Supplementary Information

Unprecedented Detection of Inherent Chirality in Uranyl-Salophen Complexes.

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Syntheses of complexes

Compounds **2** and **3** were prepared according to the procedure described in Scheme 1.

3-Isopropylsalicilaldehyde, prepared from 2-isopropyl phenol (Aldrich) according to a general procedure,[1] showed spectral data in agreement with those described in the literature.[2] 1,2-diamino-3,4,5,6-tetramethylbenzene was prepared according to a literature procedure.[3] 1,2-diaminobenzene (Aldrich) was recrystallized from chloroform prior to use.

[[1-Phenylene[nitrilomethylidyne(2-hydroxy-3-isopropyl phenyl)]-2-phenylene[nitrilomethylidyne(2-hydroxyphenyl)]](2-)-N,N',O,O']dioxouranium (1) A solution of salicylaldehyde (0.46 mmol), 3-isopropylsalicilaldehyde (1 equiv), and 1,2-diaminobenzene (1 equiv) in 5 ml of MeOH was stirred at room temperature. After 30 min 1 equiv of $UO_2(OAc)_2 \cdot 2H_2O$ was added and the solution was stirred for additional 30 min. The reaction mixture was filtered and the pale orange precipitate was purified by flash chromatography (eluent chloroform/ethyl acetate 85:15) to separate **1** from other components of the statistical mixture. Yield 30 %; elemental analysis, calcd (%) for $C_{23}H_{20}N_2O_4U$: C, 44.10; H, 3.22; N, 4.47; found: C, 44.06; H, 3.41; N, 4.12; ^1H NMR (CD_3OD, 200 MHz): δ = 9.59 (s, 1H), 9.55 (s, 1H), 7.52-7.76 (m, 8H), 7,13 (d, 1H, J=8.28 Hz), 6.72-6.82 (m, 2H), 4.13 (m, 1H, J=6.92 Hz), 1.41 ppm (d, 6H, J=6.92 Hz); ^{13}C NMR (d_6-acetone ,75 MHz): δ = 171.1, 168.6, 167.3, 167.2, 166.8, 147.7, 147.6, 140.0, 136.4, 136.2, 133.6, 132.2, 129.2, 129.1, 124.9, 124.2, 121.5, 120.4, 117.4, 117.2, 26.7, 23.0 ppm.

2-[(2-Amino-phenylimino)-phenyl-methyl]-phenol A solution of 1,2-diaminobenzene (20.2 mmol), 2-hydroxybenzophenone (1 equiv), and *p*-toluenesulfonic acid (0.2 mmol) in 10 ml of toluene was refluxed in a Dean Stark apparatus for two days. After evaporation of the solvent the crude mixture was chromatographed on silica gel (light petroleum/ethyl acetate 75:25) to give the pure product as a yellow solid, mp 139-141 °C. Yield 43 %; elemental analysis, calcd (%) for $C_{19}H_{16}N_2O$: C, 79.14; H, 5.59; N, 9.72; found: C, 79.48; H, 5.69; N, 9.80; ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 14.39$ (s, 1H), 7.04-7.40 (m, 8H), 6.66-6.86 (m, 3H), 6.41 (t, 1H, J=7.73 Hz), 6.27 (d, 1H, J=7,73 Hz), 3.83 ppm (bs, 2H); ^{13}C NMR ($CDCl_3$,75 MHz): $\delta = 176.2$, 163.3, 140.2, 135.2, 134.9, 134.3, 133.3, 130.1, 129.3, 129.2, 126.8, 122.9, 121.0, 119.1, 119.0, 118.9, 116.1 ppm.

2-[(2-Amino-3,4,5,6-tetramethyl-phenylimino)-phenyl-methyl]-phenol A solution of 3,4,5,6-dimethyl-1,2-diaminobenzene (4.7 mmol), 2-hydroxybenzophenone (1 equiv), and p-toluenesulfonic acid (0.05 mmol) in 5 ml of *m*-xylene was refluxed in a Dean Stark apparatus for two days. On cooling, the pure product precipitated from the reaction mixture as a yellow solid, mp 212-214°C. Yield 73 %; elemental analysis, calcd (%) for $C_{23}H_{24}N_2O{\cdot}H_2O$: C, 76.21; H, 7.23; N, 7.73; found: C, 76.47; H, 7.10; N, 7.72; ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 13.9$ (bs, 1H), 7.15-7.39 (m, 6H), 6.96-7.08 (m, 2H), 6.74 (t, 1H, J=7.46 Hz), 4.0 (bs, 2H), 2.10 (s, 3H), 2.08 (s, 3H), 1.97 (s, 3H), 1.83 ppm (s, 3H); ^{13}C NMR ($CDCl_3$,75 MHz): $\delta = 135.7$, 134.2, 133.7, 133.4, 132.9, 132.1, 130.1, 129.7, 128.7, 128.5, 126.9, 126.1, 123.4, 120.7, 120.6, 119.5, 119.0, 17.4, 16.9, 16.7, 14.6 ppm.

General procedure for 2 and 3 A solution of the appropriate monoimine (0.43 mmol) and 3-isopropylsalicilaldehyde (1 equiv) in 5 ml of MeOH was stirred at room temperature. After 30 min 1 equiv of $UO_2(OAc)_2{\cdot}2H_2O$ was added and the solution was stirred for additional 30 min. The pure product precipitated from the reaction mixture as a pale orange solid.

[[1-Phenylene[E-nitrilomethylidynephenyl(2-hydroxyphenyl)]-2-phenylene[nitrilomethylidyne(2-hydroxy-3-isopropylphenyl)]](2-)-N,N',O,O']dioxouranium (2): yield 46 %; elemental analysis, calcd (%) for $C_{29}H_{24}N_2O_4U{\cdot}3H_2O$: C, 46.04; H, 4.00; N, 3.70; found: C, 46.37; H, 4.19; N, 3.59; ^1H NMR (CD_3OD, 200 MHz): $\delta = 9.69$ (s, 1H), 7.44-7.66 (m, 7H), 7.15-7.27 (m, 4H), 6.71-7.02 (m, 4H), 6.51 (t, 1H, J=7.53 Hz), 4.08 (m, 1H, J=6.83 Hz), 1.33-1.45 ppm (dd, 6H); ^{13}C NMR (acetone-d_6,75 MHz): δ = 165.7, 147.9, 145.8, 140.1, 139.1, 135.0, 134.2, 133.0, 132.8, 131.8, 130.5, 129.9, 128.8, 127.4, 127.0, 126.9, 125.8, 125.1, 124.4, 121.3, 120.1, 117.2, 117.1, 116.3, 26.9, 23.4 (bs), 22.6 (bs) ppm.

[[3,4,5,6-Tetramethyl-1-phenylene[E-nitrilomethylidynephenyl(2-hydroxyphenyl)]-2-phenylene[nitrilomethylidyne(2-hydroxy-3-isopropylphenyl)]](2-)-N,N',O,O']dioxouranium (3): yield 44 %; elemental analysis, calcd (%) for $C_{33}H_{32}N_2O_4U \cdot 3H_2O$: C, 48.77; H, 4.71; N, 3.45; found: C, 49.30; H, 4.23; N, 3.59; ^{1}H NMR (acetone-d_6, 200 MHz): δ =9.55 (s, 1H), 7.44-7.67 (m, 8H), 6.95-7.05 (m, 2H), 6.63 (t, 1H, J=7.56 Hz), 6.35 (t, 1H, J=7.50 Hz), 4.02 (m, 1H, J=6.83 Hz), 2.44 (s, 3H), 2.18 (s, 3H), 1.91 (s, 3H), 1.86 (s, 3H), 1.36 (d, 3H, J=6.97 Hz), 1.24 ppm (d, 3H, J=6.83 Hz); ^{13}C NMR (acetone-d_6, 75 MHz): δ = 168.5, 144.7, 139.7, 139.1, 134.8, 134.6, 134.5, 133.8, 132.8, 132.6, 131.5, 131.3, 130.8, 130.6, 130.0, 129.1, 128.0, 127.9, 124.9, 124.7, 123.2, 122.1, 121.2, 117.1, 115.8, 104.3, 26.7, 23.7, 22.6, 17.8, 16.8, 16.3, 16.2 ppm.

Calculation details

The structure of the uranyl-salophen complex reported in Figure 1 was calculated utilising the force field MM3 as implemented in Macromodel Version 6.0. The parameters introduced for uranium, uranyl oxygens, and phenoxide oxygens are given below. Partial atomic charges were computed using the electrostatic potential (ESP) from the wavefunction obtained by an AM1 calculation in SPARTAN Version 5.0.1, whilst charge +2 on the uranium and 0 on the oxygens were used for the uranyl cation. These parameters gave good agreement with the uranyl pentahydrate cation and with several X-ray structures of salophen-uranyl complexes.

Lines added in the file atom.typ

at_typ	at_no	at_wt	name	color	vdw_rad	deloc	cat del	1-3 eqv	el_neg	wild	UA root	no_H	pdb_name	1-3 slv	fchg
201	92	238.02890	U2	19	2.20	F	F	!	1.20	F	!	!	!	!	+2
202	8	15.99940	OU	16	1.50	T	T	OM	3.50	F	!	!	!	!	0
203	8	15.99940	OL	16	1.52	T	T	OM	3.50	F	!	!	!	!	0

Lines added in the file mm3.fld

Stretching Interactions

```
1  OU = U2            1.7310     8.4600     0.0000  0000 0000            A 1
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Bending Interactions

```
2  OU = U2 = OU        180.0000     0.1400     0.0000  0000 0000 0000        A 1
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Van der Waals Interactions

```
U2     2.4000     0.0500     0.0000     2.0000                    0000    A 2

OU      1.8200     0.0590     0.0000                              0000    A 1

OL     2.1500     0.0590     0.0000    -0.4000                    0000    A 2
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[2] Casiraghi, G.; Casnati, G.; Cornia, M.; Pochini, A. *Gazz. Chim. It.* 1978, **108**, 79.

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