Supporting Information for the manuscript entitled:

Preference for Nitrogen versus Oxygen Donor Coordination in Uranyl and Neptunyl (VI) Complexes.

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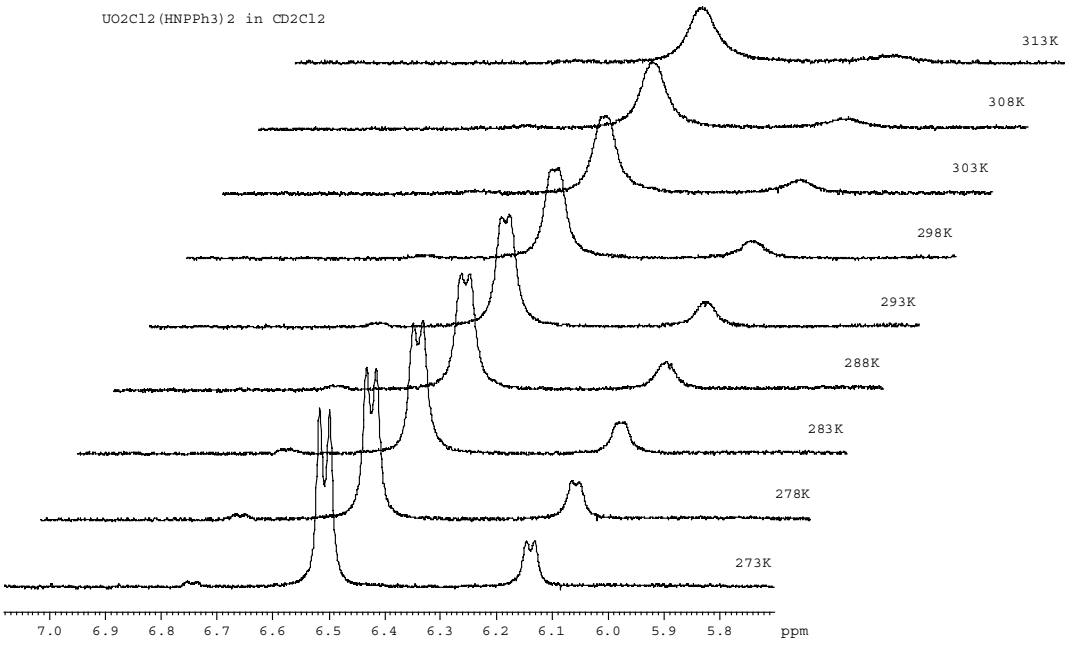
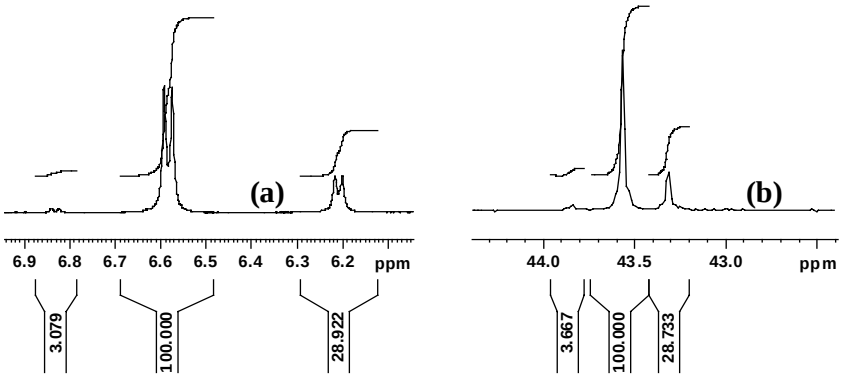
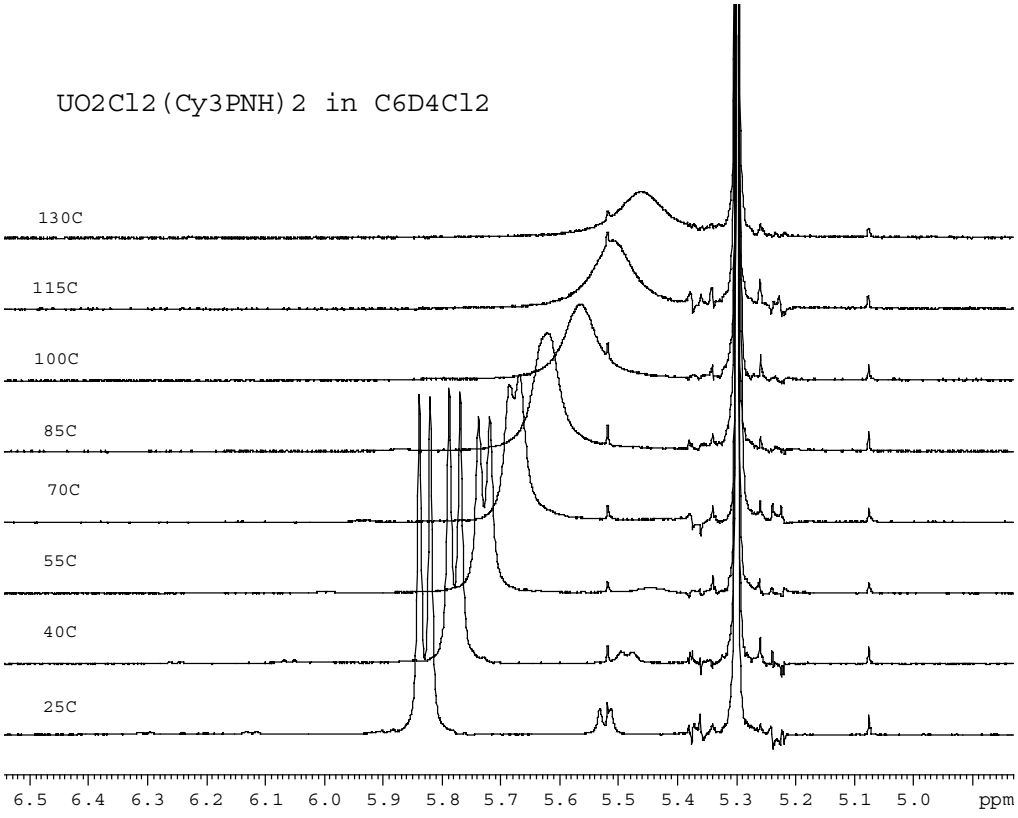


^{1}H Variable Temperature NMR spectra(P=N*H* region) of $UO_2Cl_2(Ph_3PNH)_2$ (**1**) in

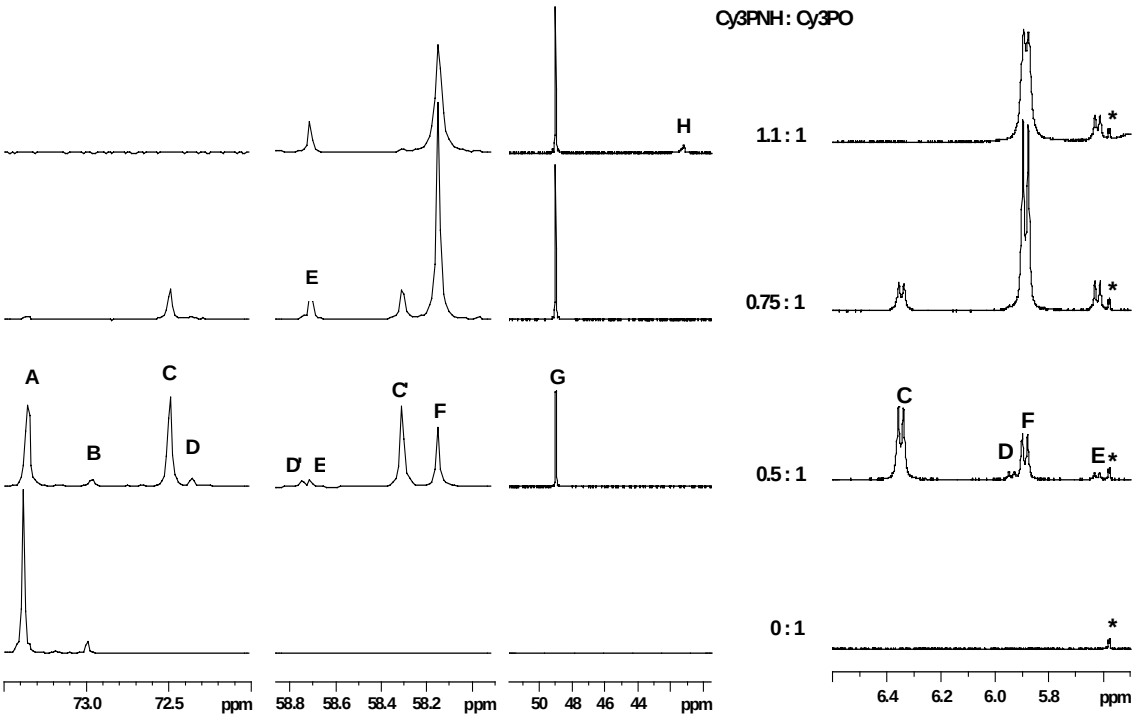


CD_2Cl_2.

(a) ^{1}H (in the PN*H* region) and (b) ^{31}P NMR spectroscopy of $UO_2Cl_2(Ph_3PNH)_2$ (**1**) (in CD_2Cl_2 at 0ºC).



^{1}H Variable Temperature NMR spectra (P=N*H* region) of $UO_2Cl_2(Cy_3PNH)_2$ (**2**) in $C_6D_4Cl_2$. The peak at 5.31 ppm is due to the residual $C_6H_4Cl_2$ solvent with ^{13}C satellites at 5.07 and 5.52 ppm.

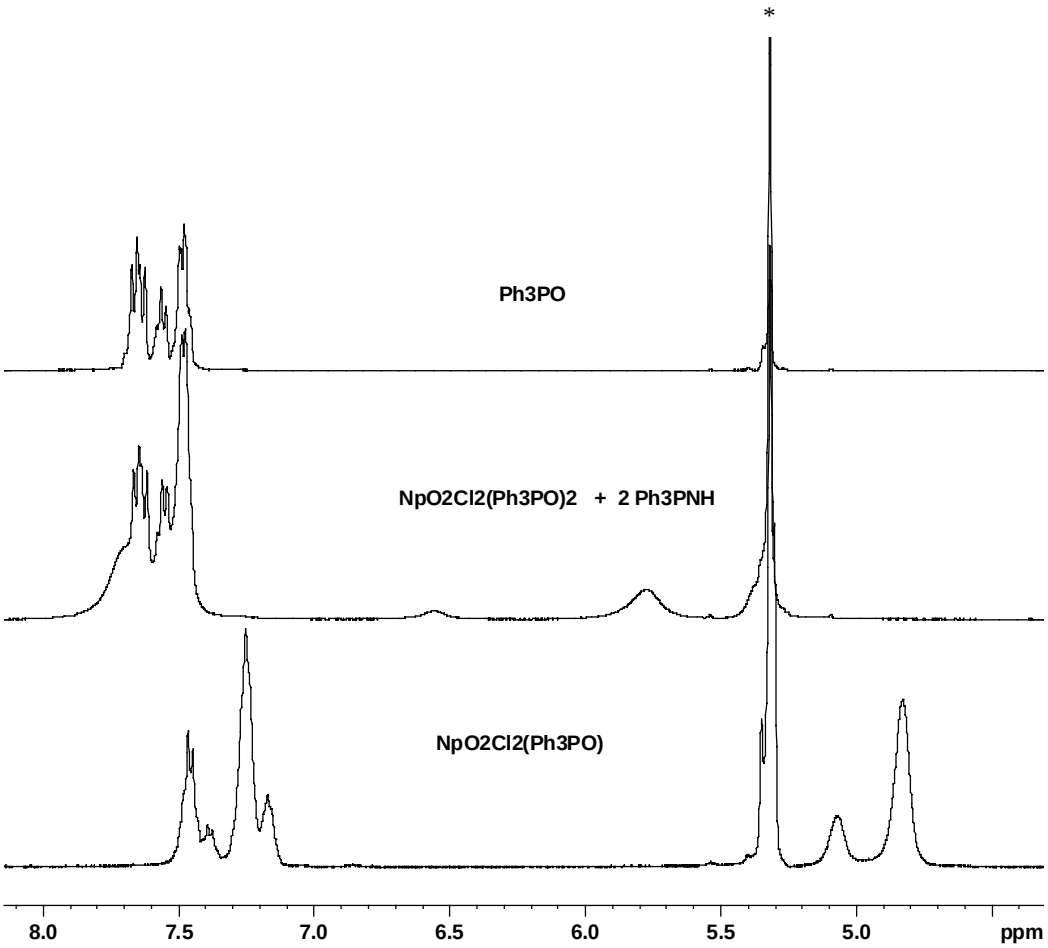


(a) ^{31}P NMR and (b) ^{1}H NMR (P=N*H* region) of the reaction between $UO_2Cl_2(Cy_3PO)_2$ (**3**) and Cy_3PNH at varying ratios of Cy_3PO : Cy_3PNH in the system. (* denotes a ^{13}C satellite of CD_2Cl_2 solvent) (see Table 1 for peak assignments).

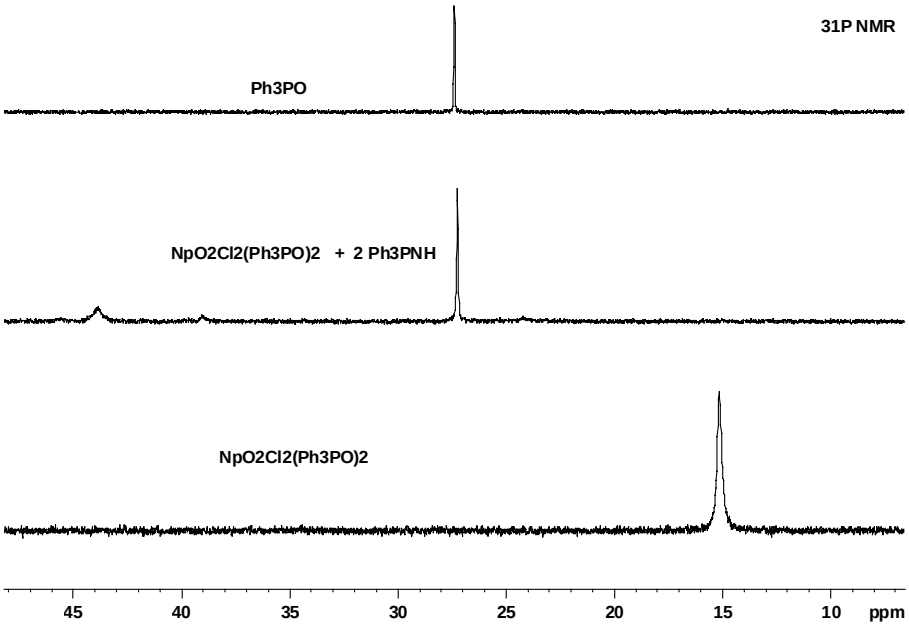
Table 1. Assignments of the chemical shifts for the above spectra. Note the assignment of *cis* and *trans* isomers are estimated on the basis that the *trans* isomer is always the higher chemical shift of the two isomers in the ^{31}P NMR spectra.

Complex	**^{31}P NMR δ (ppm)**	**^{1}H NMR δ (ppm) [J_{PH} (Hz)]**
trans-$UO_2Cl_2(Cy_3PO)_2$ (**A**)	73.4	n/a
cis-$UO_2Cl_2(Cy_3PO)_2$ (**B**)	73.0	n/a
trans-$UO_2Cl_2(Cy_3PO)(Cy_3PNH)$ (**C**,**C'**)	72.5, 58.3	6.35 [7.6]
cis-$UO_2Cl_2(Cy_3PO)(Cy_3PNH)$ (**D**,**D'**)	72.4. 58.8	5.94 [8.1]
trans-$UO_2Cl_2(Cy_3PNH)_2$ (**E**)	58.7	5.62 [7.6]
cis-$UO_2Cl_2(Cy_3PNH)_2$ (**F**)	58.2	5.89 [7.8]
Cy_3PO (**G**)	49.0	n/a
Cy_3PNH (**H**)	41.0	0.40

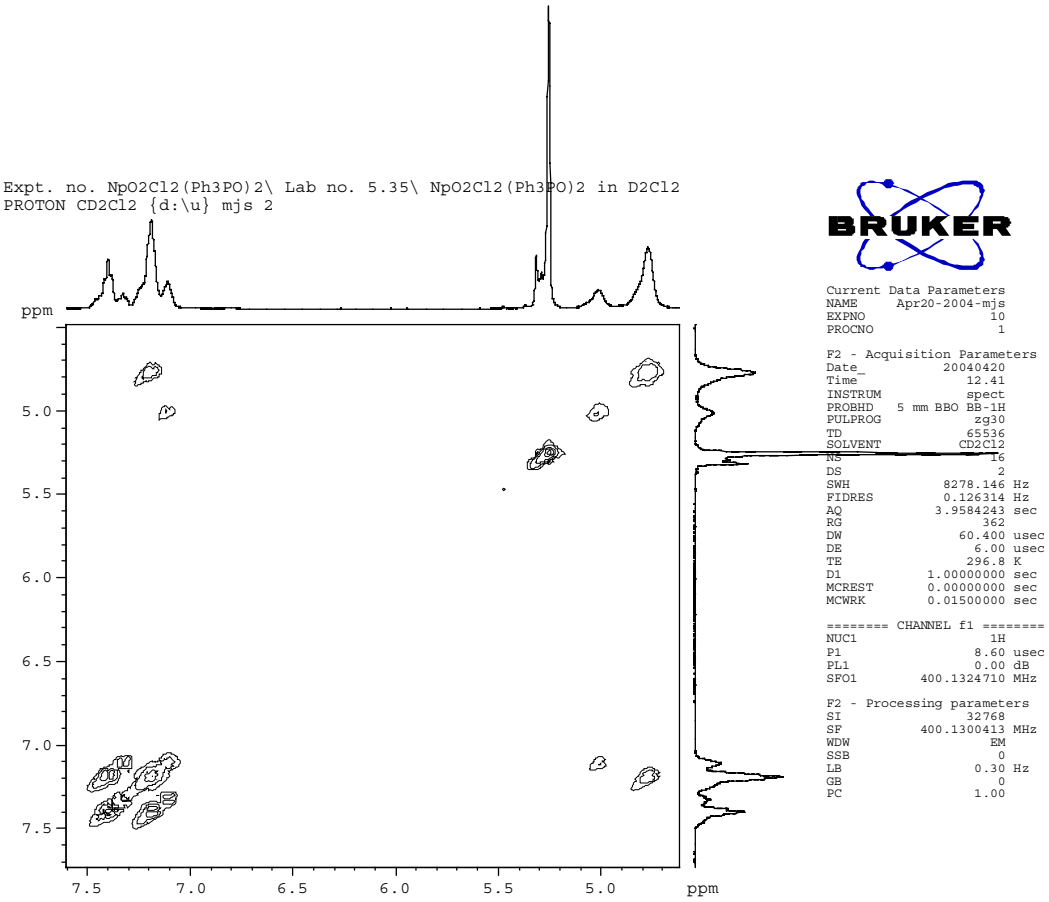
n/a = not applicable



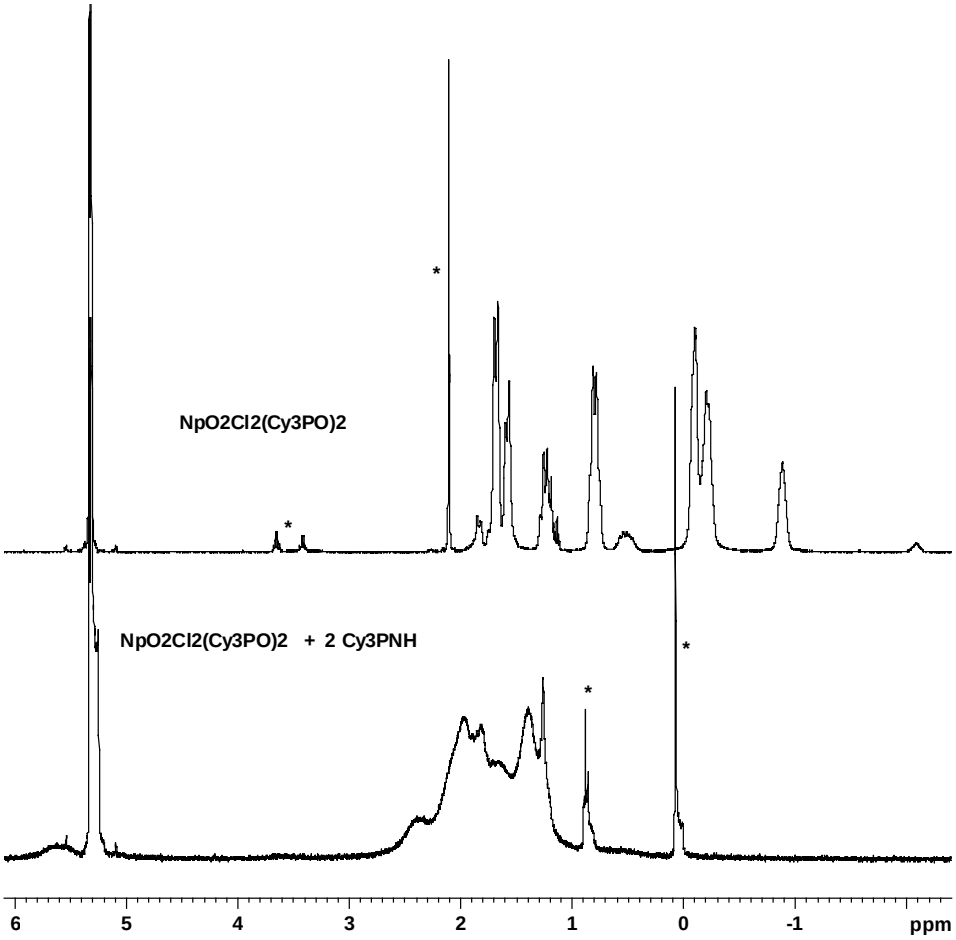
^{1}H NMR of the reaction of $NpO_2Cl_2(Ph_3PO)_2$ (**5**) with Ph_3PNH (* = residual solvent peak)



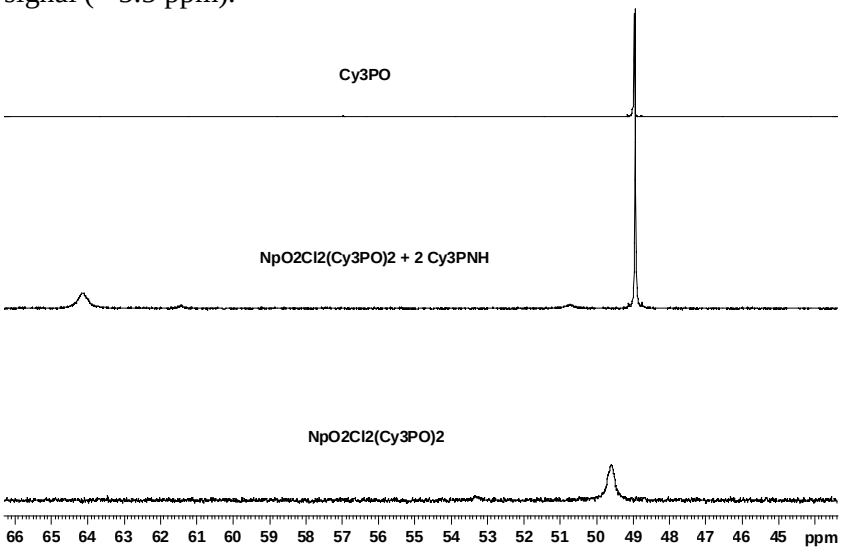
^{31}P NMR of the reaction of $NpO_2Cl_2(Ph_3PO)_2$ (**5**) with Ph_3PNH



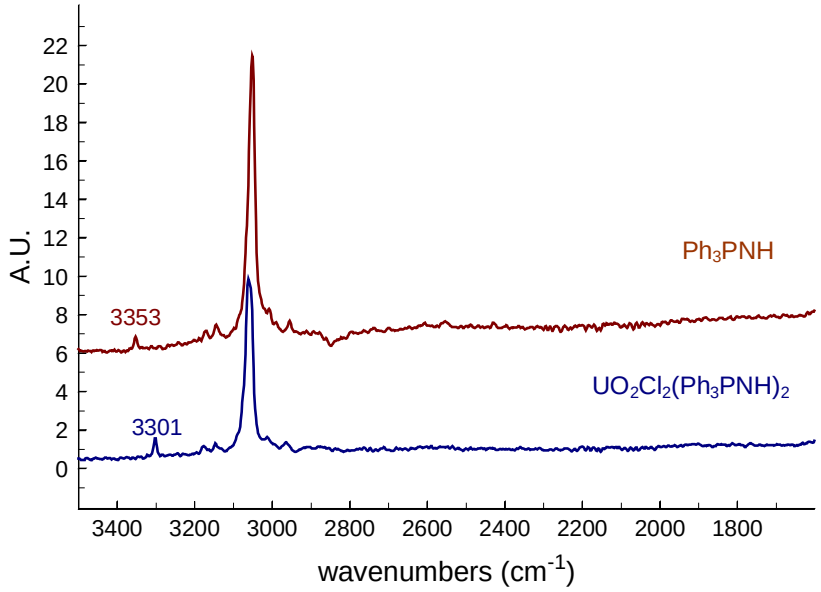
COSY spectrum of $NpO_2Cl_2(Ph_3PO)_2$ (**5**) confirming the assignment of the ortho-protons at ~ 4.8ppm.



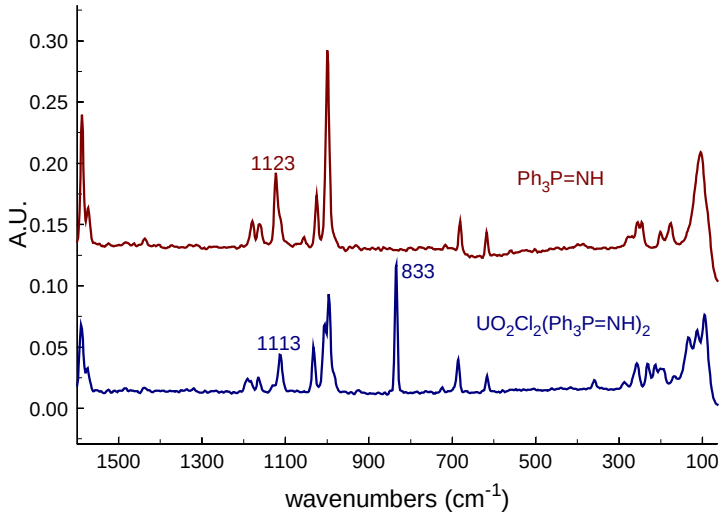
^{1}H NMR of the reaction of $NpO_2Cl_2(Cy_3PO)_2$ (**6**) with Cy_3PNH. (* denotes impurity in solvent). Note broad peak just to the left of the solvent peak is assigned the NH signal (~ 5.5 ppm).



^{31}P NMR of the reaction of $NpO_2Cl_2(Cy_3PO)_2$ (**6**) with Cy_3PNH. (Signal at 51 ppm in the middle spectrum indicates hydrolysis of some of the ligand and formation of $[Cy_3PNH_2]^+$).



Raman spectrum of $UO_2Cl_2(Ph_3PNH)_2$ (**1**) showing the change in NH stretch on going from free to complexed ligand



Raman spectrum of $UO_2Cl_2(Ph_3PNH)_2$ (**1**) showing the $O{=}U{=}O_{sym}$ stretch