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Nickel Dithiolene Chelate Rings in a New Role as η^5-Coordinating Ligands: Synthesis, Structural Characterization, and Redox Reactivity of an "Fe_2Ni" Bis-Double-Decker

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A bis-double-decker complex has been assembled from the nickel bisdithiolene complex $[Ni(S_2C_2Me_2)_2]^{1-/2-}$ and two $[Cp^*Fe]^+$ units ($Cp^* = C_5Me_5$). The complex, $[(\eta^5\text{-}Cp^*\text{-}Fe\text{-}\mu\text{-}\eta^5,\eta^5\text{-}((S_2C_2Me_2)_2Ni)Fe\text{-}\eta^5\text{-}Cp^*]^n$ (**1**^{n}), was isolated in two charge states ($n = 0, 1$). The structure of **1**$^+$ was confirmed by X-ray crystallography for **1**$^+PF_6^-$ and **1**$^+BF_4^-$, and it shows the nickel bisdithiolene units π-donating to iron centers. Both salts crystallize in a centrosymmetric space group (center of inversion at nickel). Computational (density functional theory) data indicate a highly delocalized spin density for **1**$^+$. The reaction of **1** with 1 or 2 equiv of HBF_4 leads to oxidation to form **1**$^+$ or **1**$^{2+}$, respectively. On an electrochemical time scale, reversibility is observed for the redox series **1**/**1**$^+$/**1**$^{2+}$, with an additional slower step for oxidation of **1**$^{2+}$.

Although transition-metal bisdithiolene complexes have been studied for decades, new properties and novel applications continue to be discovered. Bisdithiolene complexes show rich thermal[1] and photochemical[2] behavior. In comparatively recent work, bisdithiolenes have been considered for sensing[3] and purification[4] applications and have been incorporated into a variety of magnetic and conducting[5] materials. The unique chemical and spectroscopic properties of metal dithiolenes are related to their delocalized electronic structures. New synthetic strategies for the construction of dithiolene-derived supramolecular architectures, with extensive electronic conjugation, should lead to new properties and, likely, to new applications.

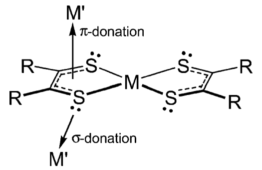

Figure 1

Using bisdithiolene complexes as ligands for other metal centers is a promising concept for the synthesis of new materials. This approach may involve appending specialized donating substituents to the dithiolene ligands (i.e., at the R groups in Figure 1).[6] Alternatively, the dithiolene ligands themselves can engage in bonding with electrophilic centers, even in the absence of ligand-appended donor groups.[7] The prototypical metal bisdithiolenes $[M(S_2C_2R_2)_2]^n$ (M = Ni, Pd, Pt; R = various substituents; $n = 0, -1, -2$) can, in principle, act as σ- or π-donor ligands. In the case of σ donation,[8] the dithiolene ligand uses electrons localized on one sulfur atom (η^1) to form a bond to a second metal (Figure 1; or other electrophiles, e.g., alkyl cations), whereas in π donation, two or more contiguous atoms of the dithiolene MS_2C_2 unit are involved in bonding (η^x with $x > 1$; e.g., η^4 or η^5; Figure 1).

π Donation of dithiolenes is quite rare. Typical examples involve homometallic complexes of ruthenium[9] or, less

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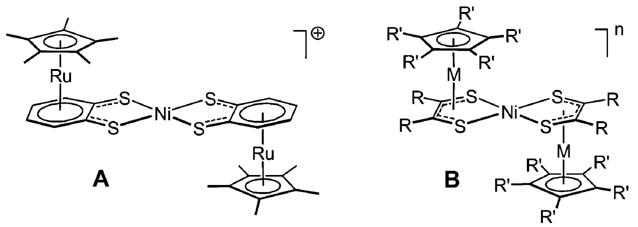

Figure 2

commonly, iron[10] or manganese,[11] as well as some heterometallic cases.[12] Sandwich compounds of nickel bisdithiolenes, with a nickel dithiolene chelate ring in an η^5 π-donating mode, have not been demonstrated so far. A report from 2000,[13] involving the monoanionic nickel bisdithiolene $[Ni(S_2C_6H_4)_2]^-$, proposed that the arene groups of the ligands, rather than the dithiolene NiS_2C_2 rings, are used for bonding to $[Cp^*Ru]^+$ fragments (Figure 2A; Cp* = pentamethylcyclopentadienyl). In fact, no structurally characterized example exists for the general nickel bis-double-decker structure shown in Figure 2B, and isoelectronic palladium and platinum complexes are also unknown. Here we describe the synthesis and redox reactivity of a novel bis-double-decker complex in which a nickel bisdithiolene complex utilizes its two chelate rings as π donors to $[Cp^*Fe]^+$ units.

The reaction of magenta-colored monoanionic nickel bisdithiolene sodium salt $Na[Ni(S_2C_2Me_2)_2]$[14] with 2 equiv of purple $[Cp^*Fe(NCMe)_3](PF_6)$[15] in acetonitrile forms the brown-green bis-double-decker complex $[\eta^5$-Cp*-Fe-μ-η^5,η^5-$((S_2C_2Me_2)_2Ni)$-Fe-η^5-Cp*](PF_6) ($1^+PF_6^-$, see Figure 2B with M = Fe, R = R′ = CH_3, and $n = 1$) in 56% yield. Compound 1^+ has an intense near-infrared (NIR) band at 1700 nm (UV−vis−NIR data discussed in the Supporting Information). The neutral analogue, compound **1**, is also accessible: the combination of the *dianionic* bisdithiolene sodium salt $Na_2[Ni(S_2C_2Me_2)_2]$[14] (dark yellow) with 2 equiv of $[Cp^*Fe(NCMe)_3](PF_6)$[15] gives green **1** (58%). The ^1H NMR spectrum of diamagnetic **1** shows all dithiolene methyl groups to be equivalent, consistent with the structure shown. The iron centers in **1** satisfy the 18-valence-electron rule: $[Ni(S_2C_2Me_2)_2]^{2-}$ is best described as Ni^{II} with two enedithiolate ligands,[16] and the π system of each enedithiolate unit should act as a 6-electron donor, similar to the cyclopentadienyl anion.

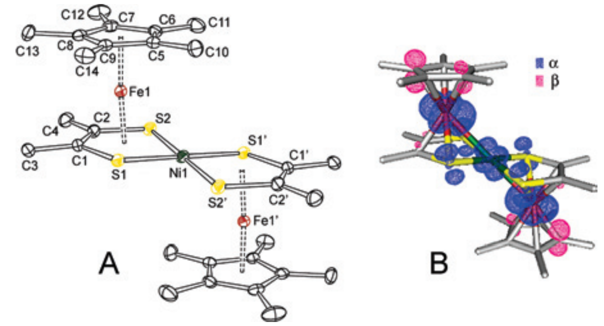

Figure 3. Structures of 1^+ (hydrogen atoms omitted). (A) Crystal structure of $1^+PF_6^-$ (PF_6^- counterion not shown), using 30% thermal ellipsoids. Ni1 resides on a crystallographic center of inversion. Selected distances and angles (Å and deg): Ni1−S1, 2.164(1); Ni1−S2, 2.163(1); C1−C2, 1.394(6); S1−Ni1−S2, 90.02(4); Fe1−S1, 2.266(1); Fe1−S2, 2.267(1); Fe1−C1, 2.072(4); Fe1−C2, 2.069(4); Fe1−Ni1, 2.6791(6); Fe1−C5, 2.090(4); Fe1−C6, 2.063(4); Fe1−C7, 2.075(4); Fe1−C8, 2.071(4); Fe1−C9, 2.088(4); Fe1−centroid (C5−9), 1.683(4); Fe1−centroid (Ni1,S1,S2,C1,C2), 1.657(3); centroid−Fe1−centroid, 175.9(1); dihedral angle Ni1−S1−S2 vs C1−C2−S1−S2, 7.9(1); dihedral Ni1−S1−S2−C1−C2 vs C5−C6−C7−C8−C9, 4.1(1). 1^+ in $1^+BF_4^-$ is extremely similar (Supporting Information). (B) Structure from UBLYP (SDD basis) geometry optimization. A spin isodensity surface corresponding to a 0.0013 value is superimposed.

Crystals of $1^+PF_6^-$ were obtained by diffusion of diethyl ether into a dichloromethane solution of $1^+PF_6^-$, and the results from a single-crystal X-ray structure determination[17] are shown in Figure 3A. The dithiolene units are almost planar. Deviations from the best plane are smaller than 0.06 Å and are caused by a very slight (ca. 8°) bending along the S−S axes. The pentamethylcyclopentadienyl plane and the nickel dithiolene plane are oriented in a parallel fashion, and the deviation from a perfectly parallel arrangement is only 4° (see the legend of Figure 3). Furthermore, the iron center resides almost directly between the center of the cyclopentadienyl ring and the center of the nickel dithiolene (C1−C2−S1−S2−Ni1) unit. Irrespective of the nature and strength of the iron−nickel interaction (the 2.6791 Å interatomic distance is well within the bonding distance[18]), the structural data[19] demonstrate that the C1−C2−S1−S2−Ni1 rings coordinate to the iron centers in an η^5 fashion.

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Concerning the electronic structure of the odd-electron species $\mathbf{1}^+$, it is relevant that oxidation of the bridging unit, $[Ni(S_2C_2Me_2)_2]^{2-}$, without the $[FeCp^*]^+$ groups, would lead to removal of one electron from an essentially ligand-based highest occupied molecular orbital (delocalized over both ligands, with a small coefficient at nickel).[1,16] It appears likely that the unpaired electron in $\mathbf{1}^+$ is delocalized over the whole molecule, including the dithiolene groups. Complex $\mathbf{1}^+$, in the crystallographically characterized $\mathbf{1}^+PF_6^-$, has a center of inversion (point group C_i), rendering both iron fragments equivalent. The core [iron−nickel bisdithiolene−iron] approximates even higher (C_{2h}) symmetry. The presence of an inversion center in the structure of $\mathbf{1}^+PF_6^-$ seems to provide evidence against a localized Fe^{II}/Fe^{III} description, but it cannot be regarded as conclusive proof of a truly delocalized ground state. Crystallographic disorder and/or rapid intramolecular electron transfer between the iron centers in a Fe^{II}/Fe^{III} localized state could also account for the center of inversion observed for $\mathbf{1}^+PF_6^-$. However, there is no evidence for disorder caused by a valence-trapped Fe^{II}/Fe^{III} state in the structure of $\mathbf{1}^+PF_6^-$ (i.e., no abnormalities observed for the iron or Cp* carbon ellipsoids). We crystallographically characterized $\mathbf{1}^+$ as its BF_4^- salt as well[17] (see the Supporting Information) and obtained a structure for $\mathbf{1}^+$ that is virtually identical to its structure in $\mathbf{1}^+PF_6^-$: again, the nickel atom lies on a center of inversion, and iron and Cp* ellipsoids show no signs of disorder. Thus, experimental evidence indicates that $\mathbf{1}^+$ is either truly centrosymmetric, with a delocalized electronic ground state, or, if the electronic structure is localized as Fe^{II}/Fe^{III}, electron transfer between the iron atoms is very facile and occurs with minimal structural reorganization.[20] Theory supports a truly delocalized ground state: a spin-unrestricted DFT (UBLYP) computation was performed for $\mathbf{1}^+$. A geometry optimization (*Gaussian03*,[21] LANL2MB basis), without symmetry imposed, converges toward C_i symmetry. A calculation using a larger basis set (SDD, with added polarization functions on the sulfur atoms) predicts C_i symmetry (closely approximating C_{2h}) and yields structural parameters very similar to those seen in the crystal structures of $\mathbf{1}^+$. The calculated structure of $\mathbf{1}^+$ is shown in Figure 3B, along with the computed spin density, which is delocalized over both iron centers with significant spin contributions on the nickel bisdithiolene unit. Using a simplified model (methyl groups replaced with hydrogen atoms) of $\mathbf{1}^+$, an unsymmetrical valence-trapped state was enforced by geometry optimization in the presence of a simulated electric field; when the field was removed, the structure reverted back to the fully delocalized state (see the Supporting Information for details).

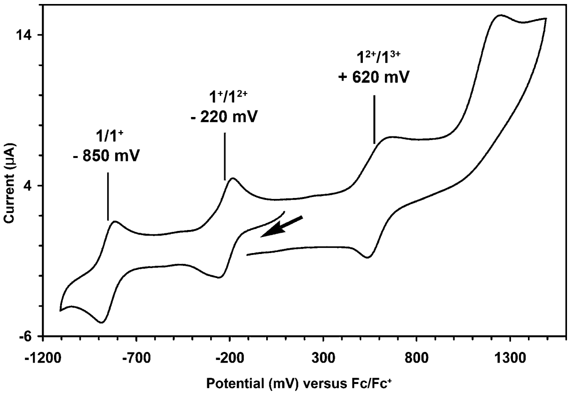

Figure 4. Cyclic voltammogram for $\mathbf{1}^+PF_6^-$ (∼1 mM in acetonitrile, 0.1 M NBu_4PF_6 as the supporting electrolyte, scan rate = 100 mV/s). Potentials are relative to the ferrocene/ferrocenium couple. See the text for a comment on "$\mathbf{1}^{3+}$" and see the Supporting Information for experimental details.

Complex **1** is rapidly[22] oxidized by 1 equiv of HBF_4 to $\mathbf{1}^+$; monocationic $\mathbf{1}^+$ can be further oxidized to $\mathbf{1}^{2+}$ by treatment with another 1 equiv of HBF_4 (in dichloromethane). Dicationic $\mathbf{1}^{2+}$ can also be generated by oxidation of $\mathbf{1}^+$ with 1 equiv of ferrocenium hexafluorophosphate. Cyclic voltammetry on $\mathbf{1}^+PF_6^-$ (Figure 4) reveals three one-electron-transfer events (see the Supporting Information). Rapid and reversible electron transfer is observed between $\mathbf{1}/\mathbf{1}^+/\mathbf{1}^{2+}$ (peak assignments in Figure 4[23]). Oxidation of $\mathbf{1}^{2+}$ is less facile and requires a relatively slow scan rate (100 mV/s or slower), indicating significant structural rearrangement. In Figure 4, the oxidation product is assigned as "$\mathbf{1}^{3+}$", but partial loss of $[Cp^*Fe]^+$ in this highly oxidized species appears possible. However, the oxidation of $\mathbf{1}^{2+}$ is fully reversible at slower (≤100 mV/s) scan rates.

In summary, we have synthesized a trimetallic bis-double-decker complex with a new structural motif in which two dithiolene ligands act as π donors to iron centers. Structural and computational data indicate a highly delocalized electronic structure for $\mathbf{1}^+$. Consistent with delocalized frontier orbitals, compounds $\mathbf{1}^n$ exhibit rich redox reactivity, as shown by cyclic voltammetry and by oxidation of **1** and $\mathbf{1}^+$ with H^+. These highly conjugated, redox-active species will be investigated for potential applications.

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Supporting Information Available: Crystallographic data for $\mathbf{1}^+PF_6^-$ and $\mathbf{1}^+BF_4^-$ (CIF format) and text containing experimental (syntheses, reactions involving H^+, and cyclic voltammetry) and computational (DFT) details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Conversion to $\mathbf{1}^+$ is complete in <2 min (room temperature) by UV−vis spectroscopy ($[HBF_4]_0 = [\mathbf{1}]_0 = 0.3$ mM in CH_2Cl_2).

(23) Peak assignments are based on the observation that $\mathbf{1}^+$ is oxidized by ferrocenium hexafluorophosphate, in a stoichiometric chemical oxidation experiment.