Synthesis, Structure, and Spectroscopy of New Thiopyrone and Hydroxypyridinethione Metal Complexes

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Supplementary Material

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Crystallization of Metal Complexes

[Ni(maltolato)$_2$(H$_2$O)$_2$]. Pale green crystals of [Ni(maltolato)$_2$(H$_2$O)$_2$] suitable for X-ray diffraction were grown by slow evaporation of a solution of the complex in a mixture of acetone and methanol. Five water molecules were found in the asymmetric unit. Two water molecules were found coordinated to the nickel(II) ion. The structure possesses crystallographically imposed symmetry with the nickel(II) ion on an inversion center. The hydrogen atoms in this structure were found in the difference map and therefore the position of all hydrogen atoms were refined isotropically.

[Co(thiomaltolato)$_2$]. Wine-red crystals of [Co(thiomaltolato)$_2$] suitable for X-ray diffraction were grown by slow diffusion of pentane into a solution of the complex in benzene. No solvent molecules were found in the unit cell.

[Cu(thiomaltolato)$_2$]. Wine-red crystals of [Cu(thiomaltolato)$_2$] suitable for X-ray diffraction were grown by slow evaporation of a solution of the complex in acetone. One water molecule was found in the asymmetric unit. The structure possesses crystallographically imposed symmetry with the copper(II) ion on an inversion center. The 2.46 e/Å^3 residual peak is located at 0.1466/0.2716/0.3471 (1.52 Å from O1).

[Zn(thiomaltolato)$_2$]. Yellow crystals of [Zn(thiomaltolato)$_2$] suitable for X-ray diffraction were grown by slow evaporation of a solution of the complex in acetone. No solvent molecules were found in the unit cell.

[Fe(3,4-HOPTO)$_3$]. Navy blue crystalline needles of [Fe(3,4-HOPTO)$_3$] suitable for X-ray diffraction structural determination were grown from layering a solution of the ligand, 3,4-HOPTO, dissolved in chloroform with a solution of iron(III) chloride hexahydrate dissolved in water. No solvent molecules were found in the unit cell. The structure possesses crystallographically imposed symmetry with the iron(III) ion on a 3-fold axis.

[Ni(3,4-HOPTO)$_2$]. Orange crystal plates of [Ni(3,4-HOPTO)$_2$] suitable for X-ray diffraction structural determination were grown from a solution of the complex dissolved in a mixture of DMSO and methanol diffused with ether. One molecule of methanol per complex cocrystallized with the [Ni(3,4-HOPTO)$_2$]. The hydroxyl hydrogen atom on the co-crystallized methanol molecule was found in the difference map and therefore its position was refined isotropically.

[Cu(3,2-HOPTO)$_2$]. Olive green crystals of [Cu(3,2-HOPTO)$_2$] suitable for X-ray diffraction structural determination were grown by slow evaporation from a solution of the complex dissolved in methanol. No solvent molecules were found in the unit cell.

[Zn(3,2-HOPTO)$_2$]. Light yellow crystals of [Zn(3,2-HOPTO)$_2$] suitable for X-ray diffraction structural determination were grown by slow evaporation from a solution with the complex dissolved in a mixture of methanol and acetone. No solvent molecules were found in the unit cell. The structure possesses crystallographically imposed symmetry with the zinc(II) ion on a 2-fold axis.

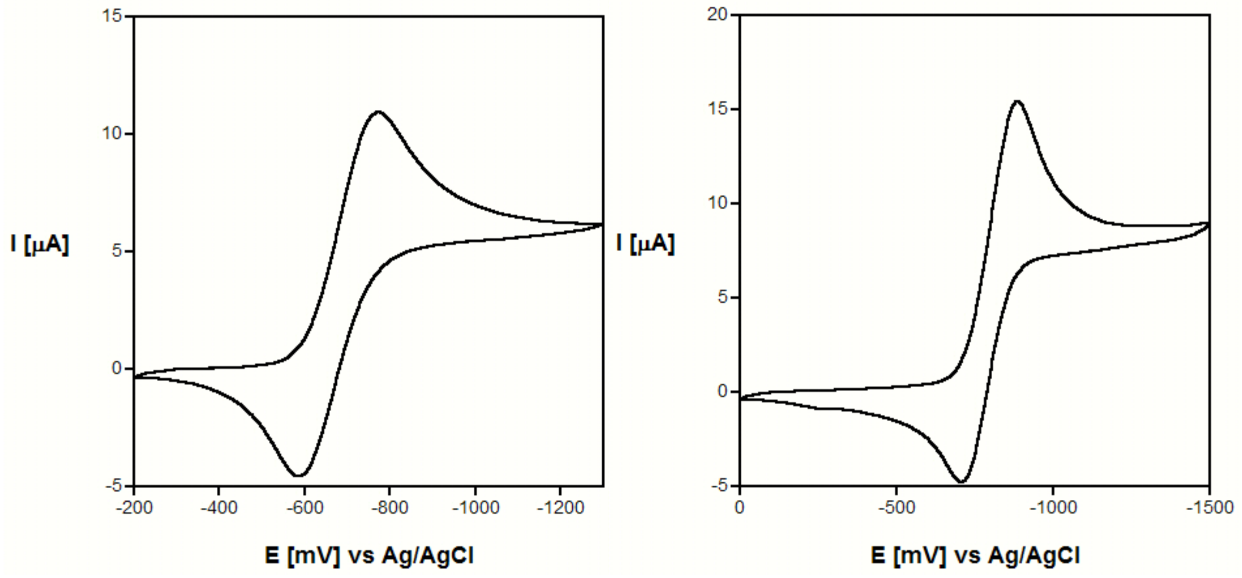

Figure S1. Cyclic voltammogram of [Cu(thiomaltolato)$_2$] (left) and [Cu(3,2-HOPTO)$_2$] (right) in CH_2Cl_2 (I = 0.1 M, scan rate = 50 mV s^{-1}, T = 25 °C).

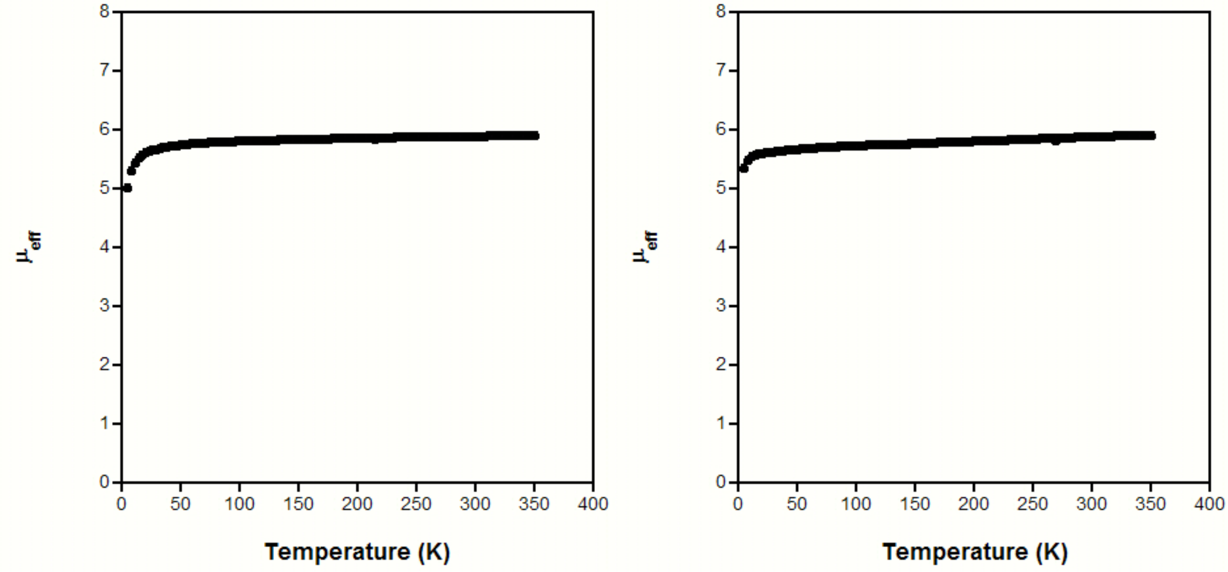

Figure S2. Temperature dependent magnetic moment (10 kG) of [Fe(3,2-HOPTO)$_3$] (left) and [Fe(3,4-HOPTO)$_3$] (right).

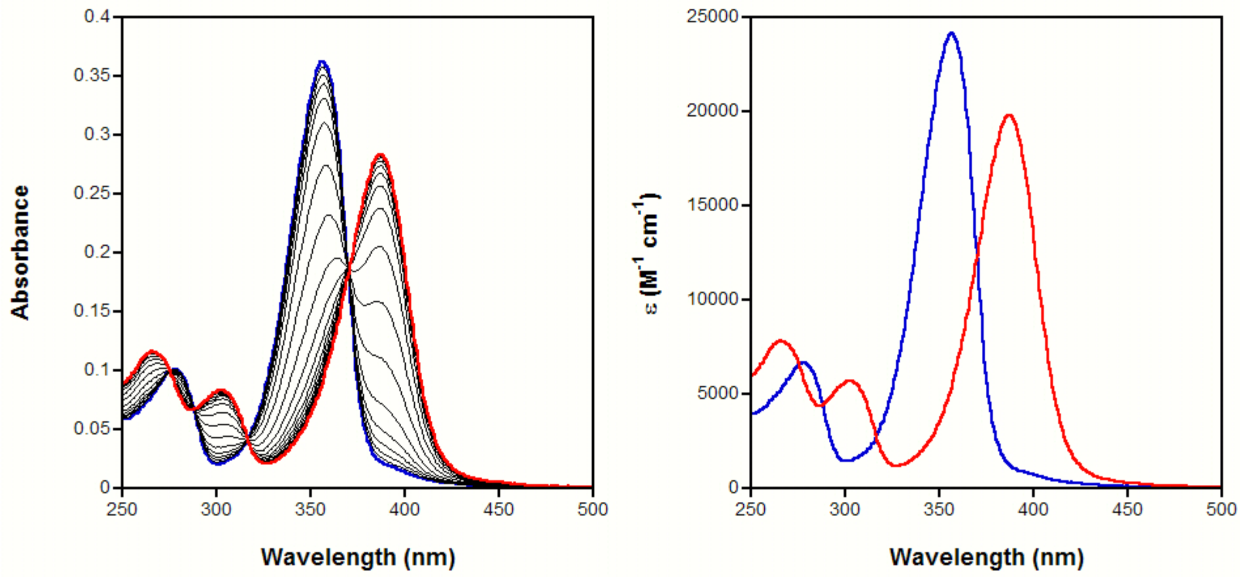

Figure S3. Experimental spectra (left) from a representative spectrophotometric titration of thiomaltol. The initial (low pH) spectrum is shown in blue and the final (high pH) spectrum is shown in red (*I* = 0.1 KCl; *T* = 25 °C). Calculated spectra (right) from factor analysis for protonated (blue) and deprotonated (red) thiomaltol.