Supporting Information

for

Synthesis and Structural Characterization of a Uranyl(VI) Complex Possessing Unsupported Unidentate Thiolate Ligands

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Experimental Section

General Considerations. Unless otherwise stated all manipulations were conducted under an inert atmosphere of dry, oxygen-free dinitrogen in a MBraun Labmaster 130 glovebox equipped with a MB 20G purification system or in standard Schlenk-type glassware on a dual vacuum/dinitrogen line. Toluene, diethyl ether and hexanes (Fisher) were dried by passage through an MBraun solvent purification system (MB-SPS) consisting of one column of activated alumina and one column of activated copper catalyst (toluene, hexanes), or two columns of alumina (diethyl ether). Tetrahydrofuran (THF) was distilled over sodium benzophenone ketyl. ^{1}H NMR spectra (referenced to non-deuterated impurity in the solvent) were recorded on a Bruker AMX-250 or -300 spectrometer. Chemicals shifts are reported in ppm and all coupling constants are reported in Hz unless otherwise noted. Infrared spectra were obtained as a mull in a mixture of type NVH and type B immersion oil pressed between KBr plates on a Thermo Nicolet Nexus 670 FT-IR spectrometer. 2,6-dichlorobenzene thiol and NaH (Aldrich) were used as received. The uranyl precursors $UO_2Cl_2L_2$ (**1**) were synthesized according to literature procedures.[1]

Synthesis of $UO_2(S\text{-}2,6\text{-}Cl_2C_6H_3)_2L_2$ (2a). To a stirred THF solution of 2,6-dichlorobenzene thiol (60 mg, 0.33 mmol) was added NaH in THF (8.1 mg, 0.33 mmol). This solution was added slowly to a stirred solution of **1a** (116 mg, 0.17 mmol) in THF. The resulting red-brown solution was stirred 12 hr and evaporated to dryness, and the solid residue extracted with CH_2Cl_2 and filtered to remove insoluble salts. The volume of the solution was reduced to 2 mL and layered with hexanes (1 mL). Slow evaporation yielded red brown crystals of **2a**, which were washed with hexane and dried. Yield: 100 mg (63%). ^{1}H NMR (23 °C, C_6D_6): δ 0.79 (d, 12H, $^3J_{HH}$ = 7 Hz, CH(CH_3)$_2$), 1.10 (d, 12H, $^3J_{HH}$ = 7 Hz, NCH(CH_3)$_2$), 1.54 (d, 12H, $^3J_{HH}$ = 7 Hz, NCH(CH_3)$_2$),

2.38 (sept, 2H, $^3J_{HH}$ = 7 Hz, C*H*(CH_3)$_2$), 2.84 (sept, 2H, $^3J_{HH}$ = 7 Hz, NC*H*(CH_3)$_2$), 3.56 (sept, 2H, $^3J_{HH}$ = 7 Hz, NC*H*(CH_3)$_2$), 6.81 (t, 2H, $^3J_{HH}$ = 7 Hz, $Cl_2C_6H_3$, para), 7.32 (d, 4H, $^3J_{HH}$ = 7 Hz, $Cl_2C_6H_3$, meta). IR: ν(U=O) 912 cm^{-1}, ν(C=O) 1570 cm^{-1}.

Synthesis of UO_2(S-2,6-$Cl_2C_6H_3$)$_2L_2$ (2b). The procedure followed was analogous to that for **2a** above, using 70 mg (0.39 mmol) of 2,6-dichlorobenzene thiol, 9.4 mg (0.39 mmol) of NaH, and 145 mg (0.20 mmol) of **1b**. Yield: 179 mg (90%). ^{1}H NMR (23 °C, C_6D_6): δ 0.76 (t, 24H, $^3J_{HH}$ = 7 Hz, $NCH_2CH(CH_3)_2$), 1.51 (d, 12H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$), 1.75 (sept, 2H, $^3J_{HH}$ = 7 Hz, $NCH_2CH(CH_3)_2$), 2.62 (sept, 2H, $^3J_{HH}$ = 7 Hz, $NCH_2CH(CH_3)_2$), 2.84 (sept, 2H, $^3J_{HH}$ = 7 Hz, C*H*(CH_3)$_2$), 2.90 (d, 4H, $^3J_{HH}$ = 7 Hz, $NCH_2CH(CH_3)_2$), 3.74 (d, 4H, $^3J_{HH}$ = 7 Hz, $NCH_2CH(CH_3)_2$), 6.22 (t, 2H, $^3J_{HH}$ = 7 Hz, $Cl_2C_6H_3$, para), 7.33 (d, 4H, $^3J_{HH}$ = 7 Hz, $Cl_2C_6H_3$, meta). IR: ν(U=O) 912 cm^{-1}, ν(C=O) 1562 cm^{-1}.

Table S1. Summary of X-ray Crystallographic Data

	UO_2(S-2,6-$Cl_2C_6H_3$)$_2L_2$ (**2b**)
Empirical formula	$C_{36}H_{56}Cl_4N_2O_2S_2U$
Formula Weight	992.78
Space group	$P2_1/n$
a, Å	16.8244(14)
b, Å	15.2484(12)
c, Å	17.1435(14)
β, °	98.7500(10)
V, Å^3	4346.9(6)
Z	4
ρ_{calc}, g cm^{-3}	1.517
T, K	173(2)
μ, mm^{-1}	4.107
θ range, °	1.80-27.12
total reflections	30142
unique reflections	9534
parameters	452
R1	0.0221
wR2	0.0466
max, min peaks, e Å^{-3}	0.986, -0.775
GOF	1.041

References.

(1) Kannan, S.; Barnes, C. L.; Duval, P. B., *Chem. Commun.*, in press.

Figure S1. ^{1}H NMR spectrum of **2a**.

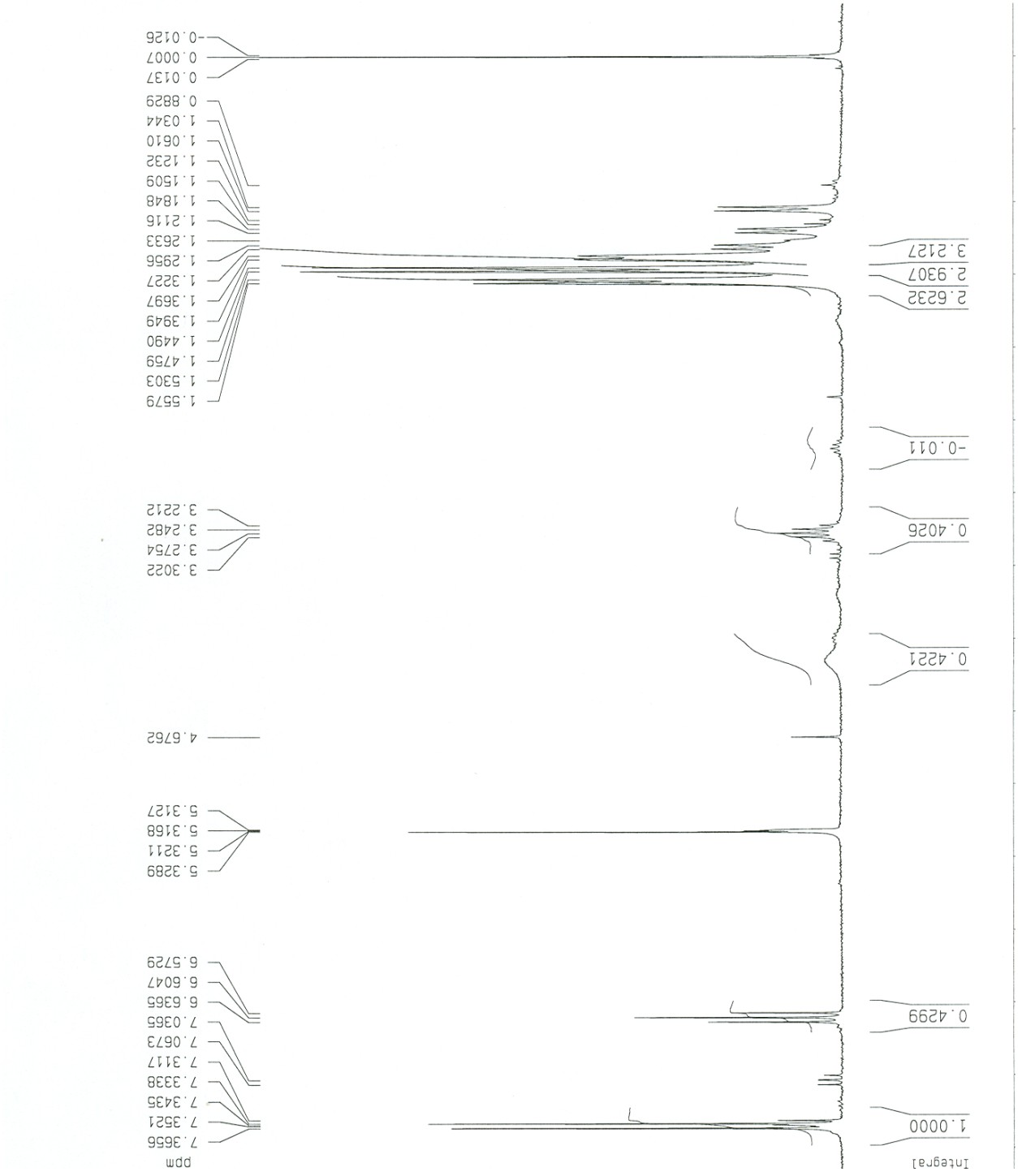

Figure S1. ^{1}H NMR spectrum of **2b**.