Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplemental Information for:

Synthesis of First Row Transition Metal Selenomaltol Complexes

Michael T. Spiegel, Amanda Hoogerbrugge, Shamus Truksa, Andrew G. Smith,

Kevin L. Shuford, Kevin K. Klausmeyer and Patrick J. Farmer*.

Baylor University, Waco TX 76798

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SM 1. Crystallographic Data

Supplemental Table 1. Crystallographic Data for $Fe(sma)_3$, $Ni(sma)_2$, $Zn(sma)_2$ and Hsma

	$Fe(sma)_3$	$Ni(sma)_2$	$Cu(sma)_2$	$Zn(sma)_2$	Hsma
Molecular formula	$C_{18}H_{15}O_6Se_3Fe$	$C_{12}H_{12}NiO_5Se_2$	$C_{12}H_{10}CuO_4Se_2$	$C_{12}H_{10}ZnO_4Se_2$	$C_6H_6O_2Se$
Formula weight	620.03	452.85	439.66	441.49	189.07
T/K	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Trigonal	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	R3c	$P2_1/c$	$P\ 2_1/c$	$P2_1/c$	$P2_1/c$
λ/Å (Mo Kα)	0.71073	0.71073	.71073	.71073	0.71073
a/Å	14.8261(12)	8.2986(6)	7.4765(3)	7.6565(3)	5.4980(2)
b/Å	14.8261(12)	24.7783(14)	13.1079(5)	23.8778(11)	8.8047(5)
c/Å	16.0571(13)	6.9641(5)	6.9501(2)	7.4531(3)	13.7294(7)
α/°	90	90	90	90	90
β/°	90	101.042(3)	100.9898(13)	91.8542(16)	100.429(2)
γ/°	120	90	90	90	90
V/Å^3	3056.7(6)	1405.48	668.63(4)	1361.87(10)	653.64(6)
Z	6	4	2	4	4
Density (Mg/M^3)	2.021	2.140	2.184	2.153	1.921
Crystal size, mm	.198x.184x.125	.136x.089x.020	0.242x0.113x0.083	.404x.141x.101	.293 x.14 x.116
Reflections collected	10165	15045	6801	14978	5861
Independent Reflections	1651	3482	1663	3370	1618
R(int)	0.0426	0.0946	.0212	0.0316	0.0281
Data/Restraints/Param	1651/1/86	3482/0/189	1663/0/89	3370/0/174	1618/0/87
GOF on F^2	1.129	1.028	1.144	1.067	1.054
R_1, wR_2 [I>2σ(I)]	0.0185, 0.0404	0.0399, 0.0552	0.0199, 0.0489	0.0222, 0.0477	0.0228, 0.0527
R_1, wR_2 [all data]	0.0195, 0.0406	0.0802, 0.0628	0.0218, 0.0499	0.0282, 0.0502	0.026, 0.0544
largest peak/hole difference, A^{-3}	.594 and -.190	.848 and -.742	0.600 and -.237	.486 and -.344	.477 and -.388

SM 2. Select data for reported structures

Supplemental Table 2: Select metal bond angles

Compound	O1-M-O2	Se1-M-Se2	Se1-M-O1	Se2-M-O2	Se1-M-O2	Se2-M-O1
$Zn(sma)_2$	120.00(6)	125.612(13)	89.89(4)	90.30(4)	116.58(5)	117.58(5)
$Cu(sma)_2$	180	180	88.74(4)	88.74(4)	91.26(4)	91.26(4)
$Ni(sma)_2$	85.81(11)	93.86(2)	90.44(8)	89.92(8)	176.10(8)	175.53(8)
$Fe(sma)_3$	91.42(9)	84.18(2)	80.51(6)	80.51(6)	107.21(6)	159.76(6)

Supplemental Table 3: Select metal ligand bond lengths

Compound	M-Se1	M-Se2	M-O1	M-O2
1 - Zn	2.2791(6)	2.2799(6)	1.879(3)	1.878(2)
2 - Cu	2.4002(2)	2.4002(2)	1.9108(13)	1.9108(13)
3 - Ni	2.2791(6)	2.2799(6)	1.879(3)	1.878(2)
4 - Fe	2.6114(6)	2.66146(6)	1.991(2)	1.991(2)

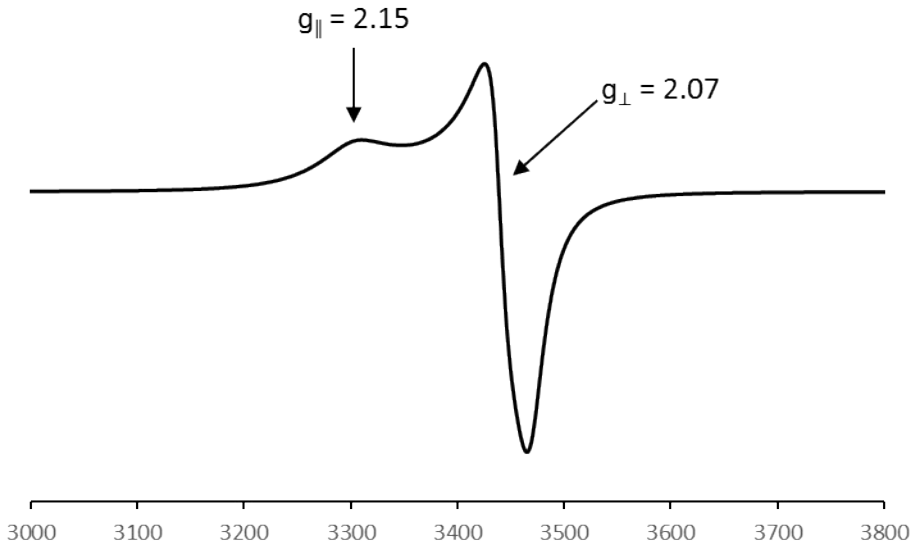
SM 3.

New synthesis of Htma

Analogous microwave method to that used for selenomaltol synthesis was used to generate thiomaltol. A 1:0.3 stoichiometric ratio of samples of maltol to Lawessons reagent were placed in anhydrous 1,4-dioxane in a 35 mL microwave reaction vessel. The resulting slurry was heated to 125 °C for 30 minutes in a microwave reactor. Water was added to the resulting black/orange mixture and the product was extracted with hexanes and subsequently evaporated to give a bright yellow powder. Purity was assessed by NMR and MS.

Synthesis of $Cu(tma)_2$

A sample of Htma was dissolved in ethanol. $Cu(OAc)_2$ was dissolved in water and stirred under nitrogen. The thiomaltol mixture was added drop wise to the copper solution to form a brown/green precipitate. The resulting mixture was filtered and washed with 5ml of hexanes twice and 5 ml of DI water and then left under vacuum to dry overnight.



Supplemental Figure 1. A crystalline powder sample of Cu(tma) was placed in an EPR tube and spectra were collected at room temperature. Conditions: microwave frequency 9.85 GHz, microwave power 2.00 mW, modulation amplitude 4.00 G, time constant 0.01 ms, sweep width 2000 G, sweep time 20.0 ms.