyrazolate ligands (η^3 bonded), and the chains are linked by intermolecular potassium–carbon interactions (Figure 1). Discrete [Er(η^2-tBu$_2$pz)$_4$]$^-$ anions and [K([18]crown-6)(dme)(PhMe)]$^+$ cations are present in **2** (Figure 2).

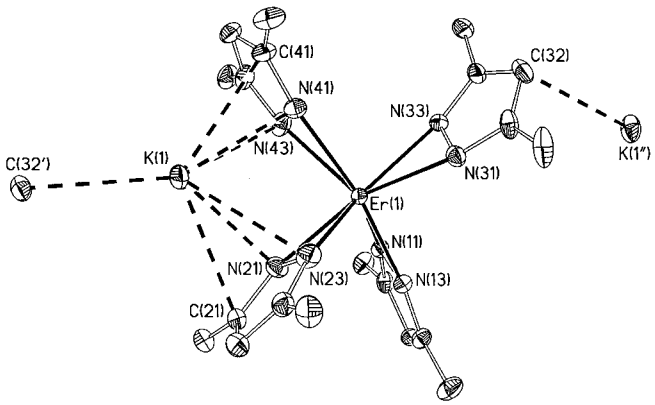

Figure 1. ORTEP plot of **1** (30% probability thermal ellipsoids; hydrogen atoms and methyl groups omitted for clarity). Selected bond lengths [Å] and angles [°]: Er–N(11) 2.342(6), Er–N(13) 2.292(6), Er–N(21) 2.346(6), Er–N(23) 2.416(6), Er–N(31) 2.350(6), Er–N(33) 2.324(6), Er–N(41) 2.361(6), Er–N(43) 2.385(6), K–N(21) 2.811(7), K–N(23) 3.077(7), K–C(21) 3.187(7), K–N(41) 2.842(6), K–N(43) 3.130(6), K–C(41) 3.093(8), K–C(32′) 3.162(7), K···C(31′) 3.665(7), K···C(33′) 3.577(7); cen(1)-Er-cen(2) 98.1, cen(1)-Er-cen(3) 102.2, cen(1)-Er-cen(4) 137.2, cen(2)-Er-cen(3) 136.7, cen(2)-Er-cen(4) 91.5, cen(3)-Er-cen(4) 98.7 (cen(x) = center of the N(x1)–N(x3) bond).

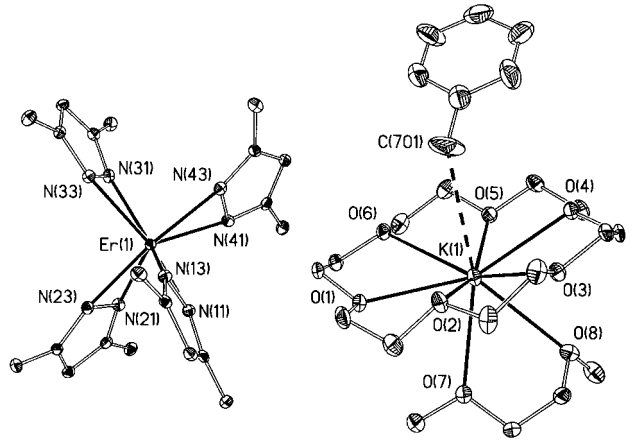

Figure 2. ORTEP plot of **2** (30% probability thermal ellipsoids; hydrogen atoms and the methyl groups of the *t*Bu substituents omitted for clarity). Selected bond lengths [Å] and angles [°]: Er–N(11) 2.332(3), Er–N(13) 2.368(3), Er–N(21) 2.359(3), Er–N(23) 2.348(3), Er–N(31) 2.332(3), Er–N(33) 2.378(3), Er–N(41) 2.396(3), Er–N(43) 2.336(6), K–O(1) 2.885(3), K–O(2) 2.868(3), K–O(3) 2.863(3), K–O(4) 2.841(3), K–O(5) 2.782(3), K–O(6) 2.900(3), K–O(7) 2.823(3), K–O(8) 3.075(3), K–C(701) 3.423(4); cen(1)-Er-cen(2) 94.7, cen(1)-Er-cen(3) 135.8, cen(1)-Er-cen(4) 99.6, cen(2)-Er-cen(3) 100.9, cen(2)-Er-cen(4) 136.7, cen(3)-Er-cen(4) 96.7 (cen(x) = center of the N(x1)–N(x3) bond).

The erbium centers of **1** and **2** are coordinated to eight nitrogen atoms of four η^2-tBu$_2$pz ligands, and the average Er–N distances (**1**: 2.35; **2**: 2.36 Å) are comparable with those of eight-coordinate [Er(η^2-tBu$_2$pz)$_3$(thf)$_2$][3a] and [Er(η^2-Ph_2pz)$_3$(Ph_3PO)$_2$][3c] (av 2.34 Å). The geometries around the erbium atom, as defined by the centers of the N(x1)–N(x3) bonds (cen(x), x = 1–4) are highly distorted from tetrahedral [cen-Er-cen 91.5–136.7 (**1**); 94.7–136.7° (**2**)]. Most likely, these deviations minimize the steric repulsions between the bulky *t*Bu groups, since in the less crowded [Ti(η^2-tBu$_2$pz)$_2$$Cl_2$][1b] the range of pseudotetrahedral angles (100.5–113.3°) is markedly narrower. The similarity of the

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geometries of the $[Er(\eta^2\text{-}t\text{Bu}_2\text{pz})_4]^-$ anions in **1** and **2** is consistent with the supramolecular nature of the $t\text{Bu}_2\text{pz}\cdots\text{K}\cdots t\text{Bu}_2\text{pz}$ interactions in **1**.

Two of the K–N distances of **1** [K(1)–N(21) and K(1)–N(41)] are comparable with the μ-η^1:η^1 and η^2 K–N distances of $[\{K(t\text{Bu}_2\text{pz})(\text{thf})\}_6]$.[5] Additionally, the adjacent nitrogen and carbon atoms of both pyrazolate ligands [e.g., N(23) and C(21) for N(21)] are only about 0.3 Å further from the potassium atom. These longer distances are similar to the K–N and K–C distances (3.122(5) – 3.255(5) Å) of a π-bound K(η^5-pyrrolyl) moiety[10] and hence are regarded as significant interactions that give overall η^3 coordination. The central K–N(21) and K–N(41) bonds of the η^3-pyrazolate ligands are virtually normal (94.2, 92.5°) to the ring planes, and this implies π-donor bonding to potassium. Notably, the potassium atom lies within the smallest of the intracentroid angles (cen(2)-Er-cen(4) 91.5°), and this also implies bonding. Since the K···C distances of the remaining two C atoms of the pyrazolate rings of each ligand are about 0.4 Å longer, it is unlikely that they are significant interactions, especially in view of the position of K^+ (see above), although they are within the range found for potassium(η^6-arene) bonding (K–C max. 3.72(1) Å; av 3.37 Å).[11, 12] The sevenfold coordination of the potassium atom in **1** is completed by a potassium – carbon (C32′) contact (3.162(7) Å) to a neighboring $[Er(\eta^2\text{-}t\text{Bu}_2\text{pz})_4]^-$ anion (see ref. [13] for a similar Ag–C(Me_2pz) interaction). The next nearest carbon atoms (see legend to Figure 1) are significantly more distant (by 0.4 Å or more) and are considered nonbonding.

The potassium cation in **2** is located in the cavity of an [18]crown-6 molecule, and a chelating dme ligand is bound on one side of the K([18]crown-6) moiety. A toluene molecule, orientated with the methyl group toward the potassium ion, occupies the vacant face opposite to dme. Formation of this supramolecular K([18]crown-6)/toluene "lock and key" interaction (K–C(Me) 3.423(7) Å) is remarkable given the excess of the potential donor dme in the crystallization solution.

Experimental Section

1: Potassium 3,5-di-*tert*-butylpyrazolate (1.20 g, 5.5 mmol) was prepared from KH and $t\text{Bu}_2\text{pzH}$ in PhMe and heated with $ErCl_3$ (0.38 g, 1.4 mmol) in 1,2,4,5-tetramethylbenzene (1.00 g) at 200 °C/10^{-3} Torr in an evacuated sealed Carius tube for 24 h. Extraction of the pink residue with light petroleum (to remove $C_6H_2Me_4$) followed by PhMe and subsequent concentration yielded large pink crystals of **1** (2.58 g, 77 %). IR (Nujol): $\tilde{\nu}$ = 1568 m, 1310 w, 1285 w, 1250 m, 1226 m, 1205 m, 1129 w, 1016 m, 993 s, 798 vs, 782 s, 728 vs, 628 w cm^{-1}; Vis/near IR (PhMe): λ_{max} (ε) = 379 (60), 490 (9), 522 (20), 595 (5), 654 (5), 980 nm (8); Λ_m (CH_2Cl_2) = 0.22 S cm^2 mol^{-1} (2.60×10^{-3} M); elemental analysis calcd for $C_{44}H_{76}N_8ErK$: C 57.23, H 8.30, N 12.13, Er 18.11; found: C 56.30, H 8.93, N 11.86, Er 18.35.

2: Compound **1** (0.10 g, 0.11 mmol) and [18]crown-6 (0.50 g, 1.9 mmol) were dissolved in PhMe (20 mL) and dme (5 mL). Cooling of the solution afforded a few pink acicular crystals of **2**. IR (Nujol): $\tilde{\nu}$ = 1606 w, 1515 m, 1486 m, 1411 m, 1319 s, 1303 m, 1285 m, 1251 m, 1225 m, 1206 m, 1191 m, 1114 br s, 1019 m, 997 s, 986 m, 960 s, 851 s, 840 s, 781 s, 776 s, 727 vs, 694 vs, 628 w cm^{-1}; Λ_m (CH_2Cl_2) = 9.7 S cm^2 mol^{-1} (1.31×10^{-3} M); elemental analysis calcd for $C_{67}H_{118}N_8O_8ErK$: C 58.74, H 8.68, N 8.18; found: C 58.08, H 7.88, N 8.35.

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[9] Crystal data for **1**: pink crystal, $0.25 \times 0.15 \times 0.15$ mm, monoclinic, space group $P2_1/c$, a = 20.7775(10), b = 12.3035(6), c = 18.8274(6) Å, β = 90.527(1)°, V = 4812.8(17) Å^3, ρ_{calcd} = 1.275 g cm^{-3}, $2\theta_{max}$ = 56.5°, N = 11516 (R_{int} = 0.072), N_o = 7754, R = 0.063, R_w = 0.132 (all data: R = 0.112, R_w = 0.147). Crystal data for **2**: pink crystal, $0.25 \times 0.13 \times 0.13$ mm, monoclinic, space group $P2_1/c$, a = 13.6803(2), b = 21.6001(2), c = 25.4376(4) Å, β = 99.445(1)°, V = 7414.8(3) Å^3, ρ_{calcd} = 1.227 g cm^{-3}, $2\theta_{max}$ = 60.1°, N = 20450 (R_{int} = 0.055), N_o = 14904, R = 0.051, R_w = 0.108 (all data: R = 0.088, R_w = 0.129). A total of N unique reflections (N_o with $(I) > 2\sigma(I)$ observed) were collected (Enraf-Nonius CCD, monochromatic $Mo_{K\alpha}$ radiation, λ = 0.71073 Å, $T \approx 123$ K) and used in least-squares refinement (anisotropic U for non-hydrogen atoms, H atoms constrained (x, y, z, U_{iso})) after structure solution and expansion by Patterson and Fourier techniques. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-112942 (**1**) and -112941 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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