







Compound	Avg Bond Length (Å)									
	MeO HN im	N _{pyr} - HO HMe	MeO-H	C=N _{im}	N _{pyr} -H	C=O	U=O _{yl}	M-N _{im}	M-N _{py}	M0
L1	2.215	1.949	0.85(2)	1.2827(18)	0.919(19)	1.2119(18)	-	-	-	-
L2	2.899	2.825	0.852(16)	1.4107(13)	0.884(15)	1.2129(14)	-	-	-	-
UO ₂ L1	-	-	-	-	-	1.238(2)	1.7739(9)	2.6952(15)	2.4377(15)	2.5575(13)
UO ₂ L2	-	-	-	-	-	1.2355(3)	1.774(2)	2.565(2)	2.4425(2)	2.6734 (19)
Zn_2L1_2	-	-	-	-	-	1.2119(18)	-	2.081(19)	1.958(19)	-
Cu ₂ L1 ₂	-	-	-	-	-	1.205(3)	-	2.048(2)	1.993(2)	-

Transition Metals

Upon metal addition the transitionmetal helicates self-assemble and adopt pseudo-tetrahedral geometries.

This binding motif is distinct from the uranyl complex (UO_2L1), despite similar radii across Cu²+, Zn²+, and UO²⁺ (87pm, 88pm, and 87pm respectively).





Figure 5. Asymmetric units of **Zn₂L1₂** and Cu₂L1₂ helicate complexes.

Synthesis and testing of selective 'pyrrophen' systems for visual uranyl detection

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coordinates to uranyl, even in competition with transition metals. Displacement of Zn^{2+} occurs even on addition of 0.5 equivalents UO_2^{2+} .

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Discussion

Industrial applications include the development of colorimetric sensors for radioactive aqueous environments. Enhanced uranyl detection methods contribute to recent demands for nuclear remediation.

Challenges in pyrrophen's development include binding competition among transition metals and matching the efficiency of current instrumental methods. Considering these constraints, the sensors must also meet the following criteria: rapid detection, selective binding, inexpensive production, and binary results.

The designed supramolecular ligand systems also provide insight on the fundamental properties of uranyl complexes. Pyrrophen's coordination offers distinct uranyl and transition metal binding motifs. The inclusion of softer donor atoms and stable planar geometry increases selectivity for UO_2^{2+} over usually-competitive transition metals.

Electrochemical data highlights more positive uranyl redox potentials in comparison to salophen complexes, demonstrating pyrrophen's advantageous "softer" binding.



Figure 2. Left: 50 µM (bottom) and 500 µM (top) solutions of L1 and metal complexes in 9:1 THF:MeOH. Right: Uranyl and zinc complexes of **L1**, 500 µM in ACN.







E (V vs Fc+/0) Figure 10. Cyclic voltammograms of a) UO₂L1 and Zn₂L1₂ and b) UO₂L2 and L2 (500uM in ACN 0.1M TBAPF₆ (scan rates in b normalized at 0.01 V/s – 0.05 V/s. ($A / v^{1/2}$)*1000 ; I = current (A), v =scan rate (V/s).

Pyrrophen

- The $UO_2^{2+/+}$ (U^{6+/5+}) redox couple is observed at $E_{1/2} = -1.27 \text{ V} (\Delta E)$ = 85 mV, QR).
- The $Zn_2^{2+/1+}$ redox couple is observed at $E_{1/2} = -1.18 \text{ V} (\Delta E =$ 250 mV, QR).

Dimethylpyrrophen

- The $UO_2^{2+/+}$ (U^{6+/5+}) redox couple is observed at $E_{1/2} = -1.28 \text{ V} (\Delta E = 90 \text{ V})$ mV, QR).
- The 10mV cathodic shift relative to UO_2L2 is a result of the electron donating methyl substituents.
- The reduction of the free ligand is observed at $E_{pc} = -1.94$ V

Uranyl redox couples of these species are significantly more positive than those of salophen species and are similar to those of macrocyclic species.

References

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