Electronic Supplementary Information

Experimental Details

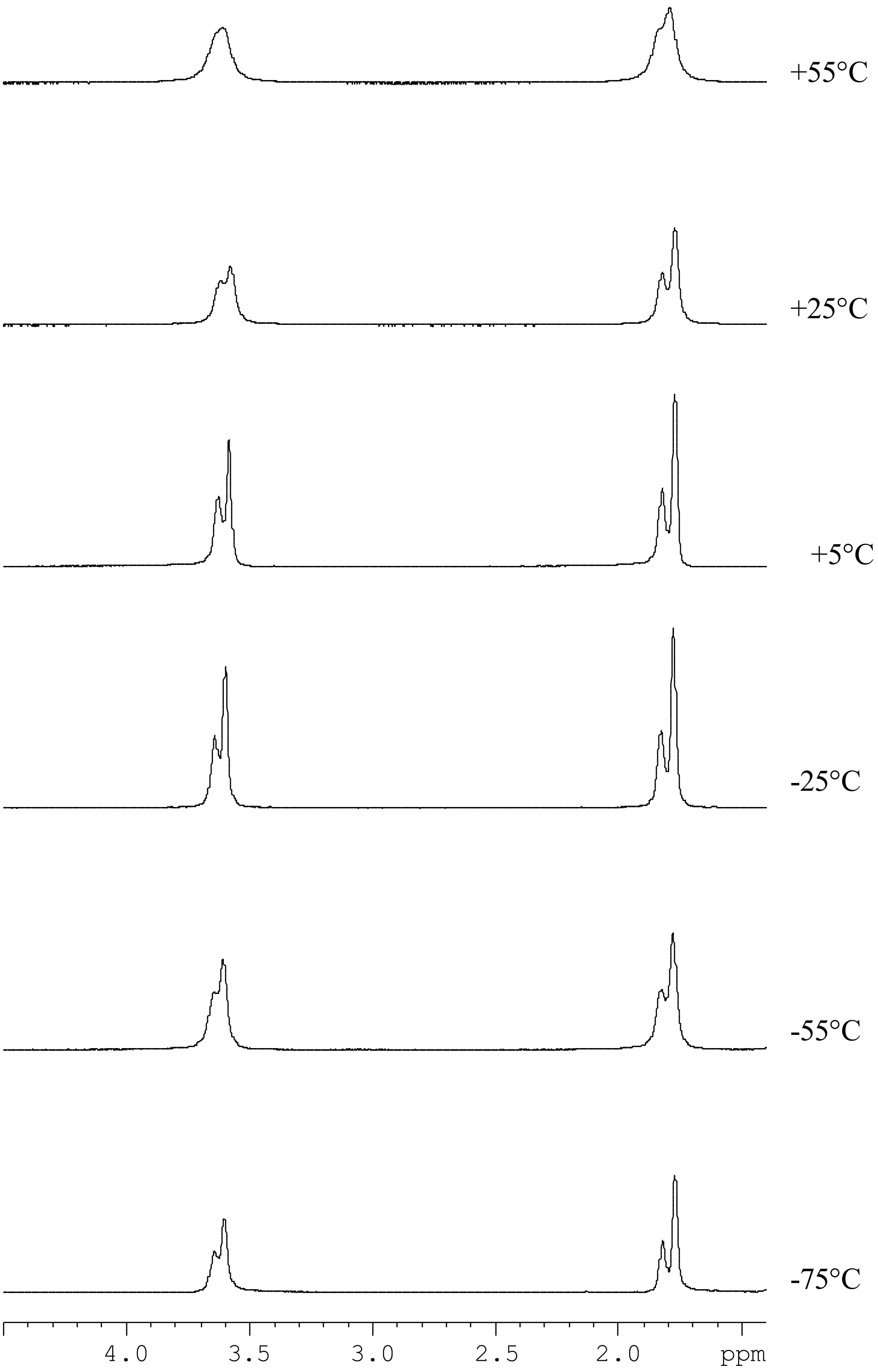
Experiments were carried out either in a radiological fume hood, under an argon atmosphere using standard Schlenk line and apparatus when necessary, or in an inert atmosphere argon glovebox. All solvents employed were reagent grade and dried by refluxing over appropriate drying agents. ^{1}H NMR spectra were recorded on a Bruker Avance Ultrashield 400 instruments at 400 MHz. UV/vis/nIR spectra were measured either on a Varian Cary 500.

The preparation of NpO_2Cl_2 in thf solution was undertaken on several occasions and a typical procedure is outlined here. Initially solid $NpO_2Cl.xH_2O$ was generated by evaporating 2.4 mL of a HNO_3 stock solution of $\{Np^{V}O_2\}^+$ (50 mg, 0.21 mmol of ^{237}Np) to dryness under a heat lamp. The stock solution was purchased from CERCA LEA (France). An aqueous $\{Np^{VI}O_2\}^{2+}$ solution was generated by dissolving of the Np(V) solid in conc. $HClO_4$ and heating to fuming. Dilution of this yellow acidic solution with 0.5 mL H_2O yielded a pink solution, with UV/vis/nIR spectroscopy used to confirm the presence of $\{Np^{VI}O_2\}^{2+}$ (major *f-f* transition at 1223 nm) and the absence of $\{Np^{V}O_2\}^+$ (major *f-f* transition at 980 nm). Brown solid neptunyl hydroxide, $NpO_2(OH)_2.xH_2O$, was precipitated from solution through the addition of NaOH. This brown precipitate of $NpO_2(OH)_2.xH_2O$ was washed twice with H_2O, once with acetone and then dried *in vacuo*. Under an argon atmosphere, the brown residue was suspended in thf (5 mL). A solution of HCl in Et_2O (2 mol L^{-1} < 1 mL) was added until the brown residue dissolved to yield a yellow solution of $NpO_2Cl_2(thf)_x$. A few drops of $SiMe_3Cl$ were then added to this solution and the resulting mixture stirred for 15 min. The solution was evaporated to dryness *in vacuo* leaving a pale yellow solid, which was redissolved in a minimum volume of thf (*c.a.* 2 mL). Vapor diffusion of hexanes into the solution afforded pale yellow crystals of **1** overnight (46 % yield), or darker crystals of **2** after a couple of days.

Computational Details

Relativistic density functional calculations were performed with the ADF code,[1] using the Zeroth Order Regular Approximation to the Dirac equation. The PBE functional[2-3] was employed, in conjunction with all-electron TZP ZORA Slater Type Orbital basis sets, and the integration parameter was set to 5.0 in all calculations.

[1] ADF2005.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.
[2] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
[3] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.



^{1}H variable temperature NMR spectra of $NpO_2Cl_2(thf)_x$ dissolved in thf–*d*$_8$.