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4 **Synthesis and selected lanthanide coordination chemistry of new ((1H-pyrazol-1-yl)methyl)pyridine**
5 **and -pyridine 1-oxide ligands**
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7 Sabrina Ouizem^{a,1}, Daniel Rosario-Amorin^{a,2}, Diane A. Dickie^a, Benjamin P. Hay^b and Robert T. Paine^{a,*}
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10 ^aDepartment of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, NM 87131,
11 USA
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13 ^bSupramolecular Design Institute, 127 Chestnut Hill Road, Oak Ridge, TN 37830, USA
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17 **ABSTRACT**
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20 Syntheses for new potentially chelating ligands, 2,6-bis((1H-pyrazol-1-yl)methyl)pyridine 1-oxide (**2**),
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22 ((6-((1H-pyrazol-1-yl)methyl)pyridin-2-yl)methyl)diphenylphosphine oxide (**4**) and 2-((1H-pyrazol-1-
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24 yl)methyl)-6-((diphenylphosphoryl)methyl)pyridine 1-oxide (**5**), that are based upon pyridine or pyridine
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26 N-oxide platforms functionalized with pyrazol-1-ylmethyl and diphenylphosphinoylmethyl substituents,
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28 are reported along with results from molecular modeling analyses that assess the strain energy
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30 encountered by the ligands in tridentate chelate interactions for gas phase [Eu(L)³⁺]complexes.
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32 Coordination chemistry with selected lanthanide nitrates is described along with X-ray crystal structure
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34 determinations for the three ligands and three representative coordination complexes.
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39 *Keywords:* pyrazole, pyridine, pyridine N-oxide, phosphine oxide ligands, lanthanides, coordination
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41 chemistry, X-ray crystallography
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44 *Corresponding author. Tel +1 505 277 1661
45

46 E-mail address: rtpaine@unm.edu (R.T. Paine)
47

48 ¹ Current address: **DIVERCHIM**, ZAC du Moulin, 6 rue du Noyer, 95700 Roissy-en-France, FRANCE
49

50 ² Current address: Centre de Recherche Paul Pascal, 115, avenue du Dr. A. Schweitzer, 33600 Pessac,
51 FRANCE
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1. Introduction

In recent years a wide variety of molecules that contain two or more interconnected heterocyclic ring systems have been prepared, and the coordination chemistry for selected examples has been surveyed. A significant number of the molecules that display useful ligation properties are based upon a pyridine ring as the central platform to which one or more secondary ring(s) are attached most often in the 2- or 2,6-positions. For example, the tris-heterocyclic ligand, 2,2':6',2''-terpyridine (terpy), and its numerous derivatives represent one of the most widely investigated classes of chelating ligands used in coordination chemistry [1-5]. Another widely studied class of tris-heterocyclic ligands is the 2,6-di(pyrazolyl)pyridines. Here, there are two sub-classes that differ by the mode of pyrazolyl ring attachment to the pyridine platform, namely N-attached 2,6-di(pyrazol-1-yl)pyridines (1-bpp, **A**) and C-attached 2,6-di(pyrazol-3-yl)pyridines (3-bpp, **B**), and the extensive derivative and coordination chemistry of these ligands has been reviewed [6-9]. Due to the direct ring-ring attachment modes, the three rings in these ligands are relatively rigidly organized, and the N-atom donor centers are ideally positioned to form strong, tridentate chelate interactions with metal cations. As a consequence, many of the complexes display extensive ligand:metal electronic communication resulting in interesting magnetic and emissive properties. Insertion of a methylene spacer between each of the pyrazole rings and the pyridine platform in 1-bpp- and 3-bpp-type frameworks would provide additional families of potentially tridentate chelating ligands namely, 2,6-bis(pyrazol-1-ylmethyl)pyridine (1-bpCp, **C**) and 2,6-bis(pyrazol-3-ylmethyl)pyridine (3-bpCp, **D**). Indeed, examples of the 1-bpCp-type ligand are known [6-9]. The ligand framework in these molecules is less pre-organized for metal binding, and inter-ring/metal electronic communication is reduced. Nonetheless, the coordination chemistry of the 1-bpCp ligands with transition metals is rich, and some control over ligand binding mode as well as complex geometry and nuclearity has been achieved [6,7]. As far as we are aware, examples of the 3-bpCp-type ligands have not been reported although the fragment appears in more complex organic compounds [10]. This no doubt results from the lack of suitable synthetic approaches for assembly of 3-bpCp fragments.

In recent contributions we have described several new multidentate phosphine oxide ligands based upon pyridine and pyridine N-oxide platforms including ligands of types **E-I**, as shown in Figure 1, and their coordination chemistry with *f*-element ions has proven to be interesting [11-24]. In particular, the N-oxide ligands, **E** and **G** (designated as NOPO) and **I** (designated as NOPOPO) appear to bind more effectively with lanthanide [Ln(III)] cations than their pyridine analogs **F** and **H**, and the more flexible ligands of types **G** and **I** coordinate more strongly than ligands of type **E** despite the larger chelate ring size utilized by the former. Ligands of type **G**, generally form bidentate O_PO_N chelates while examples of **I** produce tridentate O_PO_NO_P chelates, and both ligand classes display unique solvent extraction performance [25-28]. Lanthanide complexes with examples of the pyridine ligands of types **F** and **H** have been isolated, but so far no examples that display Ln-N binding have been structurally confirmed by X-

[Insert Figure 1 near here]

ray diffraction methods. Given these results, we have been pursuing additional donor group and architectural modifications on ligands of types **E-I** and defining their impacts on Ln(III) coordination chemistry. In this report, we describe three new ligands, **2**, **4** and **5**, that marry the pyridine and pyridine N-oxide platforms to pyrazole rings via the 1-bpCp attachment mode. It is anticipated that the presence of the 1-methylpyrazole fragment will soften the chelating environment relative to that produced by NOPO and NOPOPO-type ligands. This, in turn, may provide improved selectivity for binding actinide(III) ions over lanthanide(III) ions.

2. Experimental

2.1. Materials and general procedures

Organic reagents (Aldrich Chemical Co.) and metal salts (Ventron) were used as received, and organic solvents (VWR) were dried by using standard methods. Unless noted otherwise, reactions were performed under a dry nitrogen atmosphere by using Schlenk methods. Infrared spectra were recorded from KBr pellets on a Bruker Tensor 27 FTIR spectrometer. The FT-NMR spectra were obtained with Avance 300 and 500 spectrometers by using Me₄Si (¹H and ¹³C) and 85% H₃PO₄ as external chemical shift standards.

Downfield shifts were assigned + δ values. The atom numbering systems used in the shift assignments for the new compounds are provided in the Supplementary Data. Mass spectra were obtained from the UNM Mass Spectrometry Center, and elemental analyses were performed by Galbraith Laboratories.

2.2 Experimental procedures

2.2.1. Ligand syntheses

2.2.1.1. *2,6-bis((1H-pyrazol-1-yl)methyl)pyridine 1-oxide (2)*. A mixture of 2,6-bis((1H-pyrazol-1-yl)methyl)pyridine, **1**, (1.00 g, 4.18 mmol) [29] and *m*CPBA (77 %, 1.40 g, 6.27 mmol) in CH₂Cl₂ (50 mL) was stirred (16 h, 23 °C), and the resulting mixture was quenched with an aqueous solution of NaOH (2 M, 100 mL). After separation of the phases, the organic layer was washed with aqueous NaOH solution (2 M, 2 × 50 mL), and the combined organic layers were washed with brine (100 mL), dried over MgSO₄, filtered, and the solution evaporated to dryness leaving a white solid, **2**. Yield: 867 mg, 81 %. Mp 128-130 °C. Single crystals (colorless rods) for X-ray diffraction analysis were obtained by slow evaporation of a CH₂Cl₂ solution. ¹H NMR (300 MHz, CDCl₃): δ = 5.47 (s, 4H, *H*₄), 6.21 (t, *J*_{HH} = 2.1 Hz, 2H, *H*₆), 6.53 (d, *J*_{HH} = 7.8 Hz, 2H, *H*₂), 6.96 (t, *J*_{HH} = 7.8 Hz, 1H, *H*₃), 7.46-7.47 (m, 2H, *H*₅ or *H*₇), 7.50-7.51 (m, 2H, *H*₅ or *H*₇). ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ = 50.4 (*C*₄), 106.2 (*C*₆), 123.0 (*C*₂), 125.2 (*C*₃), 130.8 (*C*₅ or *C*₇), 140.3 (*C*₅ or *C*₇), 147.4 (*C*₁). IR (KBr, cm⁻¹): ν = 3114, 2952, 2931, 1572, 1516 ($\nu_{\text{C=N}}$), 1495 ($\nu_{\text{C=C}}$), 1448, 1430, 1394, 1354, 1288, 1242 (ν_{NO}), 1225, 1158, 1087, 1048, 972, 950, 916, 881, 848, 776, 745, 657, 618, 570, 538. HRMS (ESI): *m/z* (rel. inten., %): 256.1198 (41) [*M* + *H*⁺]. C₁₃H₁₄N₅O requires 256.1193; 278.1018 (100) [*M* + Na⁺]. C₁₃H₁₃N₅NaO requires 278.1012. *Anal.* Calc. for C₁₃H₁₃N₅O: C, 61.17; H, 5.13; N, 27.43. Found: C, 61.16; H, 5.25; N, 26.83%.

2.2.1.2. *((6-((1H-pyrazol-1-yl)methyl)pyridin-2-yl)methyl)diphenylphosphine oxide (4)*. A mixture containing 2-(diphenylphosphinoylmethyl)-6-(chloromethyl)pyridine, **3** (1.40 g, 4.10 mmol), pyrazole (335 mg, 4.92 mmol), aqueous sodium hydroxide (40%, 21 mL) and a catalytic amount of tetrabutylammonium bromide in toluene (25 mL) was stirred under a nitrogen atmosphere at reflux (5 h) and then at 23 °C (16 h). The organic layer was separated, washed with water (4 × 100 mL), dried on

MgSO₄, filtered and evaporated to dryness leaving an oil. Trituration of the oil with Et₂O afforded a tan-colored solid, **4**. Yield: 840 mg, 55 %. Mp 116-118 °C. Single crystals (pale yellow blocks) for X-ray diffraction analysis were obtained by slow evaporation of a CH₂Cl₂/Et₂O (80/20) solution. ³¹P{¹H} NMR (121.49 MHz, CDCl₃): δ = 30.2. ¹H NMR (300 MHz, CDCl₃): δ = 3.89 (d, *J*_{HP} = 14.1 Hz, 2H, *H*₂), 5.22 (s, 2H, *H*₇), 6.23 (pseudo t, *J*_{HH} = 2.1 Hz, 1H, *H*₉), 6.74 (d, *J*_{HH} = 6.8 Hz, 1H, *H*₅), 7.25 (d, 1H, *H*₈ or *H*₁₀), 7.29 (d, 1H, *H*₃), 7.37-7.51 (m, 8H, *H*₈ or *H*₁₀ and *H*_{4,13,14}), 7.69-7.72 (m, 4H, *H*₁₂). ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ = 40.7 (d, *J*_{CP} = 64.2 Hz, *C*₁), 57.2 (*C*₇), 106.1 (*C*₉), 119.9 (*C*₁₀), 124.0 (d, *J*_{CP} = 3.2 Hz, *C*₃), 128.5 (d, *J*_{CP} = 11.9 Hz, *C*₁₃), 129.8 (*C*₈), 131.2 (d, *J*_{CP} = 9.5 Hz, *C*₁₂), 131.9 (d, *J*_{CP} = 2.0 Hz, *C*₁₄), 132.2 (d, *J*_{CP} = 108.2 Hz, *C*₁₁), 137.5 (*C*₅), 139.7 (*C*₄), 152.3 (d, *J*_{CP} = 7.3 Hz, *C*₂), 156.1 (*C*₆). IR (KBr, cm⁻¹): ν = 1591 (ν_{C=N}), 1570 (ν_{C=C}), 1512, 1485, 1451, 1435, 1421, 1395, 1362, 1341, 1286, 1262, 1188 (ν_{PO}), 1123, 1098, 1085, 1046, 1026, 992, 968, 918, 838, 776, 752, 741, 719, 709, 696, 657, 639, 618, 590, 537, 526, 479. HRMS (ESI): *m/z* (rel. inten. %): 374.1414 (15) [M + H⁺]. C₂₂H₂₁N₃OP requires 374.1417; 396.1229 (100) [M + Na⁺]. C₂₂H₂₀N₃NaOP requires 396.1236; 769.2621 (54) [2M + Na⁺]. C₄₄H₄₀N₆NaO₂P₂ requires 769.2580. *Anal.* Calc. for C₂₂H₂₀N₃OP: C, 70.77; H, 5.40; N, 11.25. Found: C, 70.25; H, 5.22; N, 10.52%.

2.2.1.3. 2-((1*H*-pyrazol-1-yl)methyl)-6-((diphenylphosphoryl)methyl)pyridine 1-oxide (5). A mixture of **4** (552 mg, 1.48 mmol) and *m*CPBA (77 %, 498 mg, 2.22 mmol) in CH₂Cl₂ (20 mL) was stirred (18 h, 23 °C), and the resulting mixture was quenched with an aqueous solution of NaOH (2 M, 100 mL). After separation of the phases, the organic layer was washed with aqueous NaOH solution (2 M, 3 × 50 mL), and the combined organic layers were washed with brine (100 mL), dried over MgSO₄, filtered and evaporated to dryness. Purification by flash chromatography on silica gel (CH₂Cl₂/MeOH 100:0 to 98:2) afforded a white solid, **5**. Yield: 451 mg, 78 %. Mp 180-182 °C. Single crystals (colorless blocks) for X-ray diffraction analysis were obtained by slow evaporation of a CH₂Cl₂ solution. ³¹P{¹H} NMR (121.49 MHz, CDCl₃): δ = 30.8. ¹H NMR (300 MHz, CDCl₃): δ = 4.22 (d, *J*_{HP} = 13.8 Hz, 2H, *H*₁), 5.40 (s, 2H, *H*₇), 6.29 (t, *J*_{HH} = 2.0 Hz, 1H, *H*₉), 6.47 (d, *J*_{HH} = 7.8 Hz, 1H, *H*₅), 7.02 (t, *J*_{HH} = 8.0 Hz, 1H, *H*₄), 7.36-

7.48 (m, 8H, $H_{3,10,13,14}$), 7.54 (d, $J_{\text{HH}} = 1.8$ Hz, 1H, H_8), 7.67-7.82 (m, 4H, H_{12}). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): $\delta = 31.2$ (d, $J_{\text{CP}} = 65.9$ Hz, C_1), 51.2 (C_7), 106.5 (C_9), 122.7 (C_5), 125.1 (C_4), 126.4 (d, $J_{\text{CP}} = 3.9$ Hz, C_3), 128.6 (d, $J_{\text{CP}} = 12.1$ Hz, C_{13}), 130.9 (d, $J_{\text{CP}} = 9.7$ Hz, C_{12}), 130.9 (C_{10}), 131.9 (d, $J_{\text{CP}} = 101.7$ Hz, C_{11}), 132.2 (d, $J_{\text{CP}} = 2.3$ Hz, C_{14}), 140.5 (C_8), 143.9 (d, $J_{\text{CP}} = 5.3$ Hz, C_2), 147.6 (C_6). IR (KBr, cm^{-1}): $\nu = 3054, 2940, 2902, 1590$ ($\nu_{\text{C=N}}$), 1568 ($\nu_{\text{C=C}}$), 1513, 1489, 1437, 1423, 1410, 1398, 1351, 1332, 1288, 1264, 1242 (ν_{NO}), 1191 (ν_{PO}), 1118, 1089, 1064, 982, 961, 940, 918, 851, 835, 821, 768, 756, 742, 720, 706, 693, 620, 591, 552, 514, 468. HRMS (ESI): m/z (rel. inten., %): 390.1358 (6) [$\text{M} + \text{H}^+$]. $\text{C}_{22}\text{H}_{21}\text{N}_3\text{O}_2\text{P}$ requires 390.1366; 412.1175 (100) [$\text{M} + \text{Na}^+$]. $\text{C}_{22}\text{H}_{20}\text{N}_3\text{NaO}_2\text{P}$ requires 412.1185; 801.2512 (84) [$2\text{M} + \text{Na}^+$]. $\text{C}_{44}\text{H}_{40}\text{N}_6\text{NaO}_4\text{P}_2$ requires 801.2478. *Anal. Calc.* for $\text{C}_{22}\text{H}_{20}\text{N}_3\text{O}_2\text{P}$: C, 67.86; H, 5.18; N, 10.79. Found: C, 66.71; H, 4.92; N, 10.13%.

2.2.2. Synthesis of coordination complexes.

Coordination complexes were prepared on a 0.5 mmole scale by combination of a sample of ligand (**2**, **4** or **5**, 1 eq.), dissolved in a minimum of MeOH, with $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ($\text{Ln} = \text{Pr}, \text{Eu}, \text{Dy}, \text{Yb}$; 1 eq.), dissolved in a minimum of MeOH. The mixtures were stirred (23 °C, 2 h), and the solvent was evaporated leaving white powders. The IR spectra recorded for all of the crude 1:1 complexes are displayed in Supplementary Data, and elemental analyses (CHN) and selected IR absorptions for three representative complexes are listed here. $[\text{Eu}(\textbf{2})(\text{NO}_3)_3](\text{MeOH})(\text{H}_2\text{O})$, IR (KBr, cm^{-1}): 1504 ($\nu_{\text{C=N}}$), 1487 ($\nu_{\text{C=C}}$), 1230 (ν_{NO}). *Anal. Calc.* for $\text{C}_{14}\text{H}_{17}\text{EuN}_8\text{O}_{11}$: C, 26.14; H, 2.98; N, 17.42. Found: C, 26.15; H, 2.60; N 17.53%. $[\text{Dy}(\textbf{4})(\text{NO}_3)_3](\text{H}_2\text{O})$, IR (KBr, cm^{-1}): 1600 ($\nu_{\text{C=N}}$), 1578 ($\nu_{\text{C=C}}$), 1162 (ν_{PO}). *Anal. Calc.* for $\text{C}_{22}\text{H}_{22}\text{DyN}_6\text{O}_{11}\text{P}$: C, 35.71; H, 3.00; N, 11.36%. Found: C, 35.95; H, 3.00; N, 10.89%. $[\text{Eu}(\textbf{5})(\text{NO}_3)_3](\text{H}_2\text{O})$, IR (KBr, cm^{-1}): 1589 ($\nu_{\text{C=N}}$), 1580 ($\nu_{\text{C=C}}$), 1232 (ν_{NO}), 1095 (ν_{PO}). *Anal. Calc.* for $\text{C}_{22}\text{H}_{22}\text{EuN}_6\text{O}_{12}\text{P}$: C, 35.45; H, 2.97; N, 11.27. Found: C, 35.66; H, 2.85; N, 10.90%. Single crystals for X-ray diffraction analyses were obtained as follows. A sample of $[\text{Eu}(\textbf{2})(\text{NO}_3)_3](\text{MeOH})(\text{H}_2\text{O})$ was dissolved in CH_2Cl_2 , and the solution was allowed to slowly evaporate (0 °C) leaving colorless platelets found to have the composition $[\text{Eu}(\textbf{2})_2(\text{NO}_3)_3]$ based upon the structure solution. A sample of

[Dy(**4**)(NO₃)₃](H₂O) was crystallized by slow evaporation of a CH₂Cl₂/MeOH (50:50) solution of the complex resulting in the deposition of colorless blocks found to have the composition [Dy(**4**)(NO₃)₃(MeOH)₂] in the single crystals. Crystallization of a sample of [Pr(**5**)(NO₃)₃](H₂O) from a solution containing CH₂Cl₂, MeOH and EtOAc gave colorless blocks with a composition [Pr(**5**)₂(NO₃)₃].

2.2.3. Single crystal X-ray diffraction analyses

Single crystals of **2**, **4**·H₂O, (**5**)₂·H₂O·CH₂Cl₂, [Eu(**2**)₂(NO₃)₃], [Dy(**4**)(NO₃)₃(MeOH)₂], [Yb(**4**)(NO₃)₃(MeOH)₂] and [Pr(**5**)₂(NO₃)₃] were obtained as described above, and specimens were coated with Paratone oil and mounted on a MiTeGen support attached to a metallic pin using epoxy. The X-ray diffraction data were collected with a Bruker APEX II CCD system equipped with a graphite monochromator, MoK α sealed X-ray tube (λ = 0.71073 Å) and Oxford Cryostream 700 low temperature device. Full spheres of diffraction data were collected, integrated [30] and processed with the Bruker APEX2 software suite [31] including corrections for absorption (SADABS) [32]. The structures were solved by direct methods and refined with full-matrix least-squares on F² using SHELXTL [33]. Selected crystal data are provided in Tables 1 and 2. The non-hydrogen atom positions in the free ligands **2**, **4**·H₂O and (**5**)₂·H₂O·CH₂Cl₂ and in the complexes [Eu(**2**)₂(NO₃)₃], [Dy(**4**)(NO₃)₃(MeOH)₂], [Yb(**4**)(NO₃)₃(MeOH)₂] and [Pr(**5**)₂(NO₃)₃] were refined anisotropically. The H-atoms were placed in geometrically calculated positions and refined with $U_{iso} = 1.2 U_{eq}$ of the parent atom except for OH hydrogen atoms. These were located in diffraction maps and refined with $U_{iso} = 1.5 U_{eq}$ of the parent O-atom. The chlorine atom Cl2 for the CH₂Cl₂ lattice solvent in (**5**)₂·H₂O·CH₂Cl₂ was disordered over two positions. The relative occupancies (60/40) were freely refined without restraints on the thermal displacement parameters. For [Pr(**5**)₂(NO₃)₃], SQUEEZE [34,35] was used to account for a mixture of lattice water and methanol molecules that could not be adequately modeled otherwise. It found void spaces of 437 Å³ containing 113 electrons. The structure solution for [Yb(**4**)(NO₃)₃(MeOH)₂] shows it to be isomorphous with the structure for the Dy complex. The X-ray data for the Yb complex are deposited along with data for the other complexes at the CCDC.

2.2.4. Molecular Mechanics Calculations

Geometry optimizations of free and lanthanide-bound structures of **2** and **3** were accomplished with a MM3 force field [36-39] by using a points-on-a-sphere metal ion [39] as implemented in PCModel software [40]. Conformational searches to locate the most stable form for each structure were performed with the GMMX algorithm provided in this software.

3. Results and discussion

3.1 Ligand synthesis and characterization

The precursor for **2**, 2,6-bis((1H-pyrazol-1-yl)methyl)pyridine, **1**, was prepared in one step from a combination of 2,6-bis(chloromethyl)pyridine and pyrazole by using basic phase-transfer catalysis conditions as summarized in Scheme 1. The synthesis was described previously by Watson and coworkers [29] although in our hands the isolated yield of **1** is 68% compared to the reported yield, 90%. Oxidation of **1** with *m*CPBA in CH₂Cl₂ provides 2,6-bis((1H-pyrazol-1-yl)methyl)pyridine 1-oxide, **2**, as a white solid in good yield, 81%. The identity of **2** is supported by CHN analysis, the observation of an intense parent ion [M + H⁺] in the HRMS, and the appearance of a strong absorption, $\nu = 1242\text{ cm}^{-1}$, in the IR spectrum that is attributed to the N-O stretching vibration. The ¹H and ¹³C NMR spectra are assigned and consistent with the proposed structure. It is noted that the proton chemical shift for the methylene group in **2** is identical to that reported for **1** [29] while the carbon-13 shift ($\delta = 50.4$) appears

[Insert Scheme 1 near here]

downfield of the shift in **1** ($\delta = 57.3$). The molecular structure of **2** is confirmed by a single crystal X-ray diffraction analysis. A view of the molecule is shown in Figure 2, and selected bond lengths are summarized in Table 3. The structure is similar to that of the pyridine precursor **1** [41] except that the pyrazole ring planes in **2** are folded up and away from the N-O bond vector while they are folded down relative to the N atom in **1**. The N1-O1 bond length, 1.3178(19) Å, is identical to the corresponding bond

length in 2,6-bis[(diphenylphosphino)methyl]pyridine N-oxide, **1** (R = Ph), 1.315(6) Å [12]. The two N-N bond lengths in **2** are identical, 1.359(2) Å, and slightly longer than the average value in **1**, 1.344 ± 0.001 Å [41]. The average of the N1-C1 and N1-C5 bond lengths in **2**, 1.365 ± 0.003 Å, is also elongated relative to the average length in **1**, 1.334 ± 0.002 Å. These modifications in the pyrazole ring are in response to the N-oxidation of the pyridine ring.

[Insert Figure 2 near here]

Compound **4** was obtained in good yield (55%) from combination of 2-(diphenylphosphino)methyl)-6-(chloromethyl)pyridine, **3**, with a small excess of pyrazole under phase-transfer catalysis conditions in a fashion similar to that used for the synthesis of **1** (Scheme 2). The compound was initially obtained as a tan solid that provides pale yellow, blocky crystals after crystallization from a CH₂Cl₂/Et₂O (80/20) solution. Analytical data (CHN) for **4** suggest that samples may contain residual water since

[Insert Scheme 2 near here]

better agreement between observed data and calculated values is obtained for a composition **4**·0.3H₂O. This proposal is consistent with results obtained from X-ray diffraction analysis, *vide infra*, that reveals that single crystals are obtained with a mono-hydrate, **4**·H₂O, composition. The compound displays a low intensity parent ion [M + H⁺], intense [M + Na⁺] and [2M + Na⁺] ions and a strong infrared absorption, $\nu = 1188\text{ cm}^{-1}$, that is assigned to the phosphoryl stretch. The ³¹P NMR spectrum for **4** shows a single resonance, $\delta = 30.8$, whose value is similar to the shifts displayed by examples of compounds from the classes **E-I** that carry diphenylphosphine oxide substituent groups [11-24]. The ¹H and ¹³C NMR spectra are also consistent with the expected structure. The ¹H NMR spectrum displays a singlet at $\delta = 5.40$ that is comparable to shifts displayed by **1** and **2**, $\delta = 5.46$ and 5.47 , respectively, and these are assigned to the methylene group separating the pyridine and pyrazole rings. The ¹H NMR spectrum also contains a doublet, $\delta = 4.22$ ($J_{\text{HP}} = 13.8\text{ Hz}$), that is assigned to the methylene group spanning the pyridine ring and the diphenylphosphine oxide substituent, and these data compare favorably with data for examples of

compounds of types **E-I** [11-24]. The ^{13}C NMR spectrum contains resonances diagnostic of the two inequivalent methylene group environments: $\delta = 31.2$ ($J_{\text{CP}} = 65.9$ Hz) and 51.2. Lastly, the composition of the **4** is confirmed by single crystal X-ray diffraction analysis, and the structure solution indicates that the single crystals are obtained as a monohydrate, **4**·H₂O. A view of the molecular structure is shown in Figure 3, and selected bond lengths are listed in Table 3. The metrical parameters compare favorably with related data for **2** and for examples of free ligands from types **E-I** [12,21,23,24]. The water molecule is hydrogen bonded to the phosphine oxide O-atom, O2-H2B...O1 with O2-H2B, 0.87(3) Å, H2B...O1, 1.90(3) Å, O2...O1, 2.766(2) Å, O2-H2B...O1, 176°, and a pyrazole N-atom, O2-H2A...N3, 0.87(3) Å, H2A...N3, 2.07(3) Å, O2...N3, 2.941(2) Å, O2-H2A...N3, 174°.

[Insert Figure 3 near here]

Compound **5** was prepared by combination of **4** in CH₂Cl₂ with a small excess of *m*CBPA at room temperature. Following chromatographic purification, **5** was isolated as a white solid in 78% yield. Analytical data (CHN) for samples of **5** are in relatively good agreement with the expected theoretical composition although the observed percent carbon content is high. Improved agreement is obtained for a fractionally solvated composition **5**·0.1CH₂Cl₂·0.1 H₂O, and a mixed solvate formulation is supported by the composition determined for the single crystals used in the X-ray diffraction analysis, *vide infra*. The HRMS for **5** contains a low intensity parent ion [$\text{M} + \text{H}^+$] and very intense [$\text{M} + \text{Na}^+$] and [$2\text{M} + \text{Na}^+$] ions. The IR spectrum displays strong absorptions centered at $\nu = 1242$ and 1191 cm^{-1} that are assigned to ν_{NO} and ν_{PO} , respectively. The ^{31}P NMR spectrum shows a single resonance at $\delta = 30.8$, slightly downfield from the resonance position for **4**. This downfield shift is typical for other N-oxide derivatives **G** and **I** compared to their pyridine precursors, **F** and **H** [11,12,18,23,24]. The ^1H and ^{13}C NMR spectra are closely comparable with the data for **4**, and they are consistent with the proposed structure. The X-ray crystal structure determination clearly confirms that the compound, as isolated here, is obtained as a mixed-solvate with the composition (**5**)₂·CH₂Cl₂·H₂O wherein there are two independent molecules of **5**

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4 in the molecular unit as shown in Figure 4. Selected bond lengths for molecule #1 are provided in Table
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6 3, and these compare closely with the corresponding bond lengths in **2** and **4**·H₂O. The lattice water
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8 molecule is hydrogen bonded with the phosphoryl O-atom of molecule #2, O5-H5B...O4, with O5-H5B,
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10 0.96(2) Å, H5B...O4, 1.82(2) Å, O5...O4, 2.750(4) Å, O5-H5B...O4, 162°. The water molecule is also H-
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12 hydrogen bonded with the disordered methylene chloride molecule.
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16 [Insert Figure 4 near here]
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19 *3.2 Molecular mechanics calculations*

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22 The previously reported functionalized pyridine compound, **1**, and several of its closely related
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24 derivatives, have been demonstrated to behave as tridentate chelating ligands toward a number of
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26 transition metal ions [6,7,29], and CPK model building suggests that **2**, **4** and **5** should also be able to
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28 adopt tridentate chelate binding modes on lanthanide cations. In order to confirm this expectation and to
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30 more fully assess the impact of ligand steric energetics upon coordination, the reorganization energy of
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32 the ligands **2**, **4** and **5**, from their energy minimized free-ligand structures to their energy minimized
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34 tridentate, N_{pyrz}N_{pyrz}O_N, N_{pyrz}N_{pyrd}O_P, and N_{pyrz}O_NO_P coordination complex structures in idealized species
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36 [Eu(**2**)³⁺], [Eu(**4**)³⁺] and [Eu(**5**)³⁺] were evaluated in the gas phase. A well tested force field-based
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38 structure scoring approach [42] was employed that identifies ligand:metal structures with low
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40 conformational energies, low degrees of induced strain and few restricted bond rotations. The resulting
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42 calculated relative strain free energies (G) per donor group were then compared with data for similar
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44 ligand types. The method has been used in the evaluation of a number of other ligand systems [43]
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46 including studies of several related NOPO and NOPOPO ligands [22-24,44-48]. The energy minimized
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48 free ligand conformers for **2**, **4** and **5** are shown in Figures 5a, 6a and 7a, respectively. As expected, the
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50 donor groups in each molecule are rotated away from each other in order to minimize lone pair-lone pair
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52 donor group repulsion energies. As a result, none of the ligands is ideally pre-organized in their resting
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54 state for tridentate chelation on a metal cation. Nonetheless, the methylene spacer groups separating the
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pyridine and pyridine N-oxide rings from the secondary donor centers should be sufficiently flexible to support facile ligand reorganization. Indeed, as shown in Figures 5b, 6b and 7b, addition of a Eu(III) cation to each ligand results in formation of a tridentate chelate structure with minimal induced strain in the ligand molecule. In the case of the complex [Eu(**2**)³⁺], the tridentate interaction produces an estimated strain free energy, (G) = 2.37 kcal/mol or 0.79 kcal/mol/donor group. Replacement of one methylpyrazole substituent with a more bulky methyldiphenylphosphine oxide group and removal of the pyridine N-oxide O-atom generates **4**. Subsequent formation of the complex [Eu(**4**)³⁺] with a tridentate coordination mode occurs with (G) = 4.78 kcal/mole or 1.59 kcal/mol/donor group. Although the ligand reorganization energy is significantly higher for **4** compared to **2**, it is still lower than the value computed for the NOPOPO ligand, **I** (R = Ph), 8.8 kcal/mol or 2.93 kcal/mol/donor group [45], and it is well known that ligands of type **I** readily form strong lanthanide complexes utilizing the tridentate binding mode [22-24, 45-49]. Interestingly, addition of the N-oxide group back into the ligand framework and subsequent formation of the tridentate chelate structure [Eu(**5**)³⁺], as shown in Figure 7b, leads to a decrease in strain free energy, (G) = 3.78 kcal/mol or 1.26 kcal/mol/donor. In summary, computational modeling suggests that none of the ligands should experience serious framework strain when tridentate binding modes are adopted, and complex stability should be determined largely by relative coordinate bond enthalpies.

[Insert Figures 5, 6 and 7 near here]

3.3 Lanthanide coordination chemistry

As mentioned in the Introduction, the lanthanide coordination chemistry of numerous derivatives of 1-bpp (**A**) and 3-bpp (**B**) ligands has been extensively developed [6-9]. Based upon single crystal X-ray structure analyses, it is generally found that these bis-(pyrazole)pyridine ligands bind in a tridentate N_{pyrz}N_{pyrz}N_{pyrd} manner on Ln(III) ions. The coordination chemistry of 1-bpCp-type (**C**) ligands has been examined primarily with transition metal cations, and here too the ligands bind as tridentate N_{pyrz}N_{pyrz}N_{pyrd} chelates most often with a *meridional* configuration [6,38,40]. As far as we are aware, the coordination

chemistry of the parent of this class of ligands, **1**, with Ln(III) ions has only been sparsely studied, and confirmation of the binding mode on a Ln(III) ion, by X-ray crystallography, has not been accomplished. Of course, the lanthanide coordination chemistry for the new ligands **2**, **4** and **5**, until now, has not been examined.

Coordination complexes of **2**, **4** and **5** were prepared on a 0.5 mmole scale from equimolar combinations of each ligand, dissolved in MeOH, with hydrated lanthanide nitrates, $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ($\text{Ln} = \text{Pr, Eu, Dy, Yb}$), in MeOH. The mixtures were stirred, and the volatiles were removed by vacuum evaporation. The resulting powders were characterized by CHN analyses and IR spectroscopy. Representative CHN analyses data (Experimental section) are generally consistent with isolation of solvated, 1:1 ligand:Ln(III) compositions: $[\text{Eu}(\mathbf{2})(\text{NO}_3)_3](\text{MeOH})(\text{H}_2\text{O})$, $[\text{Dy}(\mathbf{4})(\text{NO}_3)_3](\text{H}_2\text{O})$ and $[\text{Eu}(\mathbf{5})(\text{NO}_3)_3](\text{H}_2\text{O})$. It is noted here that, as depicted, the inner- vs. outer-sphere residence of the solvent molecules, prior to crystal structure determinations, is not unambiguously known, and therefore the solvent is listed outside of the square bracket in the formulae. It is also pointed out that slightly improved agreements between calculated and found CHN data for the two Eu(III) complexes is obtained with fractional solvent compositions: $[\text{Eu}(\mathbf{2})(\text{NO}_3)_3](\text{MeOH})_{0.7}(\text{H}_2\text{O})_{0.9}$ and $[\text{Eu}(\mathbf{5})(\text{NO}_3)_3](\text{MeOH})_{0.25}(\text{H}_2\text{O})_{1.05}$. The IR spectrum for $[\text{Eu}(\mathbf{2})(\text{NO}_3)_3](\text{MeOH})(\text{H}_2\text{O})$ shows modest shifts in absorptions tentatively assigned to ν_{CC} , ν_{CN} and ν_{NO} , relative to the free ligand: $\Delta\nu_{\text{CC}} = 8\text{-}12\text{ cm}^{-1}$, $\Delta\nu_{\text{CN}} = 12\text{-}17\text{ cm}^{-1}$ and $\Delta\nu_{\text{NO}} = 12\text{-}20\text{ cm}^{-1}$, and these shifts are consistent with tridentate $\text{N}_{\text{pyrz}}\text{N}_{\text{pyrz}}\text{O}_{\text{pyrd}}$ ligand binding by **2**. Similarly, the IR spectra for $[\text{Dy}(\mathbf{4})(\text{NO}_3)_3](\text{H}_2\text{O})$ and $[\text{Eu}(\mathbf{5})(\text{NO}_3)_3](\text{H}_2\text{O})$ also display modest coordination shifts: $\Delta\nu_{\text{CC}} = 6\text{-}8\text{ cm}^{-1}$, $\Delta\nu_{\text{CN}} = 5\text{-}9\text{ cm}^{-1}$ and $\Delta\nu_{\text{PO}} = 23\text{-}31\text{ cm}^{-1}$ and $\Delta\nu_{\text{CC}} = 2\text{-}4\text{ cm}^{-1}$, $\Delta\nu_{\text{CN}} = 2\text{-}4\text{ cm}^{-1}$, $\Delta\nu_{\text{PO}} = 23\text{-}25\text{ cm}^{-1}$ and $\Delta\nu_{\text{NO}} = 8\text{-}10\text{ cm}^{-1}$, respectively. These data are clearly consistent with O_P and $\text{O}_\text{P}\text{O}_\text{N}$ ligand binding, but the small shifts in ν_{CC} and ν_{CN} make conclusions regarding the involvement of the pyrazole rings in metal binding uncertain.

3.4 Single crystal X-ray diffraction analyses for lanthanide complexes

In order to unambiguously determine the ligand and solvent binding modes in complexes of **2**, **4** and **5**, single crystal X-ray diffraction analyses were undertaken following crystallization of representative complexes. Interestingly, crystallization of [Eu(**2**)(NO₃)₃](MeOH)(H₂O) from CH₂Cl₂ leads to formation of single crystals with a 2:1 ligand: metal composition [Eu(**2**)₂(NO₃)₃] as indicated by the crystal structure determination. A view of the molecular structure of the complex is shown in Figure 8, and selected bond lengths are provided in Table 4. The Eu(III) ion is ten coordinate with coordination positions occupied by *two* bidentate ligands **2** bonded in a N_{pyrz}O_N mode and six O-atoms provided by three asymmetrically bonded bidentate nitrate ions. The second pyrazole ring in each ligand **2** is non-bonded. Interestingly, comparison of the two Eu-O_N bond lengths (2.3102(14) and 2.3764(13) Å) and the two Eu-N_{pyrz} bond lengths (2.5839(16) and 2.6574(18) Å) indicate that the two bidentate ligand molecules are not coordinated with equal strength to the central Eu(III) as the bond lengths Eu1-O1 and Eu1-N3 (ligand #1)

[Insert Figure 8 near here]

are significantly shorter than Eu1-O2 and Eu1-N8 (ligand #2). Surprisingly, this difference is not reflected in comparison of the N-O and N-N bond lengths which are identical in both bonded ligand fragments. The N-O bond lengths in the coordinated ligands are significantly longer than the N-O bond length in the free ligand, but the N-N bond lengths are unchanged compared to the free ligand. The N-N bond lengths in the bound and unbound pyrazole fragments are also the same within 3-sigma of the estimated standard deviations. For comparison, it is interesting to note that in the structure of the complex Eu(hfac)₃(1-bpp) {hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate and 1-bpp = 2,6-bis[4-(3,4-ethylenedioxythien-2-yl)pyrazol-1-yl]pyridine} the Eu(III) is nine coordinate with six positions occupied by O-atoms from three bidentate hfac⁻ anions and the remaining three positions filled by the two pyrazole N-atoms and the pyridine N-atom of the more sterically constrained 1-bpp-type ligand [49]. Herein, the Eu-N_{pyrz} bond lengths, Eu1-N1 2.559(4) Å and Eu1-N5 2.563(4) Å, are identical, indicating that the two pyrazole donors in this ligand bind with essentially equal strength. A similar structural feature is reported in the ten coordinate complex Eu(NO₃)₃(3-bpp)(DMF) {3-bpp = 2,6-bis-[5-(2,2-dimethylpropyl)-1*H*-pyrazol-3-

yl)pyridine} in which the two pyrazole rings in the tridentate 3-bpp ligand are equally coordinated to the Eu(III) as evidenced by the bond lengths Eu-N2 2.545(4) Å and Eu-N4 2.541(5) Å [50]. The formation and structure of [Eu(**2**)₂(NO₃)₃] is quite interesting since the originally formed 1:1 complex, [Eu(**2**)(NO₃)₃](MeOH)(H₂O), presumably containing **2** bound in a tridentate mode, appears to readily transform to a 2:1 complex with both ligands bonding in a bidentate manner upon recrystallization. Whether this is driven by overall complexation thermodynamics, steric energetics or a combination of both is not clear.

Crystallization of a sample of [Dy(**4**)(NO₃)₃](H₂O) from CH₂Cl₂/MeOH solution provides single crystals, and the X-ray structure determination indicates that the resulting complex has a composition [Dy(**4**)(NO₃)₃(MeOH)₂]. A view of the molecular structure is presented in Figure 9, and selected bond lengths are provided in Table 4. In this complex, under the synthesis conditions employed, the ligand **4** is bonded in a monodentate mode through the phosphoryl O-atom. The Dy(III) ion is nine coordinate with the remaining coordination sites occupied by six O-atoms from three bidentate nitrate ions and the O-atoms from two inner-sphere methanol molecules. The P-O bond length, 1.5072(18) Å, as expected, is slightly elongated relative to the bond length in the free ligand, 1.4926(14) Å. The appearance of two molecules of methanol in the inner sphere is not completely unexpected as it often replaces bound or lattice water during crystallization of lanthanide nitrate complexes when MeOH is the dominate solvent. However, it is unexpected that MeOH molecules appear to out-compete against both the pyridine and pyrazole fragments of the ligand **4** for two inner sphere coordination positions on the Dy(III) center. It is noted that one inner sphere methanol molecule hydrogen bonds with the unbound pyridine, O12-H12A...N1, in the same molecular unit with O12-H12A, 0.76(3) Å, H12A...N1, 1.91(3) Å, O12...N1, 2.664(3) Å, O12-H12A...N1, 176°, and the second MeOH hydrogen bonds with the unbound pyrazole N-atom, O11-H11A...N3, in a second molecular unit O11-H11A, 0.82(2) Å, H11A...N3, 1.89(2) Å, O11...N3, 2.696(3) Å, O11-H11A...N3, 168°.

[Insert Figure 9 near here]

Attempts to crystallize [Eu(**5**)(NO₃)₃](H₂O) from a variety of solvent combinations did not provide suitable single crystals for X-ray diffraction analysis; however, crystals of the corresponding Pr(III) complex were obtained. A view of the molecular structure is shown in Figure 10, and selected bond lengths are listed in Table 4. As found with **2**, the initially isolated 1:1 complex transforms upon crystallization to a 2:1 complex with the composition, [Pr(**5**)₂(NO₃)₃] in which the Pr(III) is ten coordinate, and both ligands adopt a bidentate O_NO_P binding mode as observed in complexes containing type-G NOPO ligands. The remaining six positions in the Pr(III) ion inner coordination sphere are occupied by six O-atoms from three bidentate nitrate ions.

[Insert Figure 10 near here]

3.5 Conclusions

Neutral, monofunctional pyrazoles and pyridines are normally classified as “intermediate” in hard-soft donor character while neutral, monofunctional pyridine N-oxides and phosphine oxides as well as nitrate anion are considered to be relatively “hard” donors. All are known to coordinate with hard Ln(III) ions; however, formation constant data for comparable Ln(L)_n(NO₃)₃ complexes, recorded under closely similar conditions, that would provide a quantitative ordering of base strengths, unfortunately are sparse to nonexistent. Nonetheless, based upon a variety of synthetic and spectroscopic observations it is possible to reasonably speculate that the qualitative strength of monodentate ligand:Ln(III) interactions increases in the order from pyridine < 1-methylpyrazole << pyridine N-oxide < phosphine oxide. The placement of pyridine N-oxides and phosphine oxides at the stronger base strength end of the series is based on the general oxophilicity of Ln(III) ion acceptors and the hard character of the O-atom donor centers in these ligands. The ready formation and stability of numerous Ln(III) complexes with monofunctional pyridine N-oxide and phosphine oxide ligands and with hybrid NOPO (**G**) and NOPOPO (**I**) ligands confirms this position [11-24]. The placement of pyridine and 1-methylpyrazole at the weaker

end of the series derives from the relatively softer character of N atom donors. In addition, limited formation constant and solvent extraction data for these ligands with Ln(III) ions supports their classification as weak donors. Indication that neutral 1-alkyl pyrazoles are slightly stronger nucleophiles (bases) than pyridine is derived from a very interesting and useful empirical scale, developed by Huynh and coworkers [51,52]. This scale is based on ^{13}C NMR chemical shifts of the carbene carbon atom in donor-acceptor complexes formed by the *trans*-dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) reference acceptor fragment. Of course, the Pd(II) site in these complexes is a much softer acceptor than a Ln(III) ion, so base-strength reversal may result with the lanthanide ions. Indeed, base strength reversal of a similar nature has been observed years ago by Alton [53], Parry [54] and Shore [55] in their studies of the comparative Lewis donor-acceptor chemistry of BH_3 and BX_3 (X = halide) toward hard and soft donors.

Given these features, it has been of interest to explore how hybrid ligands, that contain two or more of these monofunctional ligand fragments, might coordinate with Ln(III) ions. Since it was already known that hybrid ligands of types 1-bpp (**A**), 3-bpp (**B**), and 1bpCp (**C**) form tridentate chelate complexes with a range of transition metal ions and **A**, **B** and NOPOPO (**I**) ligands produce tridentate chelate structures with lanthanide ions, it was anticipated that **2**, **4** and **5** might also adopt tridentate interactions with Ln(III) ions. Indeed, molecular modeling studies reported here for **2**, **4** and **5** indicate that, based upon steric strain energy analyses, all three ligands should readily accommodate maximal tridentate interactions on a Ln(III) ion without serious framework reorganization energy. Furthermore, it is observed experimentally that 1:1 ligand:Ln(III) combinations of **2**, **4** and **5** in MeOH solutions produce complexes with apparent compositions $[\text{Eu}(\mathbf{2})(\text{NO}_3)_3](\text{MeOH})(\text{H}_2\text{O})$, $[\text{Dy}(\mathbf{4})(\text{NO}_3)_3](\text{H}_2\text{O})$ and $[\text{Eu}(\mathbf{5})(\text{NO}_3)_3](\text{H}_2\text{O})$ based upon CHN analyses. IR spectroscopic analyses indicate pyridine N-oxide fragment binding by **2** and **5** and phosphine oxide coordination by **4** and **5**. However, potential pyrazole and pyridine N-donor interactions with the Ln(III) ions are not unambiguously confirmed. Hence, ligand denticity could not been assigned in these putative complexes. In an effort to overcome this shortcoming, samples of the coordination

complexes were crystallized in appropriate organic solvents and single crystal X-ray diffraction analyses completed. In each complex, the composition changed from that in the bulk sample. In the case of [Eu(**2**)(NO₃)₃](MeOH)(H₂O), the crystal contains a 2:1 complex, [Eu(**2**)₂(NO₃)₃], in which the Eu(III) is ten coordinate and both molecules of **2** act as *bidentate* N_{pyrz}O_N chelates. The fact that one pyrazole fragment in each ligand remains unbound and that they do not displace one or more inner-sphere nitrate ions is consistent with low nucleophilicity for the pyrazole relative to a phosphine oxide fragment and a nitrate anion. This conclusion is reached based upon the performance of NOPOPO ligands which bind as tridentate chelates, displacing one to three nitrate anions from the Ln(III) inner coordination sphere [11,13,18,21,22]. In [Dy(**4**)(NO₃)₃](H₂O), the ligand:metal combining ratio remains 1:1, but water, whose inner- vs. outer-sphere location is not known, is replaced with two inner-sphere MeOH molecules resulting in a crystal composition [Dy(**4**)(NO₃)₃(MeOH)₂]. In this complex, the ligand **4** is found to be *monodentate*, bound to Dy(III) by only the phosphine oxide O-atom. Single crystals of [Eu(**5**)(NO₃)₃](H₂O) were not obtained, but the structure of its Pr(III) analog was determined, and the composition in the crystal found to be [Pr(**5**)₂(NO₃)₃]. The structure determination reveals that both ligands, **5**, coordinate with a *bidentate* O_NO_P mode by using only the phosphine oxide and pyridine N-oxide donor centers.

The fact that, under the synthetic conditions explored, **2**, **4** and **5** do not adopt tridentate binding modes on Ln(NO₃)₃ species in the solid state indicates that the relative donor strengths of the pyrazole fragments in **2** and **5** and the pyridine and pyrazole fragments in **4** are comparatively low. They are, except in the case of one pyrazole fragment of each ligand **2** in [Eu(**2**)₂(NO₃)₃], unable to replace either inner sphere solvent molecules or nitrate anions. This does not necessarily preclude that the new ligands could not behave as useful solvent extraction reagents. In particular, it was anticipated that the placement of a methyl pyrazole fragment on the NOPO ligand framework (**G**) might provide a softer coordination environment in the resulting ligand **5** than that in NOPOPO (**I**) thereby leading to improved Am/Eu separation factors by **5** compared to **I**. However, preliminary screenings of the solvent extraction

performance of the ligands in 1,2-dichloroethane, for Eu(III) and Am(III) in aqueous nitric acid solutions, indicate that the ligands are only very weakly extracting and the Am/Eu separation performance is poor. This may reflect the low propensity to form maximal chelate interactions and/or poor phase transport of complexes formed in the aqueous phase to the organic phase. Although the separations performance is disappointing, the outcomes suggest alternative synthetic targets that may lead to strong extraction accompanied by good Am/Eu partitioning and that work is in progress.

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Appendix A. Supplementary material

CCDC-1045435-1045441 contain the supplementary crystallographic data for **2**, **4**·H₂O, (**5**)₂·CH₂Cl₂·H₂O, [Eu(**2**)₂(NO₃)₃], [Dy(**4**)(NO₃)₃(MeOH)₂], [Yb(**4**)(NO₃)₃(MeOH)₂] and [[Pr(**5**)₂(NO₃)₃]. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or email: deposit@ccdc.cam.ac.uk. Supplementary spectroscopic data associated with this article can be found in the online version at <http://xxxxxxx>

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Table 1. Crystallographic Data for **2**, **4**·H₂O and **(5)**₂·CH₂Cl₂·H₂O

	2	4 ·H ₂ O	(5) ₂ ·CH ₂ Cl ₂ ·H ₂ O
Empirical formula	C ₁₃ H ₁₃ N ₅ O	C ₂₂ H ₂₂ N ₃ O ₂ P	C ₄₅ H ₄₄ Cl ₂ N ₆ O ₅ P ₂
Crystal size (mm)	0.110 x 0.184 x 0.226	0.240 x 0.454x 0.513	0.216 x 0.361 x 0.416
Formula weight	255.28	391.40	881.70
Crystal system	orthorhombic	orthorhombic	triclinic
Space group	Pbcn	P2 ₁ 2 ₁ 2 ₁	P-1
Unit cell dimensions			
<i>a</i> (Å)	22.023(6)	7.0062(3)	9.0778(14)
<i>b</i> (Å)	7.6072(18)	16.1432(6)	14.795(2)
<i>c</i> (Å)	14.917(3)	16.9188(6)	16.264(2)
<i>α</i> (°)	90	90	86.115(8)
<i>β</i> (°)	90	90	79.152(8)
<i>γ</i> (°)	90	90	86.793(8)
<i>V</i> (Å ³)	2499.1(10)	1913.56(13)	2138.3(5)
<i>Z</i>	8	4	2
<i>T</i> , (K)	100(2)	100(2)	100(2)
<i>D</i> _{cald} (g cm ⁻³)	1.357	1.359	1.369
<i>μ</i> (mm ⁻¹)	0.092	0.167	0.281
Min/Max transmission	0.9790/0.9900	0.9190/0.9610	0.8920/0.9420
Reflection collected	8362	17227	29740
Independent reflections [<i>R</i> _{int}]	2559 [0.0673]	5488 [0.0282]	10592 [0.0364]
Final <i>R</i> indices [<i>I</i> > 2σ (<i>I</i>)] <i>R</i> 1 ^a (<i>wR</i> 2) ^b	0.0457(0.0798)	0.0384(0.0856)	0.0552(0.1526)

Final R indices (all data) R1(wR2)	0.1009(0.0966)	0.0470(0.0894)	0.0790(0.1704)
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$$\text{a) } R1 = (\sum ||F_o| - |F_c||) / \sum |F_o|, \text{ b) } wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

Table 2. Crystallographic Data for [Eu(2)(NO₃)₃], [Dy(4)(NO₃)₃(MeOH)₂] and [Pr(5)(NO₃)₃]

	[Eu(2)(NO ₃) ₃]	[Dy(4)(NO ₃) ₃ (MeOH) ₂]	[Pr(5)(NO ₃) ₃]
Empirical formula	C ₂₆ H ₂₆ EuN ₁₃ O ₁₁	C ₂₄ H ₂₈ DyN ₆ O ₁₂ P	C ₄₄ H ₄₀ N ₉ O ₁₃ P ₂ Pr
Crystal size (mm)	0.128 x 0.228 x 0.601	0.235 x 0.240 x 0.256	0.172 x 0.198 x 0.237
Formula weight	848.56	785.99	1105.70
Crystal system	orthorhombic	monoclinic	triclinic
Space group	Pbca	P2 ₁ /c	P-1
Unit cell dimensions			
<i>a</i> (Å)	19.4046(4)	8.1160(9)	12.8024(9)
<i>b</i> (Å)	13.5243(3)	19.223(2)	13.4365(8)
<i>c</i> (Å)	23.9122(6)	19.635(2)	15.5126(10)
<i>α</i> (°)	90	90	80.264(3)
<i>β</i> (°)	90	96.880(2)	87.883(4)
<i>γ</i> (°)	90	90	86.515(4)
<i>V</i> (Å ³)	6275.4(2)	3041.3(6)	2624.2(3)
<i>Z</i>	8	4	2
<i>T</i> , (K)	100(2)	100(2)	100(2)
<i>D</i> _{calcd} (g cm ⁻³)	1.796	1.717	1.399
<i>μ</i> (mm ⁻¹)	2.081	2.579	1.056
Min/Max transmission	0.3680/0.7770	0.5580/0.5820	0.7880/0.8390

Reflection collected	71159	29252	27466
Independent reflections [R _{int}]	9459 [0.0454]	6969 [0.0381]	10633 [0.0417]
Final R indices [I > 2σ (I)] R ₁ ^a (wR ₂) ^b	0.0243(0.0484)	0.0245(0.0489)	0.0338(0.0831)
Final R indices (all data) R ₁ (wR ₂)	0.0379(0.0537)	0.0332(0.0518)	0.0444(0.0883)

a) $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$, b) $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

Table 3. Selected Bond Lengths (Å) for **2**, **4**·H₂O and **5**·CH₂Cl₂·H₂O

Bond Type	2		4 ·H ₂ O		5 ·CH ₂ Cl ₂ ·H ₂ O ^a	
P-O			P1-O1	1.4926(14)	P1-O2	1.4929(16)
P-C(H ₂)			P1-C10	1.8147(19)	P1-C10	1.819(2)
N-O	N1-O1				N1-O1	1.314(2)
	1.3178(19)					
N-N	N2-N3	1.359(2)	N2-N3	1.354(2)	N2-N3	1.353(2)
	N4-N5	1.359(2)				
N _{pyr} -C	N1-C1	1.363(2)	N1-C1	1.340(3)	N1-C1	1.376(2)
	N1-C5	1.368(2)	N1-C5	1.347(3)	N1-C5	1.369(3)
N _{pyrz} -C	N2-C7	1.351(2)	N2-C7	1.347(3)	N2-C7	1.355(3)
	N4C11	1.340(3)				
	N3-C9	1.334(2)	N3-C9	1.337(3)	N3-C9	1.337(3)
	N5-C13	1.333(3)				
N _{pyrz} -C(H ₂)	N2-C6	1.449(2)	N2-C6	1.467(3)	N2-C6	1.450(3)
	N4-C10	1.440(3)				
C-C(H ₂)N	C5-C6	1.499(3)	C5-C6	1.505(3)	C5-C6	1.502(3)
	C1-C10	1.504(3)				
C-C(H ₂)P			C1-C10	1.511(3)	C1-C10	1.503(3)

^a Molecule 1

Table 4. Selected Bond Lengths (Å) for [Eu(**2**)₂(NO₃)₃], [Dy(**4**)(NO₃)₃(MeOH)₂] and [Pr(**5**)₂(NO₃)₃]

Bond Type	[Eu(2) ₂ (NO ₃) ₃]		[Dy(4)(NO ₃) ₃ (MeOH) ₂]		[Pr(5) ₂ (NO ₃) ₃]	
M-O _P			Dy1-O1	2.2577(17)	Pr1-O2	2.393(2)
					Pr1-O4	2.434(2)
M-O _N	Eu1-O1	2.3102(14)			Pr1-O1	2.502(2)
	Eu1-O2	2.3764(13)			Pr1-O3	2.482(2)
M-N _{pyrz}	Eu1-N3	2.5839(16)				
	Eu1-N8	2.6574(18)				
M-O _{nitrate}	Eu1-O _{nitrate}		Dy1-O _{nitrate}		Pr1-O _{nitrate}	
avg	2.55 ± 0.07		2.46 ± 0.03		2.62 ± 0.04	
range	2.467(2)-2.698(2)		2.423(2)-2.493(2)		2.556(2)-2.668(2)	
M-O _{solvent}			Dy1-O11	2.3669(17)		
			Dy1-O12	2.3501(18)		
P-O			P1-O1	1.5072(18)	P1-O2	1.499(2)
					P2-O4	1.495(2)
P-C(H ₂)			P1-C10	1.823(2)	P1-C10	1.803(3)
					P2-C32	1.816(3)
N-O	N1-O1	1.332(2)			N1-O1	1.327(3)
	N6-O2	1.331(2)			N4-O3	1.317(3)
N-N	N2-N3	1.360(2)	N2-N3	1.357(3)	N2-N3	1.353(4)
	N4-N5	1.355(2)			N5-N6	1.348(4)

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N _{pyrd} -C	N7-N8	1.359(2)				
	N9-N10	1.351(3)				
	N1-C1	1.355(3)	N1-C1	1.357(3)	N1-C1	1.365(4)
	N1-C5	1.361(3)	N1-C5	1.344(3)	N1-C5	1.361(4)
	N6-C14	1.362(2)			N4-C23	1.370(4)
N _{pyrz} -C	N6-C18	1.364(3)			N4-C27	1.365(4)
	N2-C7	1.352(2)	N2-C7	1.351(3)	N2-C7	1.355(4)
	N3-C9	1.341(3)	N3-C9	1.331(4)	N3-C9	1.335(4)
	N4-C11	1.346(3)			N5-C29	1.337(5)
	N5-C13	1.336(3)			N6-C31	1.348(5)
	N7-C20	1.349(3)				
	N8-C22	1.344(2)				
	N9-C26	1.356(3)				
	N10-C24	1.334(3)				
N _{pyrz} -C(H ₂)	N2-C6	1.460(3)	N2-C6	1.445(3)	N2-C6	1.449(4)
	N4-C10	1.444(3)			N5-C28	1.450(4)
	N7-C19	1.464(3)				
	N9-C23	1.448(2)				
C-C(H ₂)N	C5-C6	1.501(3)	C5-C6	1.515(4)	C5-C6	1.503(4)
	C1-C10	1.504(3)			C27-C28	1.510(4)
	C18-C19	1.497(3)				
	C14-C23	1.505(3)				

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C-C(H ₂)P	C1-C10	1.503(4)	C1-C10	1.498(4)
			C23-C32	1.490(4)

Scheme 1. Synthesis of compounds **1** and **2**.

Scheme 2. Synthesis of ligands **4** and **5**.

Figure 1. Chelating pyridine and pyridine N-oxide ligand structure types **A-I** and ligands **2**, **4** and **5**.

Figure 2. Molecular structure and atom labeling scheme for **2** with H-atoms omitted. Thermal ellipsoids are shown at the 50% level.

Figure 3. Molecular structure and atom labeling scheme for **4·H₂O** with H-atoms omitted except for the hydrogen-bonded lattice water molecule. Thermal ellipsoids are shown at the 50% level.

Figure 4. Molecular structure and atom labeling scheme for $(\mathbf{5})_2 \cdot \text{CH}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ with H-atoms omitted except for H-atoms for the hydrogen-bonded lattice water molecule. Thermal ellipsoids are shown at the 50% level.

a)

b)

Figure 5. Computed geometry optimized lowest energy gas phase structure for a) free ligand **2** and b) 1:1 tridentate, N_{pyrz}N_{pyrz}O_N : Eu(III) chelate complex, [Eu(**2**)³⁺].

a)

b)

Figure 6. Computed geometry optimized lowest energy gas phase structure for the a) free ligand **4** and b) 1:1 tridentate, $N_{\text{pyrz}}N_{\text{pyrd}}O_P$: Eu(III) chelate complex, $[Eu(\mathbf{4})^{3+}]$.

a)

b)

Figure 7. Computed geometry optimized lowest energy gas phase structure for the a) free ligand **5** and b) 1:1 tridentate, $N_{\text{pyrz}}O_NOp$: Eu(III) chelate complex, $[\text{Eu}(\mathbf{5})^{3+}]$.

Figure 8. Molecular structure and atom labeling scheme for $[\text{Eu}(\mathbf{2})_2(\text{NO}_3)_3]$ with H-atoms omitted. Thermal ellipsoids are shown at the 50% level.

Figure 9. Molecular structure and atom labeling scheme for $[\text{Dy}(\mathbf{4})(\text{NO}_3)_3(\text{MeOH})_2]$ with H-atoms omitted except on the hydrogen bonded methanol molecules. Thermal ellipsoids are shown at the 50% level.

Figure 10. Molecular structure and atom labeling scheme for [Pr(**5**)₂(NO₃)₃] with H-atoms omitted. Thermal ellipsoids are shown at the 50% level.

Graphical Synopsis and Artwork

Hybrid donor ligands, based upon pyridine and pyridine N-oxide platforms decorated with 1-methylpyrazole and diphenylphosphine oxide substituents, have been prepared, and their coordination chemistry with selected lanthanide nitrates have been surveyed.

Scheme 1. Synthesis of compounds **1** and **2**.

Scheme 2. Synthesis of ligands **4** and **5**.

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a)

b)

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b)

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