

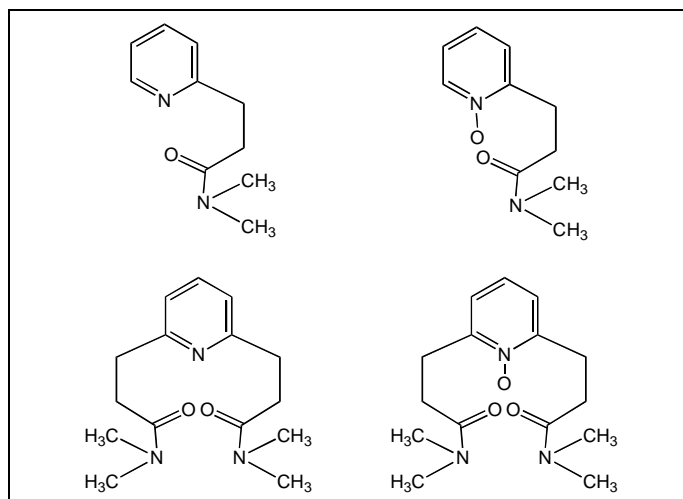
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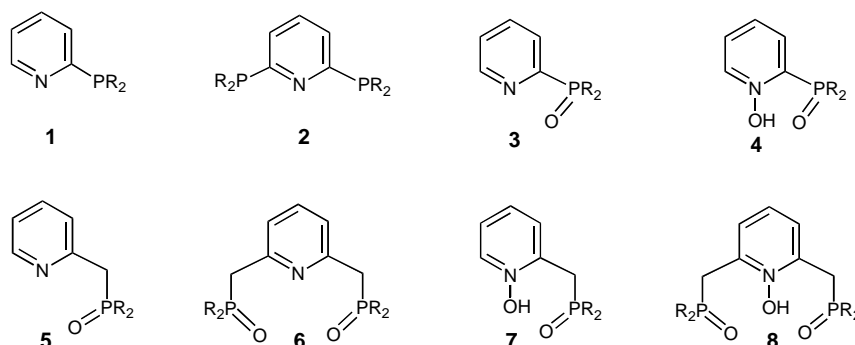
A new set of pyridine and pyridine *N*-oxides functionalized with *N,N*-dimethylpropionamide pendant groups in the 2- and 2,6-positions have been prepared from the combination of 2-chloromethylpyridine and 2,6-bis(chloromethyl) pyridine with α -lithio *N,N*-dimethyl acetamide. The coordination interaction between 2-(*N,N*-dimethylpropionamide) pyridine *N*-oxide (**10**) and $\text{Tb}(\text{NO}_3)_3$ has been unambiguously defined *via* single crystal X-ray diffraction analysis of $\text{Tb}(\mathbf{10})(\text{NO}_3)_3(\text{H}_2\text{O})$.

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INTRODUCTION

Pyridine and pyridine *N*-oxide rings offer the possibility to serve as platforms for the assembly of a variety of useful chelating ligands. Numerous investigators have described the syntheses of 2-(phosphino)pyridines, **1** and 2,6-bis(phosphino)pyridines, **2** and these generally act as good ligands toward the softer transition metal cations [1,2]. Recently, we have described syntheses for analogous 2-phosphine oxide substituted pyridine, **3**, and pyridine *N*-oxide, **4**, molecules and these are found to effectively chelate with harder metal ions such as represented by lanthanide and uranyl ions [3-6]. We have

also reported that 2-(methylphosphine oxide) and 2,6-bis-(methylphosphine oxide) substituted pyridines **5**, **6** and pyridine *N*-oxides **7**, **8** can be prepared. The latter two ligand types act as especially strong chelating ligands toward lanthanide and actinide ions despite the fact that the chelate rings contain seven atoms [7-18]. Indeed, representatives of the ligand **8** have proven to be very effective liquid-liquid extractants for trivalent lanthanide and actinide ions [19-21]. Due to the interesting ligation behavior of these ligands we have continued to seek synthetic approaches for functionally varied pyridine and pyridine *N*-oxide compounds that might serve as useful



ligands. In this report, we describe the facile synthesis of 2-(*N,N*-dimethylpropionamide) pyridine **9**, 2-(*N,N*-dimethylpropionamide) pyridine *N*-oxide **10**, 2,6-bis(*N,N*-dimethylpropionamide) pyridine **11**, and 2,6-bis(*N,N*-dimethylpropionamide) pyridine *N*-oxide **12** as well as crystal structure determinations for free ligand **10** and a 1:1 complex formed with $\text{Tb}(\text{NO}_3)_3$.

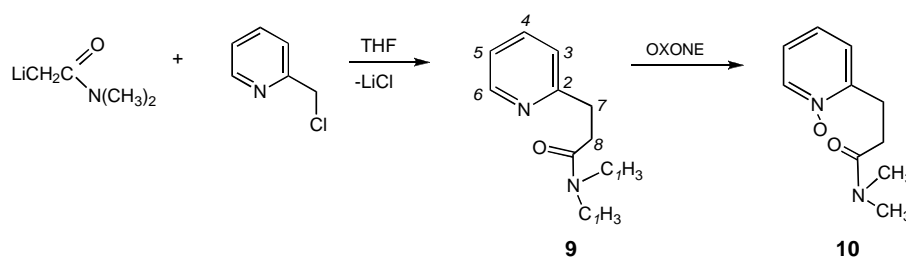
RESULTS AND DISCUSSION

The synthetic methodology involves combinations of α -lithio *N,N*-dimethylacetamide [22] with 2-chloromethyl pyridine (1:1) and 2,6-bis(chloromethyl) pyridine (2:1) in THF. These combinations produce, in moderate yields, 2-(*N,N*-dimethylpropionamide) pyridine, **9**, and 2,6-bis(*N,N*-dimethylpropionamide) pyridine, **11**, as a light yellow oil and a white powder, respectively (Schemes 1 and 2). Subsequent oxidations with OXONE give, in high yields, 2-(*N,N*-dimethylpropionamide) pyridine *N*-oxide,

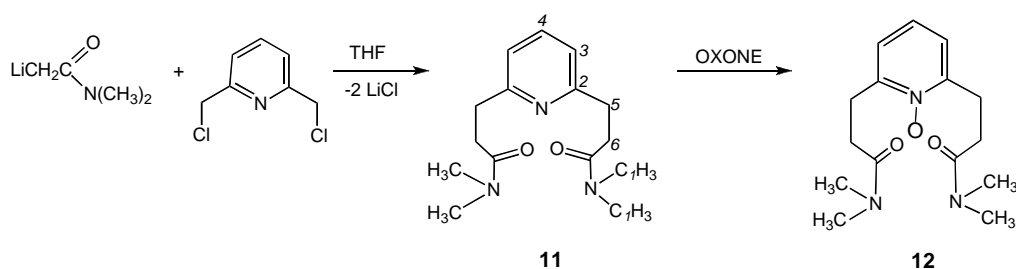
are clearly absent in the spectra recorded for compounds **9** and **11**.

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for **9** – **12** confirm the purity of the compounds. The ^1H NMR line widths for the *N*-oxide compounds are slightly broadened relative to the line widths observed for the pyridine progenitors, consequently several long range J_{HH} interactions less than 2 Hz are not resolved for **10** and **12**. Assignments were made with the use of COSY and HMQC methods. The amido groups have inequivalent methyl group environments resulting from hindered rotation within the $-\text{C}(\text{O})-\text{NMe}_2$ units. Hence, two methyl resonances appear in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra. The *exo* C_2H_4 arms in each molecule produce two triplets in the ^1H NMR spectra: one upfield of the NMe_2 resonance that is assigned to C_8H_2 in **9** and **10** or C_6H_2 in **11** and **12**, and one downfield of the NMe_2 resonance due to C_7H_2 in **9** and **10** or C_5H_2 in **11** and **12**. Upfield shifts of the

Scheme 1



Scheme 2



10, and 2,6-bis(*N,N*-dimethylpropionamide) pyridine *N*-oxide, **12**, as a colorless oil and white solid, respectively.

Compounds **9** – **11** are obtained in analytically pure form while **12** is isolated as a hydrate $(\mathbf{12})_2 \cdot \text{H}_2\text{O}$. The compounds have been fully characterized by spectroscopic methods and the data are consistent with the proposed formulations. FAB-MS spectra show $(\text{M} + \text{H}^+)$ and (M^+) ions at appropriate m/z values. Infrared spectra of the oil, **9**, and powder, **11**, dispersed in KBr pellets show an adsorption at 1647 cm^{-1} and 1643 cm^{-1} , respectively, that are assigned to ν_{CO} of the amide group. The *N*-oxidized molecules **10** and **12** show adsorptions at 1644 and 1243 cm^{-1} and 1644 and 1257 cm^{-1} , respectively. These bands are assigned to ν_{CO} and ν_{NO} . The ν_{NO} bands

$^{13}\text{C}\{^1\text{H}\}$ resonances assigned to C_2 and C_7 in **10** and C_2 and C_5 in **12** relative to the corresponding resonances in **9** and **11** are diagnostic of the *N*-oxidation of the pyridine ring.

The molecular structure of **10** was unambiguously determined by single crystal X-ray diffraction methods and a view of the molecule is shown in Figure 1 [23]. The pyridine *N*-oxide and amide groups have normal bond lengths and angles: N1-O1 $1.3091(9)\text{\AA}$, C8-O2 $1.2286(15)\text{\AA}$, C8-N2 $1.3547(13)\text{\AA}$, C9-N2-C10 $116.61(13)^\circ$, C8-N2-C9 $119.27(14)^\circ$, C8-N2-C10 $123.96(13)^\circ$, C7-C8-N2 $116.36(11)^\circ$, O2-C8-N2 $121.89(11)^\circ$, O2-C8-C7 $121.75(9)^\circ$. Interestingly and somewhat surprisingly, the N1-O1 and C8-O2 bond

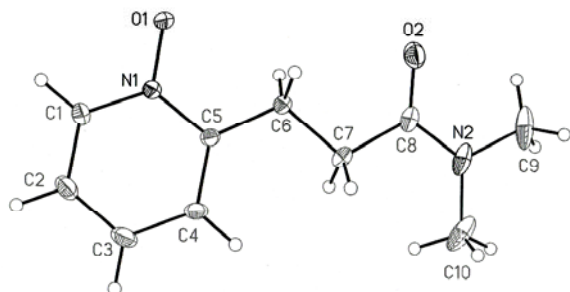


Figure 1. Crystal structure of **10** with atom labeling scheme (50% thermal ellipsoids).

vectors reside on the same side of the molecule: the atoms C1O1N1C5C6C7C8O2N2 nearly lie in a single plane (mean deviation, 0.065 Å) and planes defined by N1O1C5C6 and C6C7C8O2 are twisted by 5.6° relative to each other. This conformation is likely stabilized by crystal packing forces. Conformational analysis of the free ligand [24] reveals several low energy forms in the gas phase. The five most stable conformers are shown in Figure 2. The global minimum energy structure and the next three higher energy structures have the N-O and C=O bond vectors rotated away from each other as would be

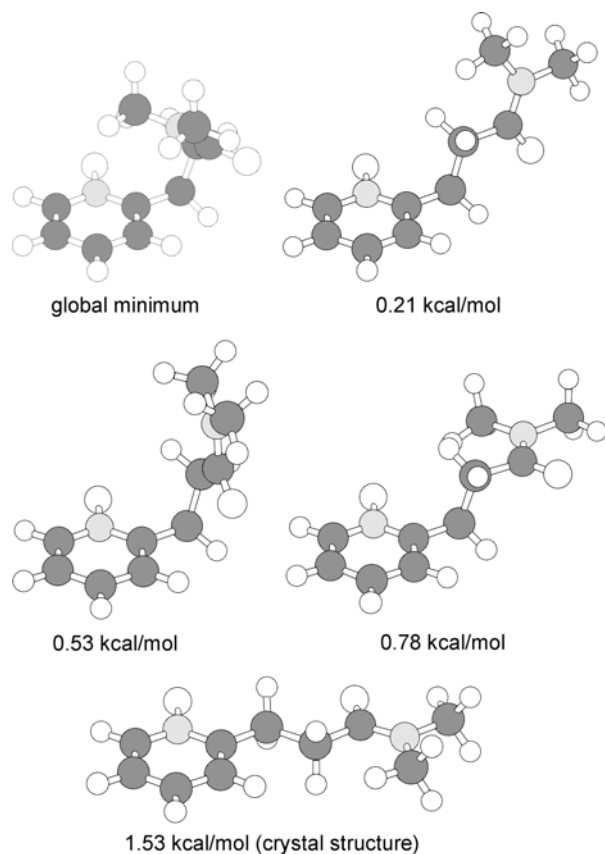


Figure 2. The five lowest energy gas-phase conformers for **10**.

expected for a molecule with such large bond dipoles. The fifth structure, 1.53 kcal/mole in energy above the computed lowest energy structure, corresponds to the structure found in the solid state. Given this result, it is not unreasonable to expect that **10** might further rearrange to a structure suitable for chelate formation.

Since we are interested in the extraction performance of ligand types represented by **10** and **12**, we have begun to explore the coordination chemistry of the ligands with lanthanide ions. Initially, we examined 1:1 and 2:1 combination of **10** with $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in $\text{MeOH}/\text{CH}_2\text{Cl}_2$ solutions. In both cases, following standard work-up, white powders were obtained. Infrared spectra recorded from KBr pellets showed evidence for ligand binding, e.g. $\Delta\nu_{\text{CO}} = 30\text{--}40\text{ cm}^{-1}$ and $\Delta\nu_{\text{NO}} = 15\text{--}30\text{ cm}^{-1}$; however, CHN analyses gave consistently low results suggesting that solvent of crystallization in the lattice was unaccounted for. All attempts to obtain suitable crystallographic quality crystals for X-ray analysis failed. At this point, a ligand deficient mixture, 1:2 (**10**:Tb), was employed from which an oily complex was obtained. Single crystals slowly deposited in the oil and they were recovered by washing with isopropyl alcohol. Subsequent single crystal X-ray diffraction analysis showed that a 1:1 complex formed and a view of the structure is shown in Figure 3 [25]. The Tb(III) is nine-coordinate with the inner sphere coordination polyhedron generated by six oxygen atoms from three bidentate nitrate anions, one oxygen atom from a coordinated water molecule and two oxygen atoms from one bidentate chelating ligand **10**. The key metrical parameters include Tb-O1 2.272(2) Å, Tb-O2 2.290(2) Å, N1-O1 1.326(4) Å, C8-O2 1.253(3) Å and these are consistent with the bidentate chelation. The resulting

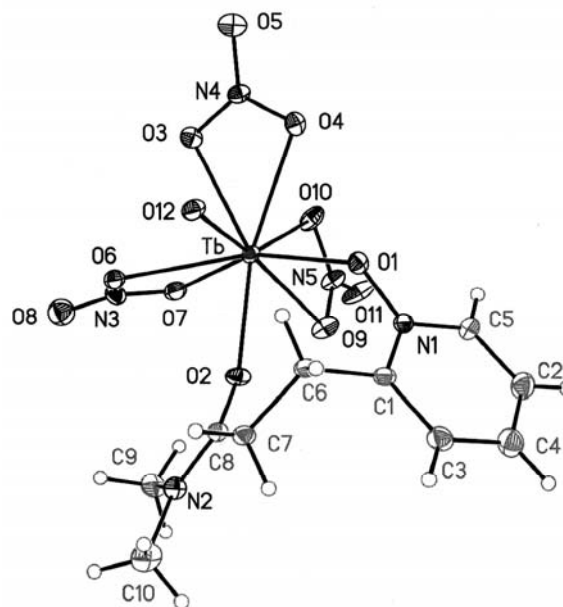


Figure 3. Crystal structure of $\text{Tb}(\mathbf{10})(\text{NO}_3)_3(\text{H}_2\text{O})$ with atom labeling scheme (50% thermal ellipsoids).

eight-membered chelate ring is somewhat unusual as such large rings are usually found supported by a smaller five- or six-member chelate ring formed by other donor groups present in a multifunctional ligand. It is worth noting that a molecular mechanics calculation for the ligand conformation adopted in the complex (metal removed) is 3.035 kcal/mole higher in energy than the energy of the global minimum energy structure and 1.50 kcal/mole higher in energy than the structure of the free ligand found in the solid state. The modest reorganization energy clearly favors the formation of the metal chelate structure.

The infrared spectroscopic data collected for the complex dispersed in a KBr pellet show small down-frequency coordination shifts relative to the free ligand, $\Delta\nu_{\text{CO}} = -28\text{cm}^{-1}$ and $\Delta\nu_{\text{NO}} = -29\text{cm}^{-1}$, consistent with the formation of the chelate structure. Analytical data (CHN) for the complex are low in carbon which historically has also been observed by us in lanthanide complexes of **7** and **8** and this may result from incomplete combustion/competing formation of lanthanide carbides.

Attempts were made to isolate 1:1 or 2:1 complex of **12** with lanthanide nitrates and characterization data for one 2:1 complex proposed as $\text{La}(\mathbf{12})_2(\text{NO}_3)_3(\text{H}_2\text{O})_2$ are provided. The IR data are consistent with the formation of a bis-tridentate chelate complex: coordination shifts $\Delta\nu_{\text{CO}} = -33\text{cm}^{-1}$ and $\Delta\nu_{\text{NO}} = -48\text{cm}^{-1}$. However, suitable single crystals of this complex have not yet been obtained and a crystal structure determination that would confirm this proposal remains to be completed.

EXPERIMENTAL

Chemicals were purchased from Aldrich and VWR. The starting material α -lithio *N,N*-dimethyl acetamide was prepared as described in the literature [22]. Melting points are uncorrected and elemental analysis data were obtained from Galbraith Laboratories. FAB-MS data were obtained from the Midwest Center for Mass Spectrometry, University of Nebraska. Infrared spectra were recorded on a Bruker Tensor 27 spectrometer and ^1H and ^{13}C NMR spectra were obtained on Bruker 250 and 500 MHz spectrometers. Chemical shifts are reported in ppm units with $+\delta$ values downfield of the reference Me_4Si .

2-(*N,N*-Dimethylpropionamide)pyridine (9). Under a dry nitrogen atmosphere, a sample of α -lithio *N,N*-dimethylacetamide (10 mmol) in dry THF (20 mL) was cooled to 0°C . A solution of freshly distilled 2-chloromethylpyridine (1.27 g, 10 mmol) in dry THF (20 mL) was injected *via* a septum capped side-arm and the resulting mixture stirred with a stir bar and warmed to 23°C (30 min.). The THF was vacuum evaporated and the residue was treated with CH_2Cl_2 (250 mL) and H_2O (50 mL). The organic phase was collected, dried over MgSO_4 and solvent vacuum evaporated leaving a yellow oil (1.4 g). The oil was dissolved in CH_2Cl_2 , combined with silica gel (70-230 mesh) and purified by column chromatography (CH_2Cl_2 :MeOH 100:1 \rightarrow 100:4 eluant). The product **9** is a light yellow oil (825 mg, 46%); soluble in CH_2Cl_2 and CHCl_3 ; insoluble in hexane.

IR(KBr): 1647cm^{-1} (ν_{CO}); ^1H NMR (CDCl_3 , 500 MHz): $\delta = 2.71$ (t, 2H, C_8H_2 $J = 7.3$ Hz), 2.82 (s, 3H, CH_3), 2.87 (s, 3H, CH_3), 3.02 (t, 2H, C_7H_2 $J = 7.3$ Hz), 6.99 (ddd, 1H, C_5H $J = 7.5$, 4.8, 1.0 Hz), 7.13 (d, 1H, C_3H $J = 7.8$ Hz), 7.45 (dt, 1H, C_4H $J = 7.6$, 1.9 Hz), 8.39 (dd, 1H, C_6H $J = 4.0$, 1.5 Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): $\delta = 32.9$ (C_8), 33.6 (C_7), 35.7 (C_1), 37.4 (C_1), 121.5 (C_3), 123.7 (C_3), 136.6 (C_4), 149.4 (C_6), 161.3 (C_2), 172.4 (C_6); MS(FAB): $m/z = 179(\text{M} + \text{H})^+$; Anal. Calcd. for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}$ (178.23): C, 67.39; H, 7.92; N, 15.72. Found: C, 66.86; H, 8.07; N, 15.83.

2-(*N,N*-dimethylpropionamide)pyridine *N*-oxide (10). A suspension of **9** (500 mg, 2.8 mmol), NaHCO_3 (0.5 g, 6.0 mmol) and OXONE (1.25 g, 2.9 mmol) in water (4 mL) and MeOH (12 mL) was stirred under a nitrogen atmosphere at $45\text{--}50^\circ\text{C}$ (24 h). The resulting mixture was filtered and the filtrate was vacuum evaporated. The residue was treated with fresh MeOH (20 mL), filtered, and solvent evaporated leaving a colorless oil (550 mg). Column chromatography (silica gel, 70-230 mesh, CH_2Cl_2 :MeOH 100:4 \rightarrow 100:8 eluant) led to recovery of a colorless oil **10** (500 mg, 92%). Soluble in CH_2Cl_2 , CHCl_3 , and MeOH. IR(KBr): 1243cm^{-1} (ν_{NO}), 1644cm^{-1} (ν_{CO}); ^1H NMR (CDCl_3 , 500 MHz): $\delta = 2.83$ (t, 2H, C_8H_2 $J = 6.8$ Hz), 2.86 (s, 3H, CH_3), 2.91 (s, 3H, CH_3), 3.17 (t, 2H, C_7H_2 $J = 7.1$ Hz), 7.12 (m, 2H, C_3H , C_5H), 7.39 (d, 1H, C_4H $J = 7.2$ Hz), 8.16 (d, 1H, C_6H $J = 5.8$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): $\delta = 28.0$ (C_8), 29.9 (C_7), 36.0 (C_1), 37.8 (C_1), 124.5 (C_3), 126.3 (C_3), 128.3 (C_4), 140.1 (C_6), 152.0 (C_2), 172.4 (C_6). MS(FAB): $m/z = 195(\text{M} + \text{H})^+$; Anal. Calcd. for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2$ (194.23): C, 61.84; H, 7.26; N, 14.42. Found: C, 60.95; H, 7.43; N, 14.17.

2,6-Bis(*N,N*-dimethylpropionamide)pyridine (11). Under a dry nitrogen atmosphere, a sample of α -lithio *N,N*-dimethylacetamide (10 mmol) in dry THF (20 mL) was cooled to 0°C . A solution of 2,6-bis(chloromethyl)pyridine (0.88 g, 5 mmol) in THF (20 mL) was injected all at once. After stirring at 23°C (30 min), the solvent was vacuum evaporated and CH_2Cl_2 (500 mL) and water (100 mL) were added. The phases were separated and the organic phase dried over MgSO_4 . The solvent was then vacuum evaporated leaving a yellow oil (1.4 g) that was purified by column chromatography (silica gel 70-230 mesh, CH_2Cl_2 :MeOH 8:1) from which a white powder (**11**) was recovered (650 mg, 46%); mp $87\text{--}88^\circ\text{C}$; soluble in CH_2Cl_2 , CHCl_3 , and MeOH. IR(KBr): 1643cm^{-1} (ν_{CO}); ^1H NMR (CDCl_3 , 500 MHz): $\delta = 2.73$ (t, 4H, C_6H_2 , $J = 7.5$ Hz), 2.90 (s, C_1H_3 , 6H), 2.95 (s, 6H, C_1H_3), 3.05 (t, 4H, C_5H , $J = 7.5$ Hz), 6.98 (d, 2H, C_3H_2 , $J = 7.6$ Hz), 7.43 (t, 1H, C_4H , $J = 7.7$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): $\delta = 33.4$ (C_6), 34.1 (C_3), 36.1 (C_1), 37.8 (C_1), 121.2 (C_3), 137.2 (C_4), 160.9 (C_2), 173.1 (C_7); MS(FAB): $m/z = 278(\text{M} + \text{H})^+$; Anal. Calcd. for $\text{C}_{15}\text{H}_{23}\text{N}_3\text{O}_2$ (277.36): C, 64.96; H, 8.36; N, 15.15. Found: C, 65.02; H, 8.42; N, 15.08.

2,6-Bis(*N,N*-dimethylpropionamide)pyridine *N*-oxide (12). A suspension of **11** (500 mg, 1.8 mmol), NaHCO_3 (0.31 g, 3.75 mmol) and OXONE (800 mg, 1.29 mmol) in water (2.7 mL) and MeOH (8.5 mL) was stirred under nitrogen at $45\text{--}50^\circ\text{C}$ (24 h). The MeOH was then vacuum evaporated and additional water was added to dissolve the salts. The product was extracted with CH_2Cl_2 (3 x 50 mL) and dried (MgSO_4). Vacuum evaporation left a white solid (**12**) $\cdot\text{H}_2\text{O}$ that was recrystallized from CH_2Cl_2 /hexane (500 mg, 92%); mp $79\text{--}80^\circ\text{C}$; soluble in CH_2Cl_2 , CHCl_3 , and MeOH. IR(KBr): 1257cm^{-1} (ν_{NO}), 1645cm^{-1} (ν_{CO}); ^1H NMR (CDCl_3 , 500 MHz): $\delta = 1.88$ (bs, H_2O), 2.80 (t, 4H, C_6H_2 , $J = 6.9$ Hz), 2.88 (s, 6H, C_1H_3), 2.96 (s, 6H, C_1H_3), 3.18 (t,

4H, C_5H_2 , $J = 6.7$ Hz), 7.06 (t, 1H, $C_4HJ = 7.0$ Hz), 7.25 (d, 2H, (C_3H) , $J = 7.6$ Hz); $^{13}C\{^1H\}$ NMR (CDCl₃, 125 MHz): $\delta = 28.39$ (C_6), 30.25 (C_5), 36.07 (C_1), 37.82 (C_1), 125.63 (C_3), 125.83 (C_4), 151.78 (C_2), 172.57 (C_7); MS(FAB): $m/z = 294$ ($M + H$)⁺; Anal. Calcd. for $C_{30}H_{18}N_6O_7$ (604.74): C, 59.58; H, 8.00; N, 13.89. Found: C, 59.32; H, 8.08; N, 13.77.

Formation of Complexes: Tb(10)(NO₃)₃(H₂O). A sample of Tb(NO₃)₃•5H₂O (2.24 g, 5.1 mmol) was dissolved in MeOH (5 mL) and combined with **10** (0.5 g, 2.6 mmol) in CH₂Cl₂. The mixture was stirred at 23 °C (1 h) and solvent evaporated. The residue was treated with a 1:1 mixture of MeOH/acetone and the solution allowed to slowly evaporate. X-ray quality crystals were obtained. IR(KBr, cm⁻¹): 1228 (ν_{NO}), 1616 (ν_{CO}). Anal. Calcd. for $C_{10}H_{16}N_5O_{12}Tb$ (557.20): C, 21.56; H, 2.89; N, 12.57. Found: C, 18.97; H, 2.94; N, 12.57.

La(12)₂(NO₃)₃(H₂O)₂. A sample of La(NO₃)₃•6H₂O (40 mg, 0.09 mmol) was dissolved in MeOH (3 mL) and combined with **5** (60 mg, 0.2 mmol) in CH₂Cl₂ (3 mL). The solution was stirred at 23 °C (30 min) and the solvent evaporated. IR(KBr): 1209.0 cm⁻¹ (ν_{NO}), 1611.2 cm⁻¹ (ν_{CO}); MS(FAB): $m/z = 849$ ($M - NO_3$)⁺; Anal. Calcd. For $C_{30}H_{50}N_5O_{17}La$ (947.63): C, 38.02; H, 5.32; N, 13.30. Found: C, 34.27; H, 4.67; N, 13.07.

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- [23] Crystal structure analysis for **10**: $C_{10}H_{14}N_2O_2$, $M_r = 194.23$ g mol⁻¹, monoclinic, space group $P2(1)/c$, $a = 9.5942(2)\text{Å}$, $b = 6.96430(10)\text{Å}$, $c = 15.2146(3)\text{Å}$, $\alpha = 90^\circ$; $\beta = 97.2160(10)^\circ$; $\gamma = 90^\circ$; $V = 1008.54(3)\text{Å}^3$, $Z = 4$, $\rho = 1.279$ g cm⁻³, $\mu = 0.090$ mm⁻¹, $F(000) = 416$, crystal size = $0.40 \times 0.38 \times 0.10$ mm³. Crystal data collected on a Bruker X8 Apex2 CCD-based diffractometer with Oxford Cryostream 700 low temperature device ($T = 223(2)\text{K}$), MoK $_{\alpha}$ radiation ($\lambda = 0.71073\text{Å}$). A full sphere of data was collected, 2282 frames, scan width of 0.5° in omega and phi at 15s/frame. A total of 20,918 reflections (2θ max = 67.80°) gave 4072 independent reflections with 3170 ($I > 2\sigma(I)$). Data were processed with SADABS [26] and corrected for absorption (semi-empirical). The structure was refined with the Bruker SHELXTL (Version 6.12) [26] software package. All non-hydrogen atoms were refined anisotropically and all H-atoms were included in idealized positions with fixed isotropic U's set to xU (equiv) of the parent atom ($x = 1.3$ for aromatic H, $x = 1.4$ for CH₂ and $x = 1.5$ for CH₃). Crystallographic data deposited at Cambridge Crystallographic Data Centre as supplementary material.
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