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Unexpected Transformation of a Schiff Base Pyridine N-Oxide in the Presence of $Pr(NO_3)_3 \cdot 6H_2O$

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UNEXPECTED TRANSFORMATION OF A SCHIFF BASE PYRIDINE *N*-OXIDE IN THE PRESENCE OF $Pr(NO_3)_3 \cdot 6H_2O$

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GRAPHICAL ABSTRACT





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Keywords Pyridine N-oxide; schiff base; lanthanide, complex

INTRODUCTION

In recent decades, considerable effort has been devoted to the development of new chelating ligands for Ln(III) and An(III) ions that would provide more efficient extractants than the well-known carbamoylmethylphosphine oxide (**CMPO**) ligands, widely employed in liquid–liquid extraction (LLE) processes (Scheme 1).¹ In continuation of our research focused on ligands derived from pyridine *N*-oxide platforms, such as illustrated by the **NOPOPO** ligands,² we developed a particular interest in the impact of the introduction of an amine group, especially a Schiff base, on coordination of such multifunctional ligands with Ln(III) ions.



RESULTS AND DISCUSSION

Amine 1^3 reacts with vanillin in the presence of catalytic amounts of sulfuric acid and pyridinium *p*-toluenesulfonate in dichloromethane to give the corresponding imine **2** in moderate yield (Scheme 2). The composition and structure of the molecule are fully supported by HRMS, IR, and ³¹P, ¹H, ¹³C NMR spectroscopies.



The coordination chemistry of **2** was initially examined with $Pr(NO_3)_3 \cdot 6H_2O$ by using a ligand/metal ratio of 1:1 in a mixture of chloroform and methanol. Since Schiff base pyridine ligands are known to be relatively soft *N*-donor ligands⁴ and lanthanide ions prefer hard donor centers, it was anticipated that **2** would preferentially coordinate to the Pr(III) via the oxygen atoms of the pyridine *N*-oxide and the phosphine oxide functional groups. In addition, it was expected that the nitrogen of the imine or possibly the hydroxyl group on the aryl ring might provide additional hemilabile interactions. However, a preliminary



Figure 1 Preliminary crystal structure determination for $[Pr(3)(3^-)](NO_3)_2$. H-atoms and outer-sphere nitrate ions removed for clarity (Color figure available online).

X-ray crystallographic molecular structure determination for the complex isolated from the 1:1 combination of **2** with $Pr(NO_3)_3$ reveals a surprising result. First, the structure shows that ligand **2** has undergone significant chemistry, forming **3**, which is not observed to occur in the absence of the Pr(III) ion. Secondly, *two* molecules of the rearranged ligand **3** coordinate to the Pr(III) ion as illustrated in Scheme 3. One of the molecules can be considered to contain a neutral isoindoline ring at its central core, while the second has an anionic isoindoline ring.





The ligand containing the anionic isoindoline fragment is bonded in a NONOPO-PON pentadentate mode with bond lengths Pr1-N1:2.648(11), Pr1-O1:2.708(7), and Pr1-O2:2.282(7) Å. The neutral isoindoline-based ligand coordinates in a NONOPOPO tetradentate mode with Pr1-O3:2.351(7), Pr1-O4:2.732(7), and Pr1...N2:3.462(11) Å (Figure 1). It is noted that the crystal used for the preliminary structure determination suffers from some disorder. The Pr(III) is disordered over two sites between the isoindoline fragments, and the OMe and OH groups in both ligands are disordered over two sites on the aryl rings. In addition, the outer sphere NO₃⁻ ions and lattice solvent molecules are severely disordered. Therefore, additional discussion of the metrical parameters from this data set is not appropriate.

The interesting ligand rearrangement and coordination chemistry encourage further study of 2 and its derivatives. Comprehensive spectroscopic and structural studies are in progress that should elucidate the formation pathway for the rearranged ligand molecule, and additional coordination chemistry of 2 and 3 with other Ln(III) ions is in progress.

REFERENCES

- (a) Horwitz, E. P.; Schulz, W. W. ACS Symp. Ser. 1999, 716, 20-50; (b) Mathur, J. N.; Murali, M. S.; Nash, K. L. Solv. Extr. Ion Exch. 2001, 19, 357-390; (c) Nash, K. L. Separation chemistry for lanthanides and trivalent actinides. In: K. A. Gschneider; L. Eyring Jr.; G. R. Choppin; G. H. Lander, (Eds.), Handbook on the Physics and Chemistry of Rare Earths; Elsevier Science: Amsterdam, The Netherlands, 1994; Ch 18, pp. 197-238; (d) Nash, K. L.; Madic, C.; Mathur, J. N.; Lacquement, J. Actinide Separation Science and Technology. In: L. R. Morss; N. M. Edelstein; J. Fuger, (Eds.), The Chemistry of the Actinide and Transactinide Elements; Springer: Dordrecht, The Netherlands, 2006; Ch 4, pp. 2622-2798.
- (a) Rapko, B. M.; Duesler, E. N.; Smith, P. H.; Paine, R. T.; Ryan, R. R. *Inorg. Chem.* **1993**, 32, 2164-2174;
 (b) Engelhardt, U.; Rapko, B. M.; Duesler, E. N.; Frutos, D.; Paine, R. T.; Smith, P. H. *Polyhedron* **1995**, 14, 2361-2369;
 (c) Bond, E. M.; Duesler, E. N.; Paine, R. T.; Nöth, H. *Polyhedron* **2000**, 19, 2135-2140;
 (d) Gan, X.-M.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.*

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2001, 40, 4420-4427 (e) Gan, X.-M.; Paine, R. T.; Duesler, E. N.; Nöth, H. *Dalton Trans.* **2003**, 153-159.

- 3. Ouizem, S.; Pailloux, S.; Ray, A. D.; Duesler, E. N.; Paine, R. T. manuscript in preparation.
- (a) Dikusar, E. A.; Potkin, V. I.; Kozlov, N. G.; Ogorodnikova, M. M. Russ. J. Org. Chem. 2009, 45, 1496-1502 (b) Ajithkumar, G.; Radhakrishnan, P. K. J. Indian Chem. Soc. 2011, 88, 635-639.