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Triggering Redox Activity in a Thiophene Compound: Radical Stabilization and Coordination Chemistry


Abstract: The synthesis, metalation, and redox properties of an acyclic bis(iminothienyl)methene L− are presented. This π-conjugated anion displays pronounced redox activity, undergoing facile one-electron oxidation to the acyclic, metal-free, neutral radical L• on reaction with FeBr2. In contrast, reaction of L• with CuI forms the unique, neutral Cu2I2(L−) complex of a ligand-centered radical, whereas reaction with the stronger oxidant AgBF4 forms the metal-free radical dication L2+.

Since the first reports on dithiolate metal complexes,[1] interest in redox-active ligands has burgeoned due to their relevance to enzymatic processes[2] and access to unusual chemical properties by coupling the redox activity of the ligand to the coordination chemistry of a metal.[3] In these cases, the ligand is no longer a classical “spectator”,[4] and a large number of ligands have been shown to exhibit redox activity and stabilize the radical species through an inductive effect or by delocalization in a conjugated π-system.

Accordingly, we have shown that an N-donor-expanded dipyrrin ligand[5] is redox active and able to mediate sequential electron transfer to a uranyl(VI) center (Figure 1). The initial reduction occurs at the ligand, forming a U(VI) ligand-centered radical prior to reduction of the uranyl center, ultimately to U(IV).[6] Ligand-centered oxidation was also seen in Ni complexes of a similar bis(phenolate)dipyrrin ligand, with the one-electron oxidation product characterized as a ligand-centered radical.[7]

In contrast to the nitrogen-containing heterocycles found in dipyrrins, porphyrinoids and sub-porphyrins,[8] studies on the redox activity of sulfur-containing heterocycles such as thiophene are more limited,[9] despite their use in tuning the electronic properties of molecular compounds[10] and polymeric materials.[11] Expanded porphyrinoids featuring five thiophene units undergo single-electron oxidations, from the aromatic mono-anion to an isolable, air-stable neutral radical, and further to an anti-aromatic mono-cation.[12] In contrast, radical cations of simple thiophenes or their analogues are stable only at low temperatures or their identity inferred from quenching reactions.[13, 14] We were keen to see if we could exploit redox activity and the ‘softer’ donor properties of the sulfur atoms in methylene-bridged thiophenes to access new transition-metal chemistry and reactivity. As such, we show here that the bis(iminothienyl)methene L− reacts with metal salts to generate the neutral radical L•; the dicatonic radical L2+[15] or the dinuclear copper(I) complex Cu2I2(L−) of a ligand-based iminothienyl radical.

Studies on the meso-C lithiation of dithiophenemethane compounds have found thermodynamic versus kinetic selectivity issues along with the formation of meso-C coupled products.[16] However, we find that deprotonation of HHL with KH in THF selectively forms the highly moisture-sensitive potassium salt KL as green crystals in high yield (Scheme 1).

The X-ray structure reveals a dimeric structural motif in the solid state (Figure 2). The two imino-thiophene ligands adopt a dinuclear mesocate arrangement at the K centers. The K-S distances appear long (> 3.3 Å), but as no other K-S(thiophene) compounds exist no comparisons can be made. The deprotonated ligand shows extended π-conjugation, evident from the planar arrangement of the ligand components linked by the sp2 hybridized meso-carbon C10; the dihedral angle between iminothienyl planes is 59° and the C9-C10 and C10-C17 distances are shortened by 0.1 Å in comparison to the sp3-hybridized HHL (SI). This unusual dinuclear coordination motif is likely related to the large separation of the imine nitrogen donor
atoms (N1…N2 = 7.357(1) Å) as a consequence of incorporating the thiophene heterocycles. This is evidenced by comparison with the X-ray crystal structure of the analogous potassium iminodipyrrin K[L(12)] in which the K cation is coordinated to all four N atoms of the ligand, with an imino N1…N4 separation of 5.513(2) Å (Figure S18).

The neutral thiophene radical has been reported to date by taking FeBr2 did not lead to the metathesis product FeBr(=)C6H4, as the two iminothienyl planes are coplanar (torsion angle of 2.2°), suggestive of extended conjugation across the molecule. The radical nature of L• is supported by its fluid-solution EPR spectrum in CH3CN, which shows a resonance at g = 2.0034, consistent with an organic radical (Figure 5). The weakly resolved hyperfine arises from coupling of the unpaired electron to six 1H (I = 1/2) and two 14N (I = 1) nuclei, simulated with A1H = 3.02 × 10–4 cm–1 and three sets of protons, A1N = 1.43, 1.24, 0.71 × 10–4 cm–1, and consistent with the calculated spin-density distribution (Figure 5). EPR spectra of samples diluted in CH2Cl2, toluene and THF suffer from perturbed molecular tumbling which leads to line broadening that conceivably arise from either the presence of the ligand radical L• and two Cu(I) centers, or from an anionic ligand with delocalized Cu(I)/Cu(II) mixed-valence cations. While mixed-valence Cu complexes have been reported and seen for the five other Cu-thiophene complexes,17 Electron Localization Function (ELF) calculations suggest that no covalent bond interaction between S and Cu occurs as the lone-pair character on S is directed away from the Cu center adopting a distorted trigonal pyramidal geometry with the thienyl-S atom axial and imino-N and bridging-I atoms equatorial (Figure 3, right). As with K and L•, the meso-carbon C10 is sp2 hybridized with the two iminothienyl fragments essentially coplanar (7.9°). While the Cu-S distance is within the range (2.336 – 3.014 Å) seen for the five other Cu-thiophene complexes,18 the fluid-solution EPR spectrum of Cu2I2(L•) shows a resonance at g = 1.9958 that is consistent with a ligand-based radical. The lowering of the g-value compared to L• is ascribed to spin-orbit contributions from the copper atoms which reduce all g-values to slightly less than gN, as described by the frozen-solution spectrum (Figure S8). The lack of hyperfine structure may stem from overlapping coupling to the many spin-active nuclei (1H, 14N, 63,65Cu, 121I) in the system. Interestingly, the EPR spectrum in CH2CN is similar to that of the radical L•, showing that the complex is labile in strong donor solvents (Figure S9).

The reaction between KL and CuI results in both a precipitate of Cu and reduction of Cu(I) to Cu metal but, unlike the reaction with Fe, the metalated product Cu2I2(L•) is isolated from toluene as a red powder. The solid-state structure was determined by X-ray crystallography and confirms its dinuclear nature16 with each Cu center adopting a distorted trigonal pyramid geometry with the thienyl-S atom axial and imino-N and bridging-I atoms.

The availability of KL allowed reactions with transition metal salts to be explored (Scheme 1). The reaction between KL and FeBr2 did not lead to the metathesis product FeBr(L•) but instead results in the neutral, toluene-soluble, metal-free radical L•. This highlights the poor coordinating ability of the thiophene ligand compared to its dipyrrole analogue. The radical L• is isolated as dichroic yellow/green crystals from toluene and its solid-state structure determined (Figure 3, left), from which it is clear that the meso-carbon C10 is sp2 hybridized with delocalized C9-C10 and C10-C17 bonds. Furthermore, the two iminothienyl planes are coplanar (torsion angle of 2.2°), suggestive of extended conjugation across the molecule. The radical nature of L• is supported by its fluid-solution EPR spectrum in CH3CN, which shows a resonance at g = 2.0034, consistent with an organic radical (Figure 5). The weakly resolved hyperfine arises from coupling of the unpaired electron to six 1H (I = 1/2) and two 14N (I = 1) nuclei, simulated with A1H = 3.02 × 10–4 cm–1 and three sets of protons, A1N = 1.43, 1.24, 0.71 × 10–4 cm–1, and consistent with the calculated spin-density distribution (Figure 5). EPR spectra of samples diluted in CH2Cl2, toluene and THF suffer from perturbed molecular tumbling which leads to line broadening that conceivably arise from either the presence of the ligand radical L• and two Cu(I) centers, or from an anionic ligand with delocalized Cu(I)/Cu(II) mixed-valence cations. While mixed-valence Cu complexes have been reported and are seen for the five other Cu-thiophene complexes,17 Electron Localization Function (ELF) calculations suggest that no covalent bond interaction between S and Cu occurs as the lone-pair character on S is directed away from the Cu center adopting a distorted trigonal pyramid geometry with the thienyl-S atom axial and imino-N and bridging-I atoms equatorial (Figure 3, right). As with KL and L• the meso-carbon C10 is sp2 hybridized with the two iminothienyl fragments essentially coplanar (7.9°). While the Cu-S distance is within the range (2.336 – 3.014 Å) seen for the five other Cu-thiophene complexes,18 the fluid-solution EPR spectrum of Cu2I2(L•) shows a resonance at g = 1.9958 that is consistent with a ligand-based radical. The lowering of the g-value compared to L• is ascribed to spin-orbit contributions from the copper atoms which reduce all g-values to slightly less than gN, as described by the frozen-solution spectrum (Figure S8). The lack of hyperfine structure may stem from overlapping coupling to the many spin-active nuclei (1H, 14N, 63,65Cu, 121I) in the system. Interestingly, the EPR spectrum in CH2CN is similar to that of the radical L•, showing that the complex is labile in strong donor solvents (Figure S9).

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within the N$_2$S$_2$ molecular cleft and interacts with the imine nitrogen atoms with approximate distances of 2.78 Å (N1···F1) and 2.88 Å (N2···F3). The EPR spectrum of L’(BF$_4$)$_2$ is simulated with $g = 2.0037$, which is identical to L’. However, the hyperfine splitting pattern is less congested and the spectral profile was modelled with coupling to the $^{14}$N nucleus ($A^N = 2.38 \times 10^{-4}$ cm$^{-1}$) and three protons ($A^H = 3.22, 1.10, 0.70 \times 10^{-4}$ cm$^{-1}$) of one iminothienyl arm. The spin-density distribution calculated for L’$^{2+}$ (Figure 5) corroborates this spectrum, showing spin density on one thiophene-imine arm only due to the twist at the meso-carbon atom (dihedral angle 50.9°) in the optimized structure. This calculated structure is different to that seen in the X-ray crystal structure of L’$^{2+}$ which is planar, presumably due to the presence of the BF$_4^-$ counter-ion which interacts with both imine nitrogen atoms.

Upon deprotonation of HL to form KL, an intense band at 654 nm appears (Figure 5), and is similar, although red-shifted, to the HOMO-LUMO transition in related dipyrromethene compounds, the band seen at 295 nm is indicative of re-protonation of KL and highlights its sensitivity to water. Oxidation of KL to the radical L’ results in a considerable hypsochromic shift of the low-energy absorption band, from 654 to 456 nm, which is explained by an increase in the SOMO($\alpha$)-LUMO($\alpha$) gap from TD-DFT calculations, from 4.41 keV in KL to 5.41 keV in L’.

Incorporation of the dinuclear core in Cu$_2$I$_2$(L’) leads to the appearance of additional absorption bands, in particular a broad absorption at 826 nm (765 nm in the calculated spectrum) mainly involving the SOMO($\beta$)-LUMO($\beta$) transition. Although the UV-vis spectra are generally well-modeled by TD-DFT simulations, the transitions in Cu$_2$I$_2$(L’) involve the participation of a multitude of orbitals and cannot be straightforwardly assigned.

While the cyclic voltammogram (CV) of HL displays a single irreversible reduction at $E_{re} = –1.46$ V versus ferrocene (Figure S11), the CV of KL consists of two reversible events, with an oxidation at $–0.12$ V and a reduction at $–1.33$ V (Figure 6). These are complimentary to the reduction wave at $–0.02$ V in the CV for L’, together with another reduction at $–1.38$ V, assigned by linear-sweep voltammetry; in this case, the data profiles are skewed, indicating quasi-reversibility in the redox properties of L’ and may also be due to a lower electrolyte concentration than for KL (0.1 M vs 0.14 M). In Cu$_2$I$_2$(L’) the general features of KL and L’ are retained, with two similar reductions seen at $+0.07$ V and $–1.00$ V; a new irreversible oxidation at $+0.83$ V is also seen and is tentatively assigned to Cu$^{2+}$/Cu$^+$ oxidation. These data, along with the computed electronic structures, show that the redox reactivity seen in Cu$_2$I$_2$(L’) is primarily ligand-based.
We have shown that the thiophene analogue of a N-donor expanded dipyrrin exhibits rich radical chemistry, forming the unusual, isolable neutral radical L−, its dicopper complex Cu2L2(L−), and the radical dication L2+. The radical chemistry of thiophenes and their complexes is relatively unexplored and primarily limited to examples in which the radical is stabilized within a macrocyclic framework. As such, this work provides the first insight into new thiophene coordination chemistry which, thanks to the redox activity of this ligand framework, could potentially lead to metal complexes with an internal electron reservoir for redox chemical processes.

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Keywords: thiophene • redox-active ligand • density functional theory • dinuclear copper • X-ray crystallography

Figure 6. Comparison of CV data for KCL (top), L+ (middle), and Cu2L2(L−) (bottom); glassy carbon working electrode, platinum gauze counter electrode, silver wire pseudo-reference electrode, 100 mV s−1, referenced to Fc/Fc+, 1 mM analyte, 0.1 M – 0.14 M [Cu2I2(L−)].


