

Helical coordination polymers and cyclic dimers formed from heteroleptic thioether-dipyrrinato copper(II) complexes†

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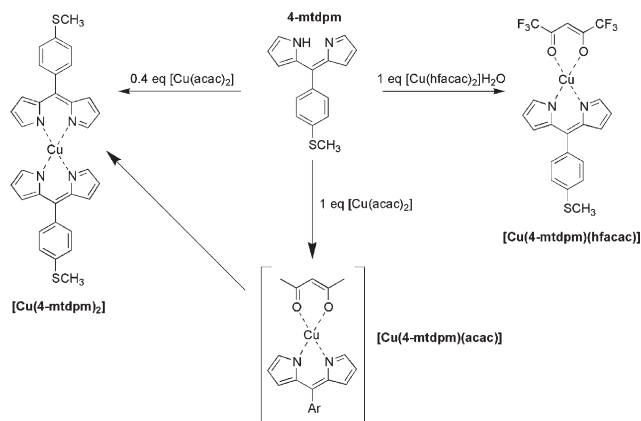
Heteroleptic copper complexes containing an acetylacetonato ligand and a thioether derivatized dipyrrinato ligand are shown to form oligomers and polymers in the solid state.

Coordination polymers represent a growing area of interest for the discovery of novel magnetic, electronic, and functionalized materials.^{1–3} Recently, dipyrrromethene (dipyrrin) complexes of copper(II) were found to form a variety of coordination polymers with several interesting morphologies.^{4,5} These polymers are constructed from self-complementary, heteroleptic copper(II) complexes containing a heteroditopic dipyrrinato ligand and an acetylacetonato (acac) ligand. Some of the compounds identified were found to trap volatile solvents,⁴ while others formed extremely unusual structures containing both discrete and extended chain components.⁵ One limitation of the systems described in these earlier studies is that only a single functional group, a *meso*-pyridyl substituent, was found to mediate formation of polymeric structures. Attempts to use other ligands, such as nitrile donors, failed to form any oligomeric structures.⁴ Herein, two new heterotopic dipyrrin ligands are described that form a self-complementary helical coordination polymer and a cyclic dimer with copper(II).

The heteroleptic dipyrrin complexes described to date result from the formation of a square planar coordination sphere established by the dipyrrin and acac chelates around a copper(II) center. The polymeric compounds are then connected by axial attachment of a peripheral donor atom found at the *meso* position of the dipyrrinato ligand from a neighboring metal complex; this generates a square pyramidal coordination environment around the copper(II) ion.^{4,5} Thioether groups are not particularly strong ligands; however, the coordination of this moiety to transition metals is well documented.⁶ In order to determine whether thioether substituted dipyrrins could form coordination polymers, the ligand 5-(4-methylthiophenyl)dipyrrromethene (4-mtdpm) was synthesized according to literature procedures.^{4,7} Complexation of 4-mtdpm with Cu(acac)₂ resulted in formation of the desired heteroleptic complex [Cu(4-mtdpm)(acac)], but this complex proved unstable (Scheme 1) and decomposed to the homoleptic [Cu(4-mtdpm)₂], which does not form a coordination polymer, consistent with earlier studies on related homoleptic complexes.^{4,†}

In order to obtain a stable, heteroleptic complex, Cu(hfacac)₂ (hfacac = hexafluoroacetylacetonato) was used to prepare the complex [Cu(4-mtdpm)(hfacac)]. Use of the fluorinated hfacac ligand was found to stabilize the heteroleptic [Cu(4-mtdpm)(hfacac)] complex, which was isolated without difficulty by silica column chromatography as a red solid.

Slow evaporation of a solution of [Cu(4-mtdpm)(hfacac)] from CH₂Cl₂ generated red crystals. X-Ray diffraction structural characterization shows the complex has a square pyramidal coordination geometry (Fig. 2).[†] The square plane of the coordination sphere is made up of the dipyrrin (Cu–N 1.94 Å) and hfacac (Cu–O 1.99 Å) chelates. The apical position of the



Scheme 1 General synthesis of (dipyrrinato)copper(II) complexes.

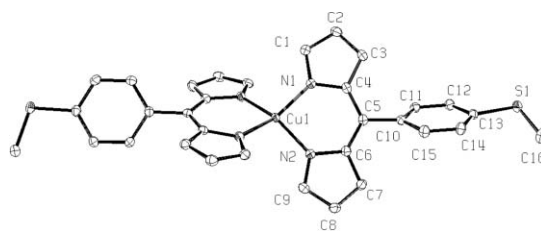


Fig. 1 Structural diagram of [Cu(4-mtdpm)₂] with partial atom numbering schemes (ORTEP, 50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

coordination sphere is occupied by the sulfur atom from the thioether moiety of a neighboring complex. The Cu–S bond length is 2.78 Å, which is long compared to most thioether–copper(II) interactions found in the Cambridge Crystallographic Data Centre (~2.3–2.5 Å). Nevertheless, several examples of long Cu–S interactions with thioether ligands have been described when coordinated axially.^{8–10}

Like earlier described pyridyl-containing dipyrrins, [Cu(4-mtdpm)(hfacac)] generates a 1-dimensional coordination polymer in the solid state. The polymer chains orient along the crystallographic *c*-axis and display a helical topology. The hfacac groups are directed out to the periphery of the polymer backbone, where they are displayed toward other hfacac groups from neighboring polymer chains. This packing arrangement, where a layered structure is formed from the localization and interdigitation of hfacac groups (Fig. S1[†]), suggests that self-segregation of these groups has a substantial influence on the packing of the polymer chains in the crystal lattice. This tendency of fluoroalkanes to phase separate has been observed in other self-assembling structures both in solution and the solid-state.^{5,11} Thermal gravimetric analysis (TGA) showed no weight loss up to ~175 °C, suggesting that the coordination polymer is thermally stable to this temperature.

In order to further probe this new polymer motif, the compound [Cu(3-mtdpm)(hfacac)] was prepared (3-mtdpm = 5-(3-methylthiophenyl)dipyrrromethene).^{7,12,13} The complex was

† Electronic supplementary information (ESI) available: synthesis, characterization, and crystallographic details for all compounds. See <http://www.rsc.org/suppdata/cc/b4/b411991f>

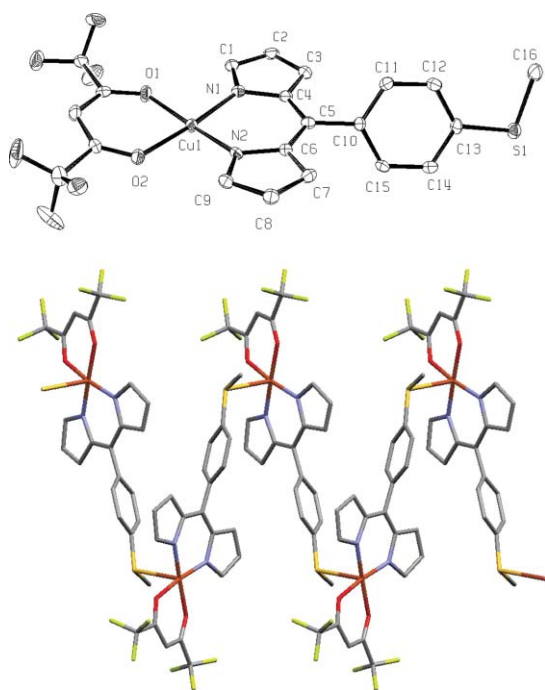


Fig. 2 Structural diagram of [Cu(4-mtdpm)(hfacac)] with partial atom numbering schemes (ORTEP, 50% probability ellipsoids). Hydrogen atoms, solvent molecules, and axial thioether ligation have been omitted for clarity (top). Stick representation (bottom) shows the 1-dimensional coordination polymer formed by the complex.

crystallized and the solid-state structure of [Cu(3-mtdpm)(hfacac)] shows the desired heteroleptic complex; however, to our surprise, the compound does not form a coordination polymer.[‡] Instead, this compound forms a head-to-tail cyclic dimer, connected through axial thioether ligands (Fig. 3). The coordination environment around the metal center is similar to [Cu(4-mtdpm)(hfacac)] with Cu–N distances of 1.94 Å and Cu–O distances of 1.97 Å. The dimer is held together by weak interactions, with the thioether moiety binding in the axial position of the coordination sphere, as found in [Cu(4-mtdpm)(hfacac)]. The Cu–S distance in [Cu(3-mtdpm)(hfacac)] is 2.86 Å, which is slightly longer than that found in the coordination polymer [Cu(4-mtdpm)(hfacac)]. A recently reported complex with 2,8-diethyl-1,3,7,9-tetramethyl-5-(2-pyridyl) dipyrromethene and zinc(II) ions forms a related cyclic binuclear structure.¹⁴

As mentioned above, the heteroleptic complex [Cu(4-mtdpm)(acac)] was found to rearrange to [Cu(4-mtdpm)₂] during isolation. We have found that the stability of these heteroleptic complexes depends strongly on the nature of the acac ligand, the peripheral *meso* donor on the dipyrin ligand, and the presence of absorbents such as alumina.^{4,15} Freshly prepared CH₂Cl₂–benzene (1 : 1) solutions of 4-mtdpm were combined with one equivalent of different copper(II) sources to generate [Cu(4-mtdpm)(acac)], [Cu(4-mtdpm)(tfacac)] (tfacac = trifluoroacetylacetonato), and [Cu(4-mtdpm)(hfacac)]. The reaction mixtures were stirred at room temperature and examined by UV–visible spectroscopy to evaluate the stability of each complex. Immediately after addition of the copper(II) sources, the expected heteroleptic complexes were formed as evidenced by a characteristic charge-transfer band centered at ~492 nm.⁴ After stirring for ~1 h, the solution containing [Cu(4-mtdpm)(acac)] had started to form [Cu(4-mtdpm)₂], which was identified by a new transition at ~467 nm. By ~17 h a stable equilibrium mixture of both the homo- and heteroleptic complexes was achieved. Complexes of [Cu(4-mtdpm)(tfacac)] and [Cu(4-mtdpm)(hfacac)] showed no change in electronic spectra over the same time period. These data indicate that the more electron-withdrawing fluorinated acac ligands stabilize these heteroleptic complexes, an observation that may

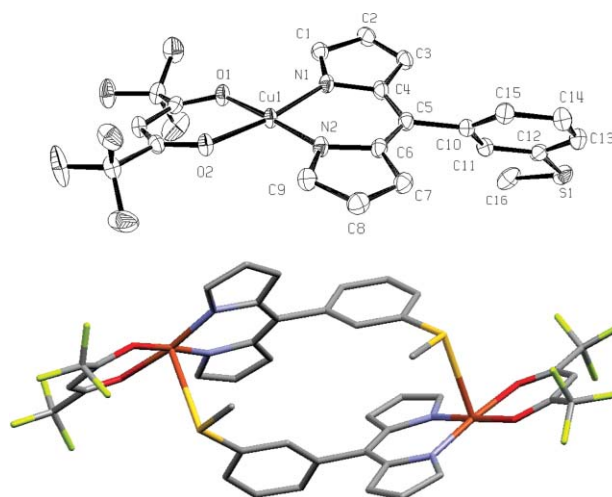


Fig. 3 Structural diagram of [Cu(3-mtdpm)(hfacac)] with partial atom numbering schemes (ORTEP, 50% probability ellipsoids). Hydrogen atoms, solvent molecules, and axial thioether ligation have been omitted for clarity (top). Stick representation (bottom) shows the head-to-tail dimer formed by the complex (viewed down the crystallographic *b*-axis).

prove useful in the preparation of related complexes and supramolecular structures. The compounds presented here show that small perturbations in ligand structure can lead not only to the formation of mononuclear and polymeric structures, as previously reported,⁴ but also discrete oligomeric structures. The stabilization of these heteroleptic complexes by electron-withdrawing spectator ligands has also been established. We anticipate that these findings will aid in the discovery of interesting solid-state topologies based on these dipyrin motifs.

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[‡] CCDC 246586–246588. See <http://www.rsc.org/suppdata/cc/b4/b411991f/> for crystallographic data in .cif or other electronic format.

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