A Versatile Route to Homo- and Heterobimetallic 5f-5f and 3d-5f Complexes Supported by a Redox Active Ligand Framework

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Content

A. Experimental section

General Considerations. Unless otherwise noted, all reactions were performed either using standard Schlenk line techniques or in an inert atmosphere glovebox under an atmosphere of purified argon (<1 ppm O_2/H_2O). Glassware was dried overnight at 130°C prior to use. Unless otherwise noted, reagents were acquired from commercial sources and used without further purification. The solvents were purchased from Aldrich or Eurisotop (deuterated solvents) in their anhydrous form, conditioned under argon and vacuum distilled from K/benzophenone or Nadispersion/benzophenone(hexane, diisopropylether, pyridine and THF) and degassed prior to use. Syntheses were performed using glass covered stirring bars. Anhydrous $CoCl_2$ et $NiCl_2$ were purchased from Sigma Aldrich and further purified by extraction in THF. The amount of THF present in the resulting [$CoCl_2$(THF)] and [$NiCl_2(THF)_{0.6}$] solvate was determined by NMR titration using naphthalene as internal reference. $UI_4(OEt_2)_2$,[1] UCl_4,[2] and [Na_2U(bis-salophen)],**1**,[3] were prepared using literature procedures. NMR experiments were carried out using NMR tubes adapted with J. Young valves. NMR spectra were recorded on Bruker 200 MHz and 400 MHz spectrometers. ^{1}H chemical shifts are reported in ppm and were measured relative to residual solvent peaks, which were assigned relative to an external TMS standard set at 0.00 ppm. EPR spectra of were measured with a Bruker Elexsys E500 spectrometer working at 9.4 GHz frequency with an oxford ESR900 cryostat for 4–300 K operation. Elemental analyses were performed under argon by Analytische Laboratorien GMBH at Lindlar, Germany and by the analytical service at EPFL. Mass spectra were acquired on a LXQ-linear ion trap (Thermo Scientific, San Jose, CA, USA), equipped with an electrospray source. Solutions of the complexes were prepared and filtered on microporous filters in the glove-box and maintained under argon until injection in the mass spectrometer. The experimental isotopic profile was compared in each case to the theoretical one. Experimental details concerning X-ray structural determinations are reported below.

Reaction of [Na_2U(bis-salophen)] with PbI_2

To a solution of **1** (10.0 mg, 0.011 mmol, 1 equiv) in THF (0.5 mL) was added a suspension of PbI_2 (5.1 mg, 0.011 mmol, 1 equiv) in THF (0,5 mL). The reaction mixture was stirred 16 hours, affording a dark brown suspension. The mixture was filtered to remove NaI salts and Pb(0) and the brown filtrate was analyzed by ^{1}H NMR. The spectrum

(200 MHz, THF-d_8, 298 K) displayed the characteristic resonances of the isomeric mixture of the previously reported [U(salophen)$_2$] complex**.**

Synthesis of [U$_2$(bis-salophen)(S)$_6$]I$_2$, 2-THF and 2-py

A deep purple solution of **1** (98.2 mg, 0.107 mmol, 1 equiv) in THF (1 mL) was added dropwise to a red solution of [UI$_4$(OEt$_2$)$_2$)] (96.2 mg, 0.107 mmol, 1 equiv) in THF (1 mL). The reaction mixture was stirred for 12 hours at room temperature, affording a deep orange/brown suspension. The reaction mixture was filtered to remove NaI and 2 mL of hexane were added to the brown filtrate. The resulting solid was collected and dried in vacuo to give [U$_2$(bis-salophen)I$_2$(THF)$_2$].3.3NaI, **2-THF.3.3NaI** as a brown powder (107.0 mg, 50% yield). Attempts to further purify this solid from NaI impurities were unsuccessful. Anal. calcd for [U$_2$(bis-salophen)(I)$_2$(THF)$_2$].3.3NaI: C, 28.86; H, 2.22; N, 2.80. Found: C, 28.58; H, 2.58; N, 3.00. ESI-MS: m/z = 1231.1 ([U$_2$(bis-salophen)I]$^+$). ^{1}H NMR (200 MHz, THF-d_8, 298 K): δ = 91.2 (brs, 2H), 74.1 (brs, 2H), 70.6 (brs, 2H), 52.2 (brs, 2H), 50.8 (brs, 2H), 39.0 (s, 2H), 36.8 (s, 2H), 35.8 (brs, 2H), 26.6 (s, 2H), 17.9 (brs, 2H), -12.8 (s, 2H), -18.3 (s, 2H), -24.5 (s, 2H), -40.4 (s, 2H). ^{1}H NMR (200 MHz, pyridine-d_5, 298 K): δ = 86.0 (brs, 4H), 83.6 (s, 2H), 72.7 (s, 2H), 68.6 (s, 2H), 55.0 (s, 2H), 50.0 (s, 2H), 43.4 (s, 2H), 41.1 (s, 2H), 32.1 (s, 2H), -19.6 (s, 2H), -21.3 (s, 2H), -24.0 (s, 2H), -27.6 (s, 2H).

Single crystals of [U$_2$(bis-salophen)(py)$_6$]I$_2$ **2-py** suitable for X-ray diffraction where obtained by slow diffusion of hexane into a pyridine solution of the complex.

Synthesis of [U$_2$(bis-salophen)(THF)$_2$Cl$_2$], 3.

A pale green solution of UCl$_4$ (17.4 mg, 0.047 mmol, 1 eq) in THF (2.5 ml) was added dropwise to a solution of **1** (43.3 mg, 0.047 mmol, 1 eq) in THF (1.5 ml). The reaction mixture was stirred for 4 hours at room temperature affording an orange/brown solution. The reaction mixture was filtered in order to remove NaCl. The filtrate was concentrated to 1 ml and 3 ml of hexane were added. Complex [U$_2$(bis-salophen)(THF)$_2$Cl$_2$], **3**, precipitated out of the solution as an orange powder that was collected and dried under vacuum (31.3 mg, 50% yield). Single crystals of **3** suitable for X-ray diffraction where obtained by slow diffusion of hexane into a THF solution of the complex. ^{1}H NMR (400 MHz, THF-d_8, 298 K): δ = 82.9 (s, 2H), 67.0 (s, 2H), 45.6 (s, 4H), 35.6 (s, 2H), 32.8 (s, 4H), 32.0 (s, 2H), 24.3 (s, 2H), 6.7 (s, 2H), -10.2 (s, 2H), -15.2 (s, 2H), -20.6 (s, 2H), -38.2

(s, 2H). Elemental analysis for [U_2(bis-salophen)(THF)$_2$Cl$_2$]: C, 43.68; H, 3.36; N, 4.24. Found: C, 43.37; H, 3.62; N, 3.85.

Reduction of 2-THF with KC_8 yields [U_2(cyclo-salophen)(THF)$_4$].

A deep purple solution of **1** (20.0 mg, 0.022 mmol, 1 equiv) in THF (1 mL) was added dropwise to a red solution of [$UI_4(OEt_2)_2$)] (19.6 mg, 0.022 mmol, 1 equiv) in THF (2 mL). The THF volume was adjusted to 4 mL and the reaction mixture was stirred for 12 hours, affording a deep orange/brown suspension of **2-THF**. A potassium chunk (1.7 mg, 0.043 mmol, 2 equiv) was added to a orange/brown suspension of **2-THF** in THF prepared in situ by reacting a solution of Na_2[U(bis-salophen)] **2** (20.0 mg, 0.022 mmol, 1 equiv) in THF (1 mL) with a solution of [$UI_4(OEt_2)_2$)] (19.6 mg, 0.022 mmol, 1 equiv) in THF (2 mL). The reaction mixture was stirred for another 12 hours resulting in a dark brown suspension. The reaction mixture was filtered and the resulting dark brown solution was taken to dryness to give the previously reported complex [U_2(cyclo-salophen)(THF)$_4$] as confirmed by ^{1}H NMR spectroscopy.[3]

Reduction of 3 with KC_8 yields [U_2(cyclo-salophen)(THF)$_4$].

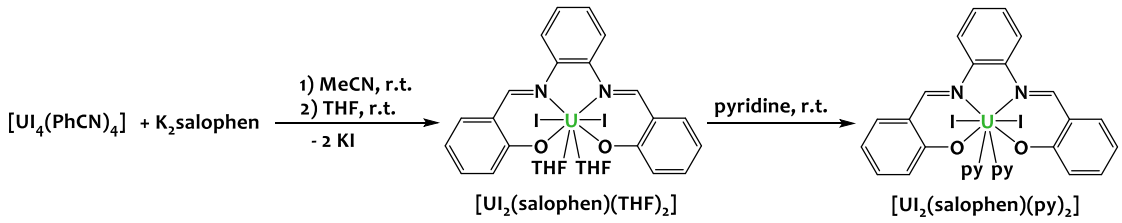
2.6 mg of KC_8 (0.019 mmol, 2 equiv) were added to a solution of **3** (12.8 mg, 0.0097 mmol, 1 equiv) in THF-d_8 (0.5ml). The reaction was stirred at room temperature overnight and then was filtered. ^{1}H NMR spectra of the resulting solution showed a complete conversion to the previously reported complex [U_2(cyclo-salophen)(THF)$_4$]. [3]

Reaction of [U_2(bis-salophen)(py)$_6$]I_2 with I_2

A solution of **2-py** (10.0 mg, 0.007 mmol, 1 equiv) in pyridine (0.5 mL) was added onto I_2 (3.7 mg, 0.015 mmol, 2 equiv). The mixture was stirred at room temperature for 12 hours, affording a red-orange solution. The ^{1}H NMR spectrum (200 MHz, pyridine-d_5, 298 K) recorded for the crude reaction mixture showed that complex [UI_2(salophen)(py)$_2$] [3] was quantitatively formed.

Synthesis of [UI_2(salophen)(S)$_2$] (S= THF, pyridine)

$[UI_2(salophen)(S)_2]$ (S = THF, pyridine) was prepared independently - by reacting the U(IV) precursor $[UI_4(PhCN)_4]$ with one equivalent of the deprotonated form of the Schiff base ligand - to ensure its correct identification.



A solution of $[UI_4(PhCN)_4]$ (272.1 mg, 0.235 mmol, 1 equiv) in acetonitrile (2 mL) was added to a yellow suspension of K_2salophen (92.2 mg, 0.235 mmol, 1 equiv) in 8 mL of acetonitrile. This suspension was stirred at room temperature for 20 min to yield a clear dark red solution. The solution was filtered and the filtrate was layered with 4 mL THF. After 2 days, 174 mg of red-orange crystals of $[UI_2(salophen)(THF)_2]$, were collected by filtration (0.183 mmol, 79% yield). Anal. Calcd for $C_{28}H_{28}I_2N_2O_4U$: C, 35.46; H, 2.98; N, 2.95. Found: C, 35.25; H, 3.13; N, 3.02. ^{1}H NMR (200 MHz, pyridine-d_5, 298 K): δ = 80.22 (s, 2H), 46.16 (s, 2H), 45.74 (s, 2H), 42.18 (s, 2H), 30.36 (s, 2H), -6.19 (s, 2H), -8.24 (s, 2H).

Reaction of $[Na_2U(bis\text{-}salophen)]$ with $CoCl_2$, synthesis of $[UCo(bis\text{-}salophen)(THF)_2]$ 4-THF

A blue solution of $[CoCl_2(THF)]$ (17.9 mg, 0.089 mmol, 1 eq) in THF (4ml) was slowly added (dropwise) to a stirred deep purple solution of **1** (80.9 mg, 0.089 mmol, 1 eq) in THF (3 ml) kept at –40 °C. The resulting deep brown reaction mixture was stirred at -40°C for 3 hours. The mixture was filtered to remove NaCl; the solvent volume was reduced to 2 ml and 3 ml of hexane were added maintaining the solution at – 40 °C. A brown solid formed after one night that was collected (13 mg). Further solvent reduction and hexane addition afforded additional product yielding overall 58 mg of $[UCo(bis\text{-}salophen)(THF)_2].0.5$ NaCl as dark brown powder (60% yield). Re-crystallization at -40 °C of this solid by slow diffusion of DIPE into a THF solution of the complex or slow diffusion of hexane into a pyridine solution of the complex afforded black single crystals suitable for X-ray diffraction of $[UCo(bis\text{-}salophen)(THF)_2]$, **4-THF** and $[UCo(bis\text{-}salophen)(py)_2]$, **4-2py** respectively. ES-MS: m/z= 1141.7 $[M+THF]^+$. ^{1}H NMR (200 MHz, THF-d_8, 298 K): δ = 64.7 (s, 1H), 59.3 (s, 1H), 43.7 (s, 1H), 43.50 (s, 1H), 40.5 (s, 1H), 37.7 (s, 1H), 31.7 (s,

1H), 27.3 (s, 1H), 26.8 (s, 1H), 26.5 (s, 1H), 22.4 (s, 1H), 20.9 (s, 1H), 11.1 (s, 1H), 8.9 (s, 1H), 7.2 (s, 2H), 3.2 (s, 1H), 2.8 (s, 1H), -0.65 (s, 1H), -0.74 (s, 1H), -2.4 (s, 1H), -13.2 (s, 1H), -13.5 (s, 1H), -14.0 (s, 1H), -14.9 (s, 1H), -21.6 (s, 1H), -28.6 (s, 1H), -37.3 (s, 1H). ^{1}H NMR (200 MHz, pyridine-d_5, 298 K): δ = 65.6 (s, 1H), 41.6 (s, 1H), 40.1 (s, 1H), 38.5 (s, 1H), 36.1 (s, 1H), 30.8 (s, 1H), 30.1 (s, 1H), 27.4 (s, 1H), 25.8 (s, 1H), 24.4 (s, 1H), 21.2 (s, 1H), 16.4 (s, 1H), 9.8 (s, 1H), 9.1 (s, 1H), 5.6 (s, 1H), 2.4 (s, 1H), -1.1 (s, 1H), -4.6 (s, 1H), -6.22 (s, 1H), -11.2 (s, 1H), -11.5 (s, 1H), -22.5 (s, 1H), -23.6 (s, 1H), -27.1 (s, 1H).

Attempts to obtain the complex **4-THF** analytically pure by recrystallization from THF/DIPE resulted always in the presence of variable amount of co-crystallized NaCl. Elemental analysis calcd. for [UCo(bis-salophen)(THF)$_2$]. 0.5 NaCl: C, 52.45; H, 4.04; N, 5.10. Found: C, 52.36; H, 4.10; N, 4.96.

Complex **4-2THF** and **4-2py** are stable in solution at room temperature. However the complex **4-2py**, presenting a tetra-coordinate square planar cobalt, slowly undergoes a rearrangement in solution affording complex [UCo(bis-salophen)(py)$_3$], **4-3py** (see following synthesis) where a penta-coordinate square pyramidal cobalt is formed upon pyridine binding to the cobalt center. After 14 days an equilibrium is reached showing a ratio **4-2py**:**4-3py** of 10:1.

If [CoCl$_2$(THF)] is rapidly added to the solution of complex Na$_2$[U(bis-salophen)] at room temperature significant amounts of the oxidation products [U(salophen)$_2$] and [U(salophen)Cl$_2$] are formed with concomitant formation of Co(0). This is probably due to the presence of local excess of [CoCl$_2$(THF)] that leads to oxidation of the uranium complex.

Reaction of [Na$_2$U(bis-salophen)] with CoCl$_2$, synthesis of [UCo(bis-salophen)(py)$_3$], 4-3py.

A -40 °C solution of [CoCl$_2$(THF)] (8.9 mg, 0.044 mmol, 1 eq) in py (2 ml) was slowly added to a -40 °C solution of **1** (39.6 mg, 0.044 mmol, 1 eq) in py (2 ml). The mixture was stirred overnight affording a red/brown solution. The solution was evaporated (0.5 ml), filtered and 6 ml of cold hexane were added at -40 °C. The resulting precipitate of **[**UCo(bis-salophen)(py)$_3$], **4-3py** (33 mg, 57 %) was collected and conserved at low temperature. Re-crystallization of this solid by slow diffusion of hexane into a pyridine solution of **4-3py** at –40 °C afforded dark red crystals suitable for X-ray diffraction. Elemental analysis for [UCo(bis-salophen)(py)$_3$]: C,56.82; H, 3.73; N, 8.43. Found: C, 56.65; H, 3.55; N, 8.43. ^{1}H NMR (400 MHz, pyridine-d_5, 298 K): δ = 61.39 (s, 1H), 48.23

(s, 1H), 47.74 (s, 1H), 43.30 (s, 1H), 35.55 (s, 1H), 34.99 (s, 1H), 32.48 (s, 1H), 28.98 (s, 1H), 28.62 (s, 1H), 28.00 (s, 1H), 20.84 (s, 1H), 17.78 (s, 1H), 6.75 (t, 1H), 5.69 (s, 1H), 2.86 (d, 1H), 2,23 (s, 1H), 0.18 (s, 1H), -3.57 (s, 1H) - 3.67 (s, 1H), - 10.28 (s, 1H), -11.98 (s, 1H), -20.76 (s, 1H), -25.13 (s, 1H), - 44.13 (s, 1H), -46.78 (s, 1H), -50.60 (s, 1H), -57.81 (s, 1H).

The proton NMR of **4-3py** in pyridine-d_5 at – 30 °C shows only the signals assigned to **4-3py** which remains the only product at -30°C for several days. After 14 days at room temperature a ratio **4-2py**:**4-3py** of 10:1 is reached.

Reaction of [Na_2U(bis-salophen)] with $NiCl_2$, synthesis of [UNi(bis-salophen)$(S)_2$], (S= py, 5-py; S=THF, 5-THF)

A cold solution (-40 °C) of [$NiCl_2(THF)_{0.6}$] (8.5 mg, 0.049 mmol, 1 eq) in py (3.5 ml) was added dropwise to a stirred cold solution of **1** (44.6 mg, 0.049 mmol, 1 eq) in py (1.5 ml). The mixture was let slowly return at room temperature and left stirring overnight to give a yellow/brown solution. The solution was evaporated (0.5 ml), filtered and 6 ml of hexane were added. [UNi(bis-salophen)$(py)_2$], **5-py** precipitated out of the solution immediately as a black solid, that was collected and dried under vacuum (38 mg, 64 %). ^{1}H NMR (400 MHz, pyridine-d_5, 298K) δ= 57.8 (s, 1H); 47.7 (s, 1H); 43.9 (s, 1H); 37.9 (s, 1H); 35.3 (s, 2H); 30.8 (s, 1H); 28.4 (s, 1H); 25.3 (s, 1H); 24.1 (s, 1H); 17.6 (s, 1H); 16.8 (s, 1H); 11.90 (s, 1H); 10.10 (s, 1H); 3.9 (s, 1H); 2.9 (s, 1H); 0.6 (s, 1H); -1.1 (s, 1H); -2.3 (s, 1H); -3.4 (s, 1H); -4.8 (s, 1H); -6.7 (s, 2H); -10.1 (s, 1H); -30.0 (s, 1H). Elemental analysis calcd. for [UNi(bis-salophen)$(py)_2$]. 0.9 py: C, 56.70; H, 3,71; N, 8.37. Found: C, 56.66; H, 3.87; N, 8.16. The coordinated py molecules were replaced by THF molecules by dissolving the product in THF and taking it to dryness for 3 time affording complex [UNi(bis-salophen)$(THF)_2$], **5-THF**. Elemental analysis for [UNi(bis-salophen)$(THF)_2$]: C, 53.90; H, 4.15; N, 5.24. Found: C, 53.64; H, 4.14; N, 5.21.

^{1}H NMR (200MHz, THF-d_8, 298K) δ= 57.9 (s, 1H); 48.3 (s, 1H); 43.4 (s, 1H); 38.2 (s, 1H); 34.6 (s, 1H); 33.9 (s, 1H); 31.1 (s, 1H); 28.6 (s, 1H); 26.1 (s, 1H); 25.5 (s, 1H); 23.9 (s, 1H); 19.0 (s, 1H); 16.0 (s, 1H); 11.3 (s, 1H); 9.8 (s, 1H); 7.3 (s, 1H); 6.6 (s, 1H); 3.9 (s, 1H); 3.2 (s, 1H); 1.9 (s, 1H); -0.3 (s, 1H); -1.5 (s, 2H); -3.1 (s, 1H); -3.8 (s, 1H); -7.2 (s, 1H); -11.3 (s, 1H); -28.4 (s, 1H).

Dark-green single crystals of **5-THF** suitable for X-ray diffraction analysis were obtained from by slow diffusion of DIPE into a THF solution of **5-THF**.

Reaction of 4-3py with CS_2

$^{13}CS_2$ (5.8 μL , 0.059 mmols, 2 equiv) was added to a solution of **4-3py** (30.0 mg, 0.0293 mmol, 1 equiv) in 0.5 ml py-d_5. The resulting suspension was stirred for 2 days until complete consumption of **4-3py**. The suspension was centrifuged to remove the formed dark solid. The ^{1}H NMR (200MHz, py-d_5, 298K) of the resulting solution shows signals assigned to the [U(salophen)$_2$] complex. The quantitative integration of the signals assigned to the [U(salophen)$_2$] show complete conversion of **4-3py** into [U(salophen)$_2$]. The ^{13}C NMR spectrum of the solution shows a signal at 248 ppm assigned to the presence of $^{13}C_2S_4^{2-}$. The dark solid formed in the reaction is partially soluble in pyridine. The X-band EPR spectrum of the solid formed in the reaction shows the presence of Co(II). The presence of $C_2S_4^{2-}$ in the solid was detected by ^{3}C NMR in agreement with the presence of [Co(C_2S_4)]. X-ray photoelectron spectroscopy (XPS) analysis of the solid showed a ratio S/Co of 1.8 suggesting that the solid contains at least an additional sulfur containing Co(II) species. The low solubility of this solid in all organic solvent prevented further analysis.

B. NMR spectroscopic data

Figure S1. ^{1}H NMR spectrum of **4-2THF** (THF-d_8, 298K, 400MHz).

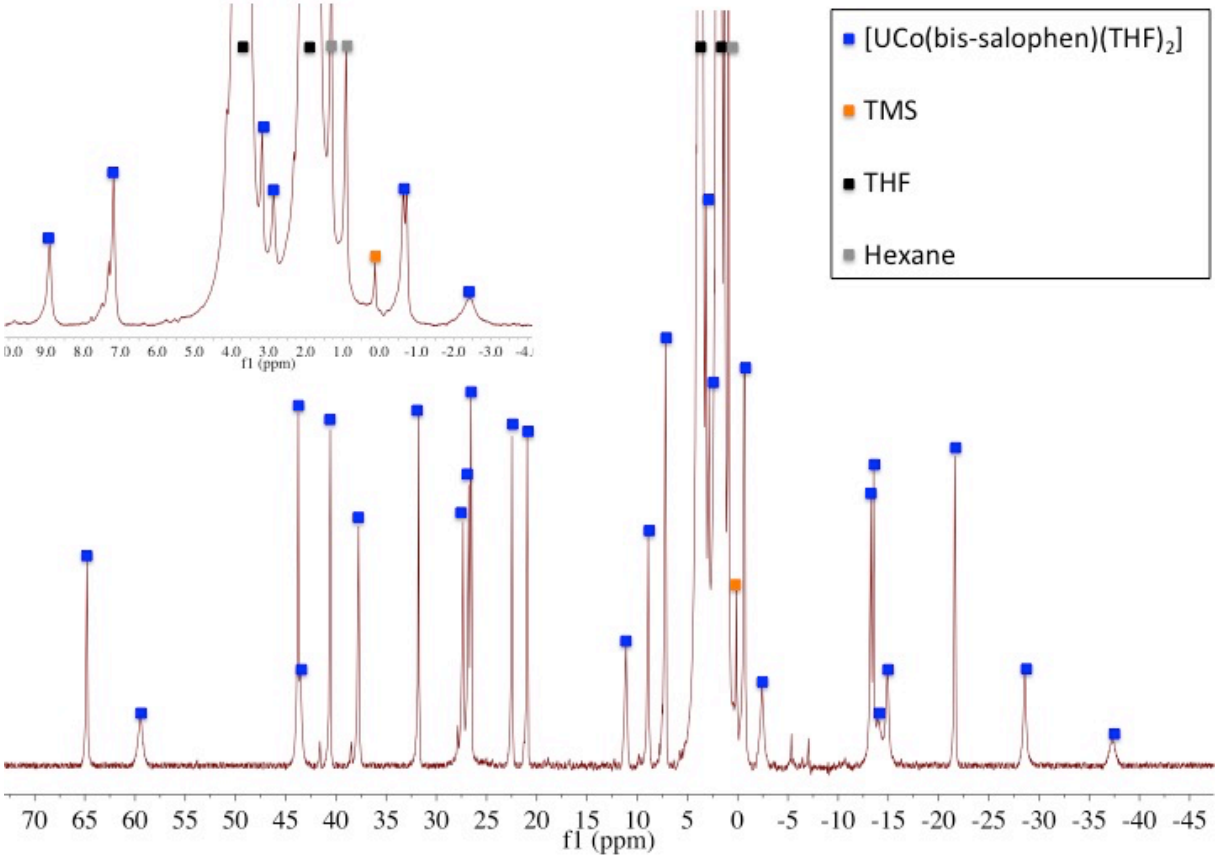


Figure S2. ^{1}H NMR spectrum of **4-2py** (pyridine-d_5, 298K, 400 MHz).

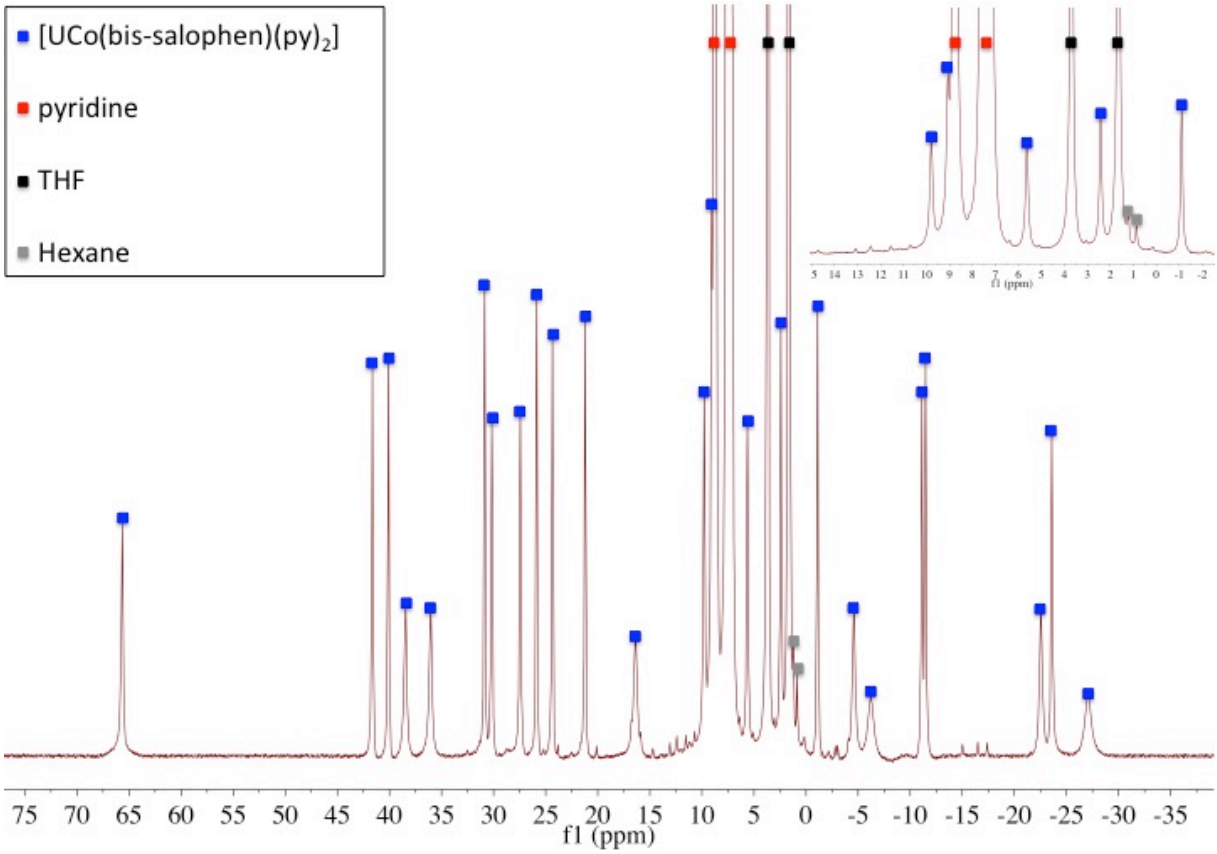


Figure S3. ^{1}H NMR spectrum of **4-3py** (pyridine-d_5, 298K, 400 MHz) immediately after dissolution in pyridine.

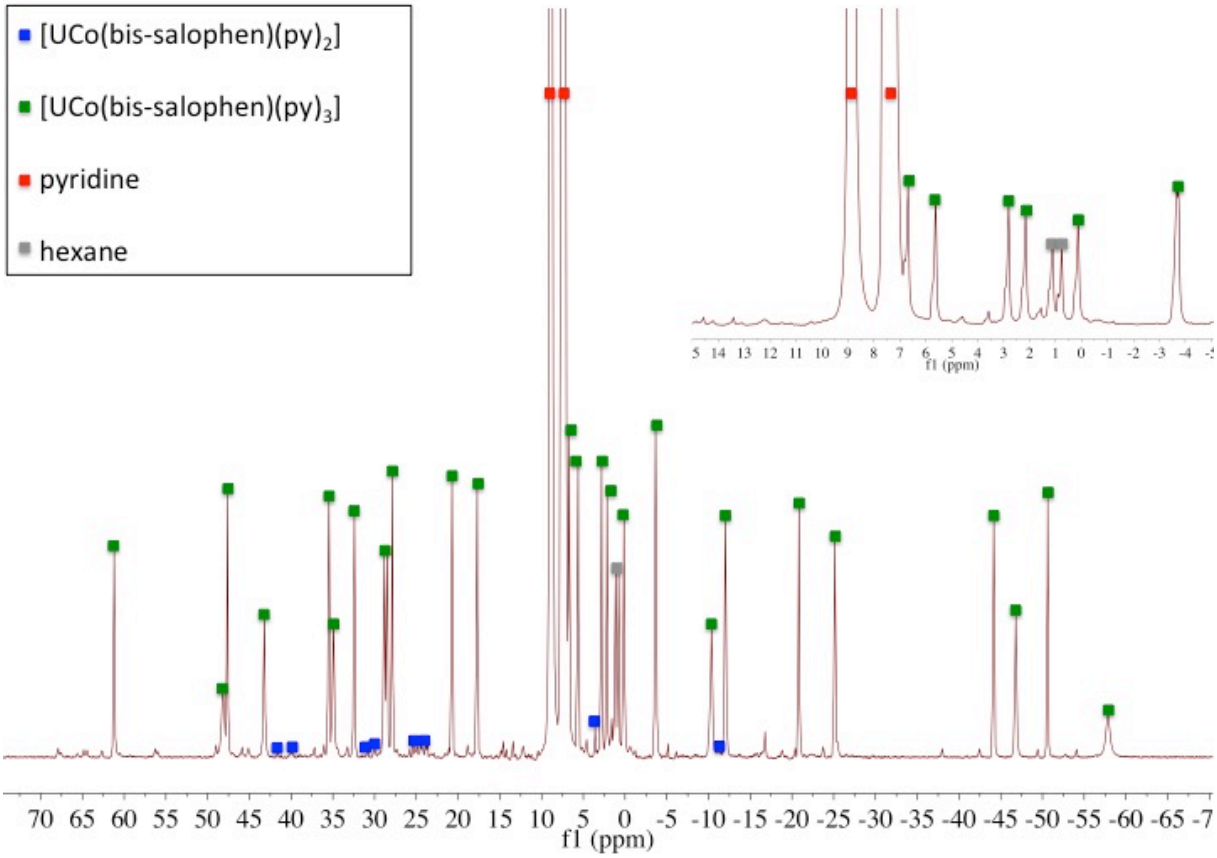


Figure S4. ^{1}H NMR spectrum of of **4-3py** after 14 days in pyridine at room temperature (pyridine-d_5, 298K, 400 MHz).

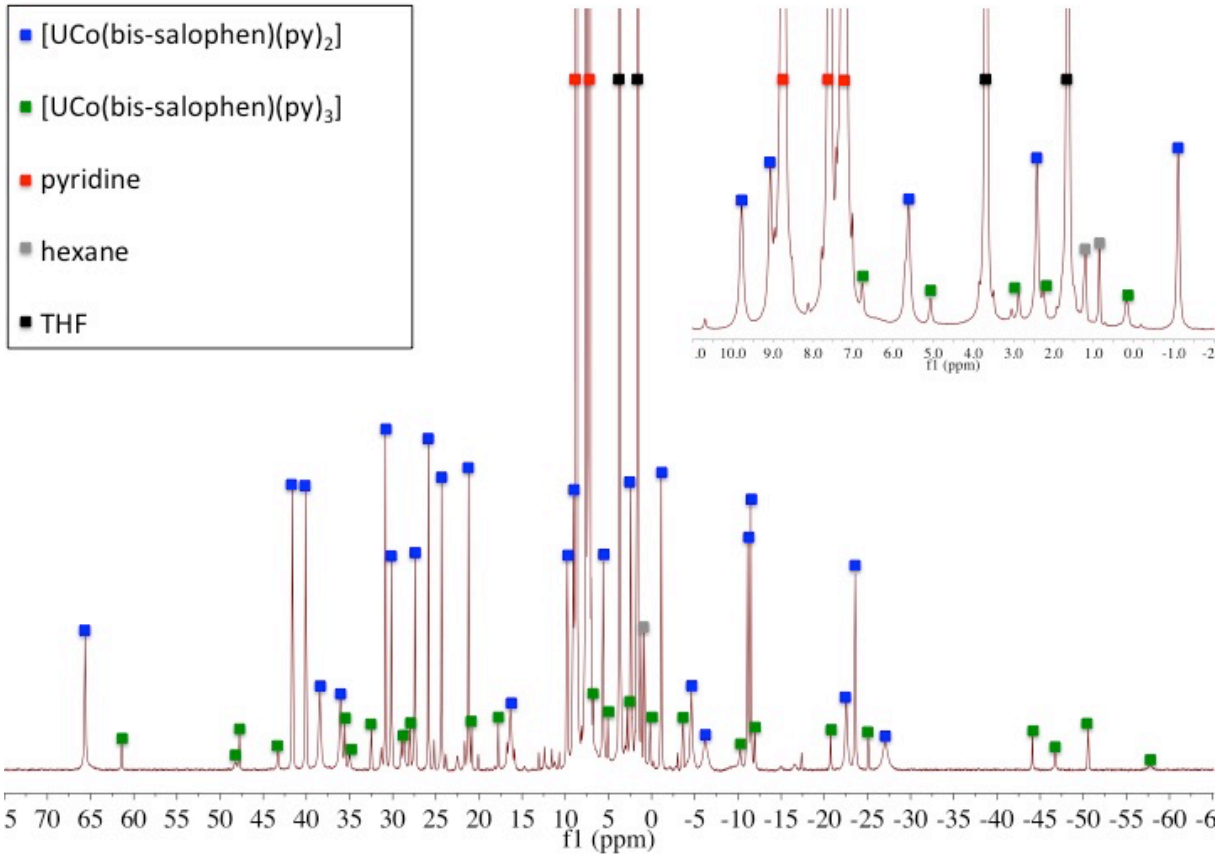


Figure S5. ^{1}H NMR spectrum of **5-py** (pyridine-d_5, 298K, 400 MHz).

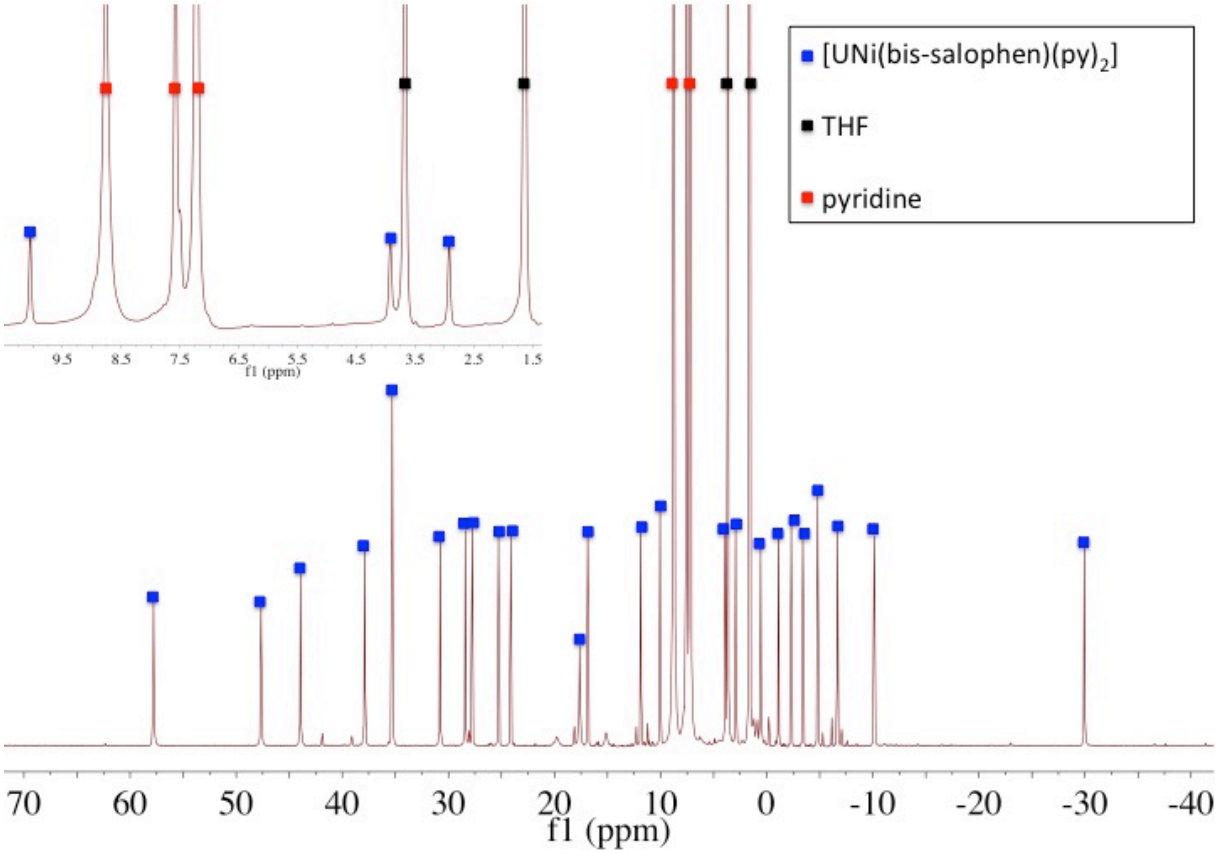

[UNi(bis-salophen)(py)2]
THF
pyridine
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5
f1 (ppm)
70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

Figure S6. ^{1}H NMR spectrum of **5-THF** (pyridine-d_5, 298K, 400 MHz).

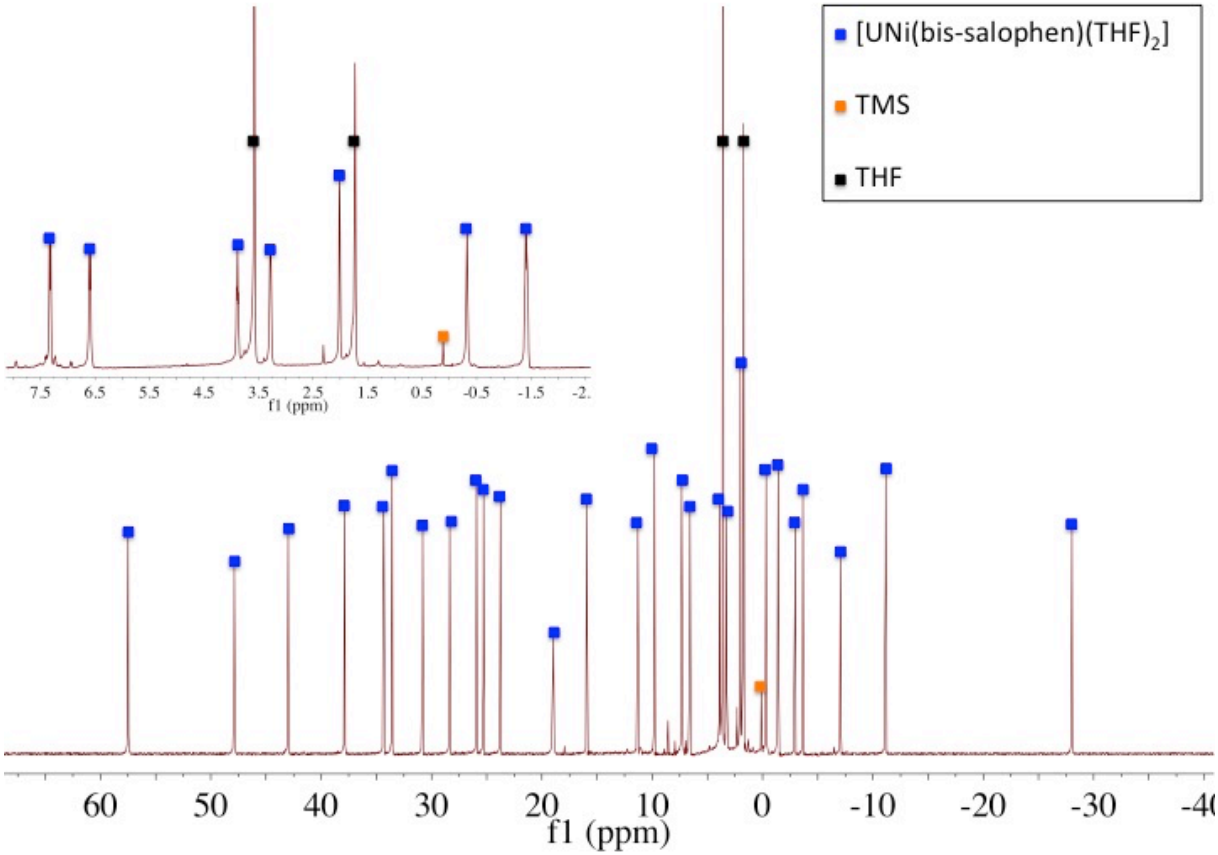


Figure S7. ^{1}H NMR spectrum after reaction of **3** with KC_8 showing only the peaks assigned to [U_2(cyclo-salophen)$(THF)_4$] (THF-d_8, 298K, 400 MHz).

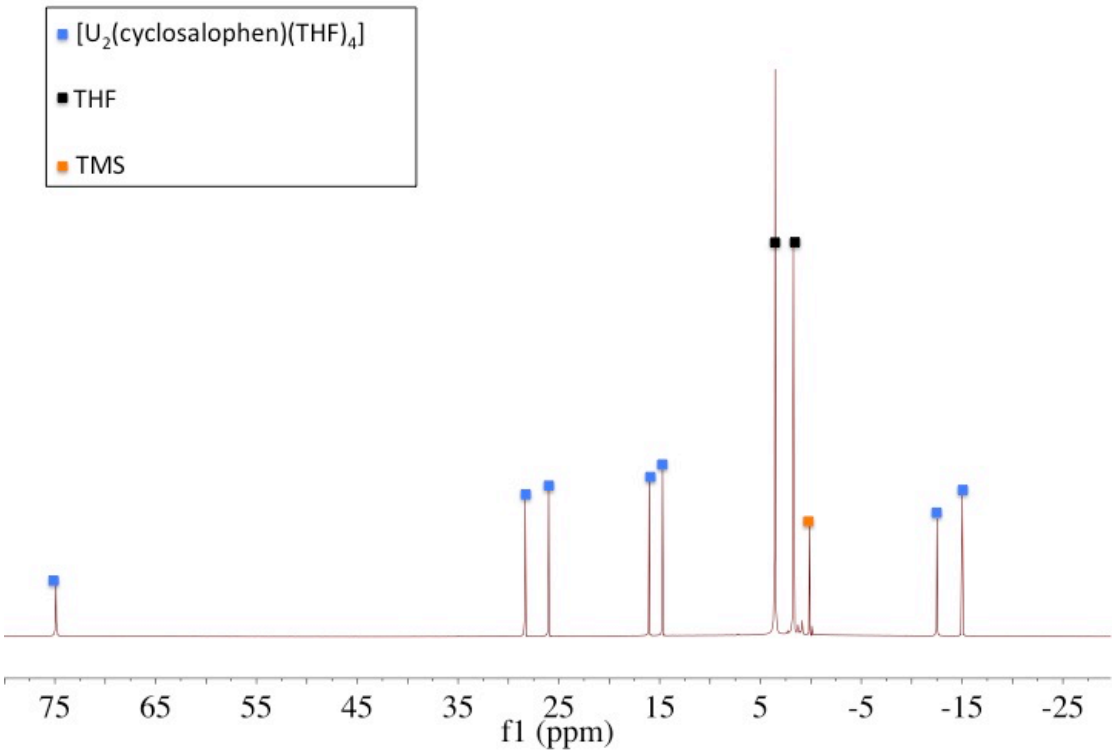

[U2(cyclosalophen)(THF)4]
THF
TMS
75
65
55
45
35
25
15
5
-5
-15
-25
f1 (ppm)

Figure S8. ^{1}H NMR spectrum before (top), immediately after (middle) and 24 hours after the reaction between **4-3py** and 2 equiv of $^{13}CS_2$ (pyridine-d_5, 298K, 400 MHz).

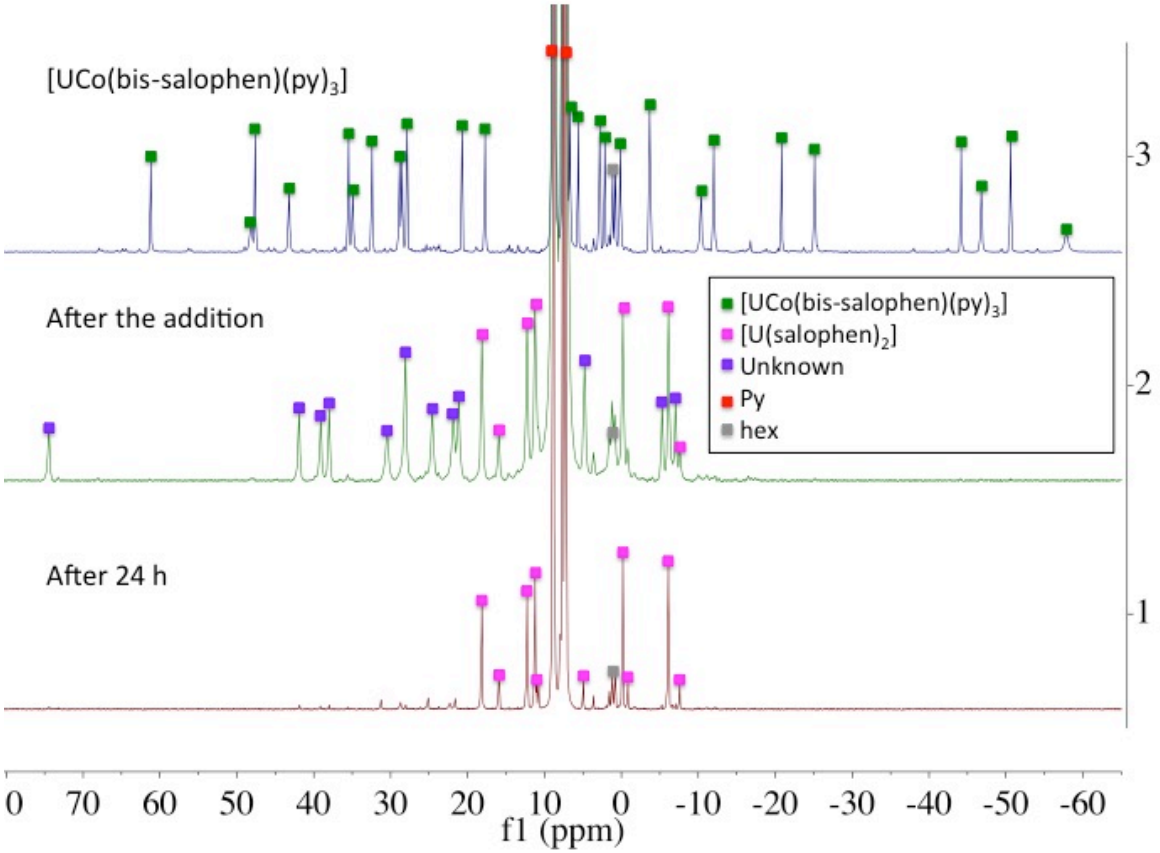
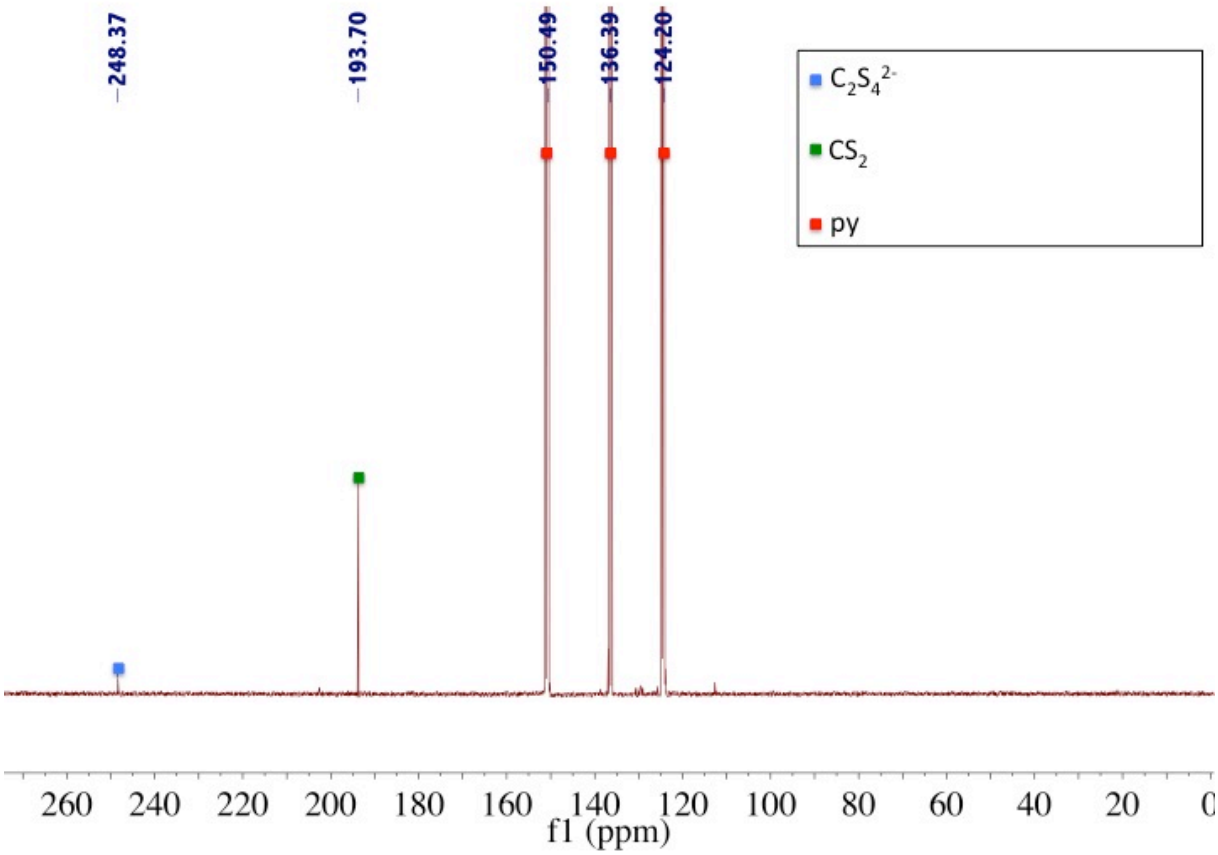


Figure S9. ^{13}C NMR spectrum of the solid obtained from the reaction of **4-3py** with $^{13}CS_2$ (pyridine-d_5, 298K, 100.6MHz).



C. ESI-MS spectrometry data

Figure S10. Experimental and simulated ESI-MS spectrum of $[U_2(\text{bis-salophen})I]^+$ (m/z Calcd for $C_{40}H_{28}N_4O_4IU_2$: 1231.2).

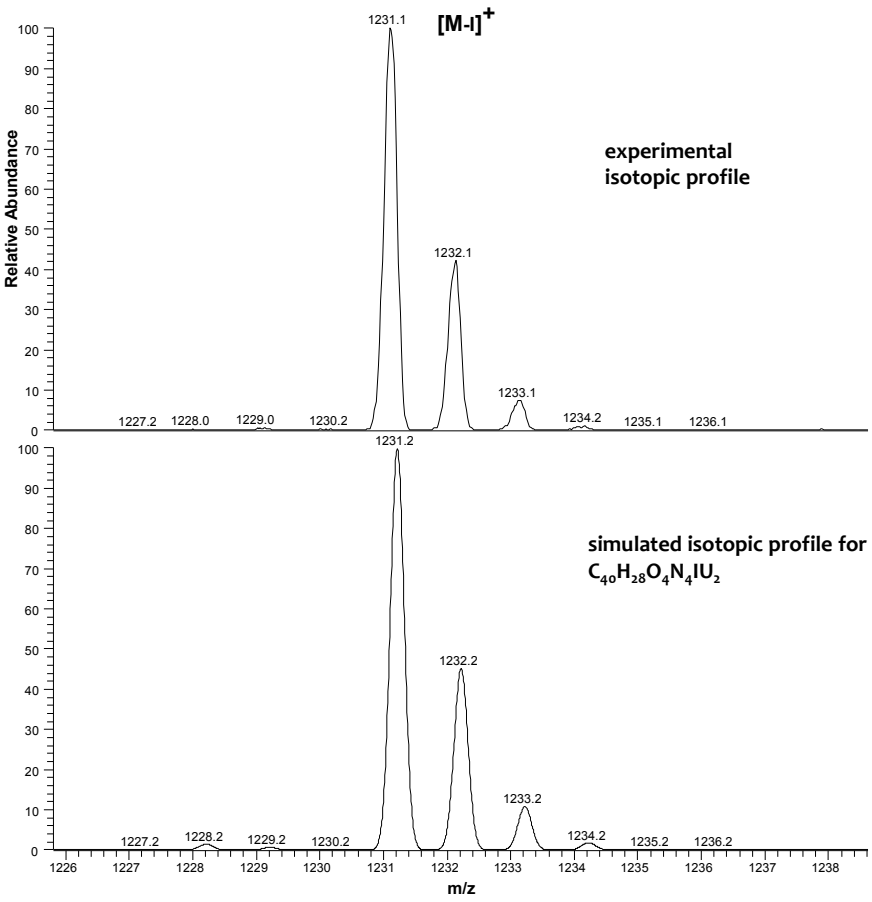

[M-I]+
experimental
isotopic profile
simulated isotopic profile for
C40H28O4N4IU2
Relative Abundance
m/z
1231.1
1232.1
1233.1
1234.2
1227.2
1228.0
1229.0
1230.2
1235.1
1236.1
1231.2
1232.2
1233.2
1234.2
1227.2
1228.2
1229.2
1230.2
1235.2
1236.2

Figure S11. Experimental and simulated ESI-MS spectrum of $[UCo(bis\text{-}salophen)(THF)_3]^+$ (m/z Calcd for $C_{52}H_{52}N_4O_7UCo$: 1141.4).

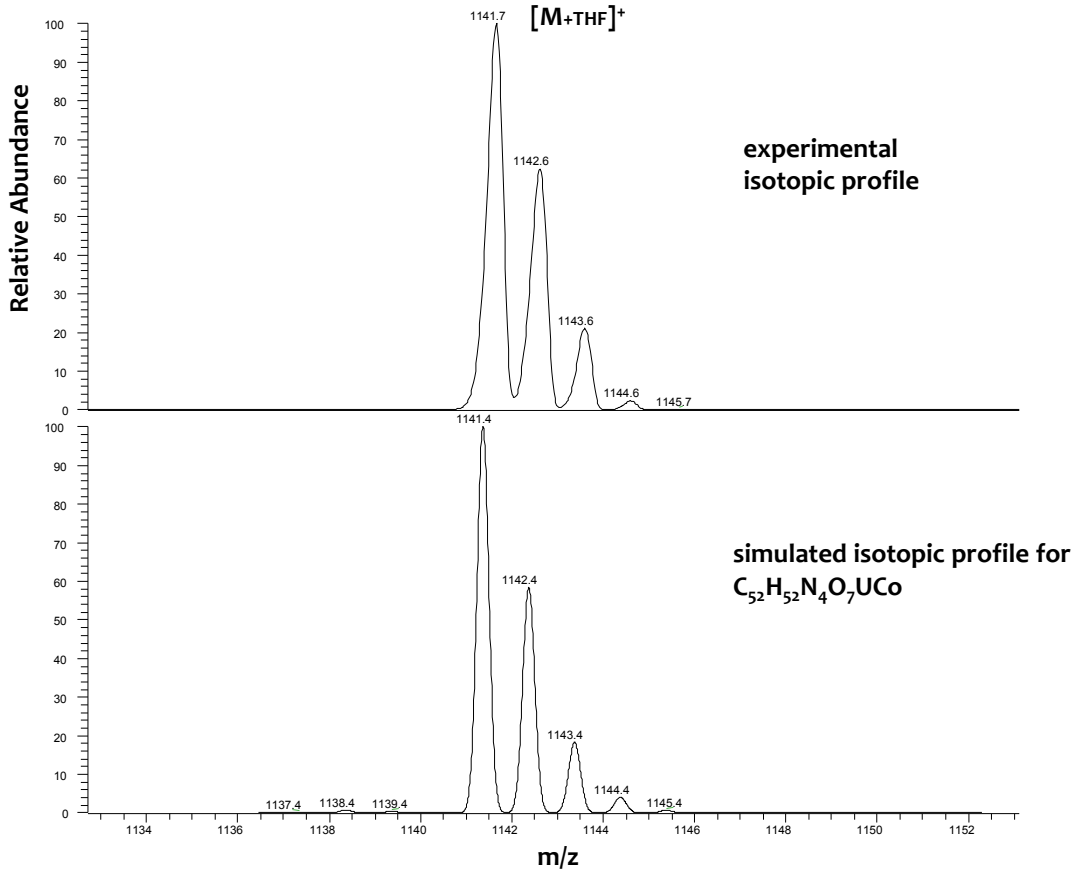
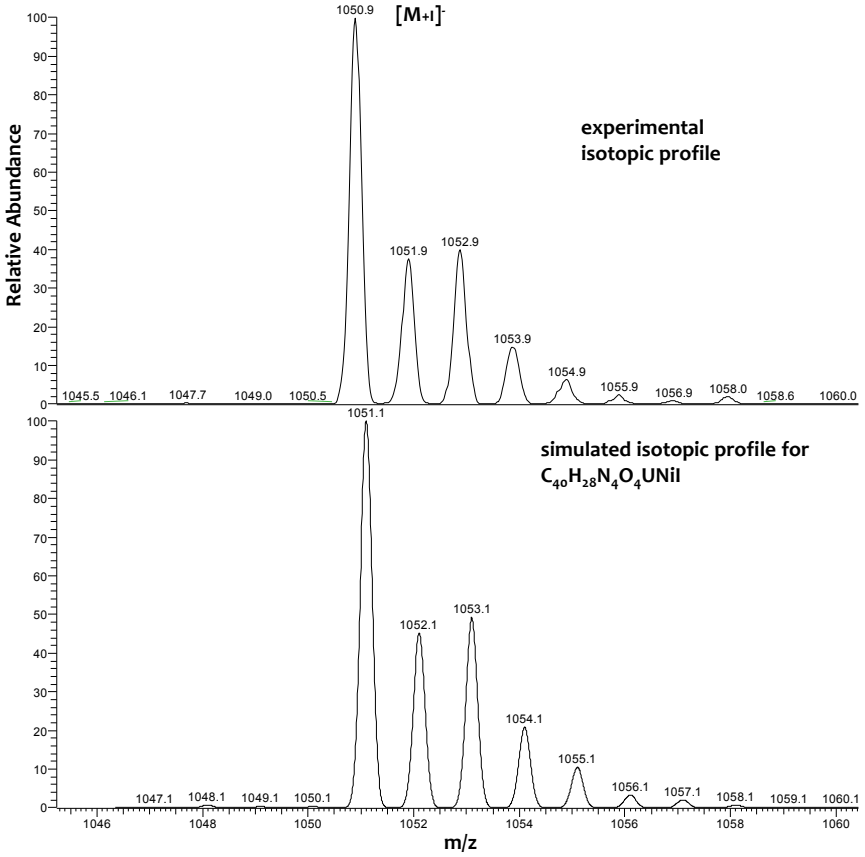


Figure S12. Experimental and simulated ESI-MS spectrum of [UNi(bis-salophen) + I]$^-$ (m/z Calcd for $C_{40}H_{28}N_4O_4UNiI$: 1051.1).



D. X-ray crystallography

Experimental details for X-ray data collections of all complexes are given in table S1. X-ray data can be obtained free of charge from the Crystallopgraphic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. CCDC numbers xxx. Figure Graphics are generated using MERCURY 2.4 Supplied with Cambridge Structural Database; CCDC: Cambridge, U.K., 2004-2009. Diffraction data for **2-py**, **4-2py**, **4-THF** and **5-THF** were taken using an Oxford-Diffraction XCalibur S or a Bruker APEX II CCD kappa geometry diffractometers (Mo-Kα radiation, graphite monochromator, λ = 0.71073 Å). The Bragg-intensities of **3** and **4-3py** were measured using Cu *K*α radiation on a Rigaku SuperNova dual system equipped with an Atlas CCD detector. To prevent evaporation of co-crystallised solvent molecules the crystals were coated with light hydrocarbon oil and the data were collected at 150 K or 100 K. The dataset were reduced and corrected for absorption with CrysAlisPro.[4] and then corrected for absorption.

The solution and refinement were performed by SHELXT.[5] The crystal structures were refined using full-matrix least-squares based on F^2 with all non hydrogen atoms anisotropically defined. Hydrogen atoms were found by Fourier transform and refined isotropically for **4-2py**, placed in calculated positions by means of the "riding" model for **2-py**, **3**, **4-THF**, **4-3py** and **5-THF**.

The crystal structure of **3** included, within the asymmetric unit, three THF solvent molecules. Two of them were correctly modelled, whereas the third one turned out to be highly disordered and, because of this, it was treated by the SQUEEZE algorithm of PLATON.[6] The crystal structure of **4-3py** displayed in the final model two pyridine molecules (as solvent). One of them was very disordered and it was treated by the split model in combination with some geometrical constraints (AFIX card) and rigid bond restraints (SIMU card), during the last stages of refinement.

Table S.1 Crystallographic parameters for complexes **2-5.**

Compound	**$[U_2$(bis-salophen)$(py)_6][I]_2$.3 py**, **2-py.3py**	**[UCo(bis-salophen)$(py)_2$] 4-2py**	**[UCo(bis-salophen)$(THF)_2$].1.5 THF 4-THF.1.5THF**	**[UNi(bis-salophen)$(THF)_2$]. 5-THF. 1.5 THF**
Formula	$C_{85}H_{73}N_{13}O_4I_2U_2$	$C_{50}H_{38}N_6O_4CoU$	$C_{56}H_{56}N_4O_{7.5}CoU$	$C_{54}H_{56}N_4O_{7.5}NiU$
Crystal size [mm]	0.43 x 0.34 x 0.06	0.38 x 0.22 x 0.09	0.42 x 0.37 x 0.27	0.17 x 0.10 x 0.08
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P 2_1/c	C 2/c	C 2/c	C 2/c
Volume [$Å^3$]	7864.2(8)	8466.5(3)	9138(5)	9151.8(4)
a [Å]	13.3578(11)	26.5567(6)	26.2903(17)	26.2314(8)
b [Å]	15.3976(7)	11.9483(2)	12.927(7)	12.9229(3)
c [Å]	38.2404(17)	26.6871(5)	27.0396(12)	27.1920(7)
α [°]	90	90	90	90
β [°]	90.910(5)	91.1024(16)	96.065(6)	96.858(3)
γ [°]	90	90	90	90
Z	4	8	8	8
Absorption coefficient [mm^{-1}]	4.958	4.267	3.965	4.008
F (000)	3984	4248	4696	4704
T [K]	150.0(1)	150(2)	150(2)	150(2)
Total no. reflexions	31445	25630	26327	28607
Unique reflexions [R(int)]	16050 [R(int) = 0.0671]	12885 [R(int) = 0.0341]	13941 [R(int) = 0.0474]	13862 [R(int) = 0.0485]
Final R indices [I>2σ(I)]	R1 = 0.0801, wR2 = 0.1345	R1 = 0.0369, wR2 = 0.0631	R1 = 0.0581 wR2 = 0.1055	R1 = 0.0467, wR2 = 0.0741
Largest diff. peak and hole [eA^{-3}]	2.35 and -2.29	1.163 and -0.827	2.382 and -1,368	1.114 and -1.166
GOF	1.108	1.022	1.058	1.027

Compound	**$[U_2$(bis-salophen)$Cl_2(THF)_2]$. THF, 3.THF**	**[UCo(bis-salophen)$(py)_3$].2py 4-3py.2py**
Formula	$C_{52}H_{52}N_4O_7U_2Cl_2$	$C_{65}H_{53}N_9O_4CoU$
Crystal size [mm]	0.145 x 0.109 x 0.079	0.138 x 0.109 x 0.098
Crystal system	Triclinic	Monoclinic
Space group	P 1	$P\,2_1/n$
Volume [$Å^3$]	5046(3)	5376.44(18)
a [Å]	11.7350(5)	11.6829(2)
b [Å]	19.9970(7)	23.5857(4)
c [Å]	22.9587(9)	20.1120(4)
α [°]	76.376(4)	90
β [°]	77.185(3)	104.034(2)
γ [°]	78.707(3)	90
Z	4	4
Absorption coefficient [mm^{-1}]	19.340	3.377
F (000)	2664.0	2628
T [K]	100.01(10)	100.01(10)
Total no. reflexions	38801	70018
Unique reflexions [R(int)]	20295 [R(int) = 0,0464]	13687 [$R_{(int)}$ = 0.0344]
Final R indices [I>2σ(I)]	R1 = 0.0449 wR2 = 0.0931	R_1 = 0.0277, wR_2 = 0.0543
Largest diff. peak and hole [eA^{-3}]	1.543 and -2.638	0.729 and -0.682
GOF	0.994	1.050

Table S2. Selected average bond lengths (Å) and angles (°) for compounds **1-3.**

Compound	U-N_{imino}	U-N_{amido}	U-$O_{phenolate}$	C-C_{link}	C-N_{amido}	C-N_{imino}
$[U(salophen)_2]$[3]	2.61(3)	/	2.22(1)	/	/	1.283(8)
Na_2[U(bis-salophen)][3] **1**	2.624(7)	2.387(8)	2.31(1)	1.559(7)	1.46(1)	1.298(3)

$[U_2$(bis-salophen)$(py)_6]I_2.(py)_3$ **2-py**	2.55(1)	2.44(2) and 2.662(3)	2.15(1)	1.599(15)	1.49(1)	1.303(3)
$[U_2$(bis-salophen)$(THF)_2Cl_2]$ **3**	2.559(5) and 2.484(5)	2.448(5) and 2.453(5)	2.156(4), 2.170(4), 2.135(5) and 2.154(4)	1.588(8)	1.467(7) and 1.482(8)	1.293(8) and 1.302(9)

Figure S13. Mercury diagram of the two independent molecules found in the structure of **3**. Ellipsoids at 50%. Hydrogen atoms and lattice solvent molecules omitted for clarity.

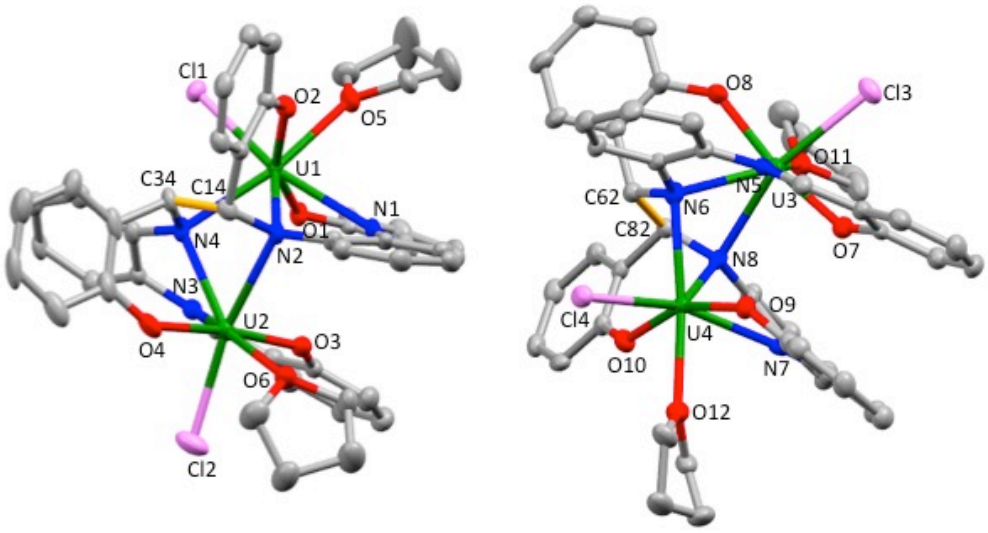
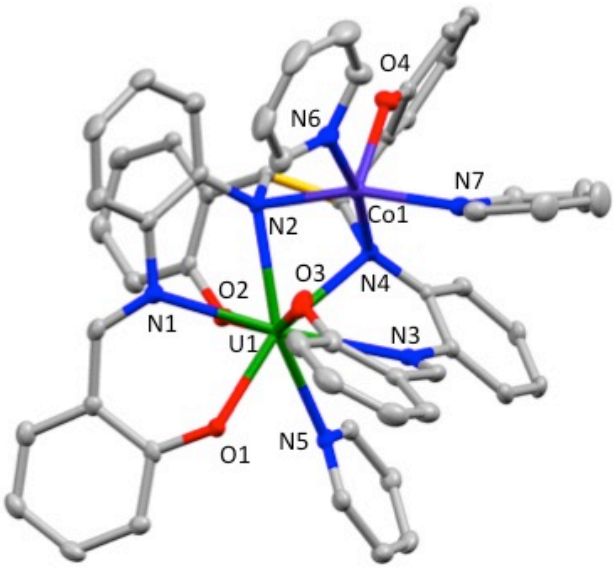
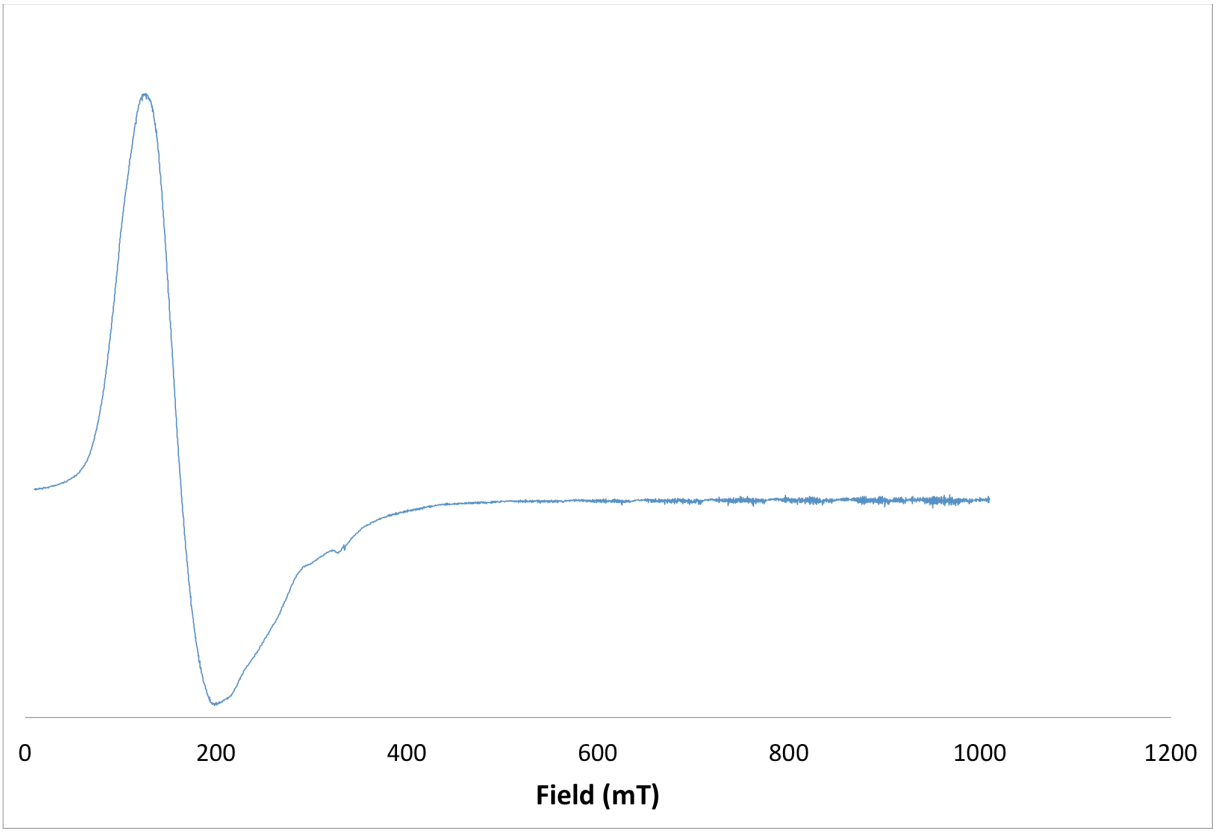


Figure S14. Mercury diagram of the structure of **4-3py**. Ellipsoids at 50%. Hydrogen atoms and lattice solvent molecules omitted for clarity.



E. EPR spectrum

Figure S15. X Band (9.40 GHz) EPR spectrum of the solid obtained from the reaction of **4-3py** with $^{13}CS_2$ in a toluene/hexane glass at 5 K (g = 4.04).



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2. (a)J. A. Hermann and J. F. Suttle, *Inorg. Synth.*, 1957, **5**, 143-145; (b)J. L. Kiplinger, D. E. Morris, B. L. Scott and C. J. Burns, *Organometallics*, 2002, **21**, 5978-5982.
3. C. Camp, V. Mougel, P. Horeglad, J. Pecaut and M. Mazzanti, *J. Am. Chem. Soc.*, 2010, **132**, 17374-17377.
4. CrysAlisPRO, Rigaku Oxford Diffraction, 2015.
5. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2015, 71, 3-8.
6. PLATON and A. L. Spek, *Acta Crystallogr., Sect. C*, 2015, 71, 9-18.