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Transition-Metal Complexes with Singly Reduced 1,2-Diketone Radical Ligands[**]

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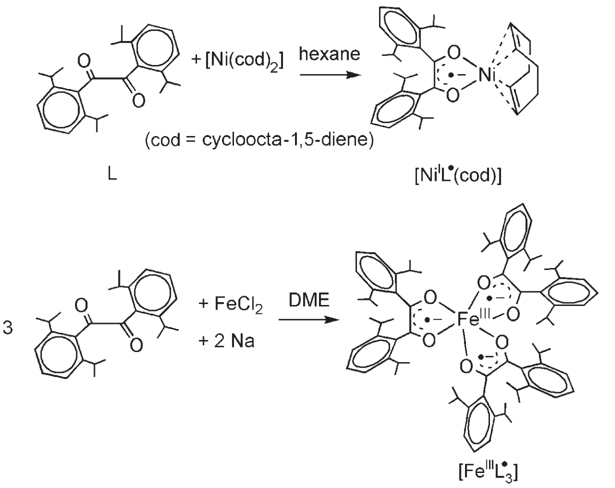
Radical-ligand metal complexes have been known for some time, with 1,2-benzosemiquinone complexes of iron and nickel being among the earliest examples.[1,2] The unpaired-electron density in these radical-anion ligands is stabilized by delocalization over the aromatic π system. In contrast, no examples of the singly reduced form of a 1,2-diketone have been isolated even though 1,2-diketones are widely used in organic synthesis and are present in a number of bioactive compounds.[3] Recently, we showed that the bulky diaryl 1,2-diketone bis(2,6-diisopropylphenyl)glyoxal (L) is a redox-active ligand which, in its doubly reduced closed-shell state, can stabilize a mixed-valent $\{Fe^{III}Fe^{II}\}$ dimer.[4] Herein we report the isolation of two complexes featuring this bulky 1,2-diketone as a singly reduced radical anion (Scheme 1).

The addition of bis(2,6-diisopropylphenyl)glyoxal, in hexane at about 25 °C, to one equivalent of $[Ni(cod)_2]$ (cod = cyclooctadiene) caused an instantaneous color change from yellow to deep red. Filtration, followed by removal of the solvent in vacuo, led to the isolation of a red–brown powder. Subsequent recrystallization from Et_2O, by slow evaporation, afforded dark red needles of $[Ni^{I}L^{\bullet}(cod)]$ (Figure 1; $(L^{\bullet})^{-}$ is the one-electron-reduced π-radical form of L) suitable for single-crystal X-ray diffraction[5], in moderate yield (approx. 40 %). The addition of three equivalents of L, in DME at about 25 °C, to one equivalent of anhydrous $FeCl_2$ and two equivalents of Na, with stirring, led to a gradual color change from pale yellow to deep green over the course of 24 h. Filtration, followed by removal of the solvent in vacuo, yielded a dark green powder. Subsequent recrystallization from Et_2O gave dark green plates of neutral $[Fe^{III}L^{\bullet}_3]$ (Figure 2) suitable for single-crystal X-ray diffraction,[5] also in moderate yield (approx. 57 %).



Scheme 1. Synthesis of $[Ni^{I}L^{\bullet}(cod)]$ and $[Fe^{III}L^{\bullet}_3]$. DME = 1,2-dimethoxyethane.

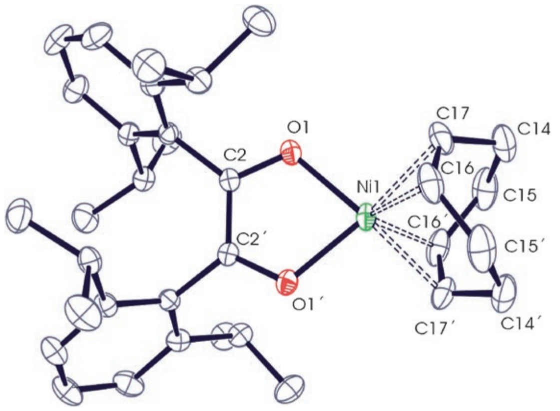


Figure 1. Thermal ellipsoid (50% probability) plot of $[Ni^{I}L^{\bullet}(cod)]$. H atoms are not shown. Selected bond lengths [Å]: Ni1–O1 1.940(1), O1–C2 1.293(1), C2–C2′ 1.432(2), Ni1–C16 2.087(1), Ni1–C17 2.060(1), C16–C17 1.377(2), C14–C17 1.511(2), C14–C15 1.547(2).

The ligand environment around the nickel center in $[Ni^{I}L^{\bullet}(cod)]$ approximates tetrahedral geometry while the molecular structure of $[Fe^{III}L^{\bullet}_3]$ consists of a distorted octahedral iron center with the three ligand units bound through all six oxygen atoms. The glyoxal carbon–carbon bond lengths (1.432–1.445 Å) in both complexes are intermediate between those observed for the free ligand (1.558 Å) and those for the doubly reduced enediolate form (1.365 Å),[4] thereby suggesting that each ligand has been singly reduced. This is also indicated by the intermediate carbon–oxygen bond lengths (1.285–1.293 vs. 1.214 Å for the neutral 1,2-diketone and 1.355–1.385 Å for the dianionic diolate form).[4] The bound cyclooctadiene has statistically identical internal bond lengths to those for $[Ni(cod)_2]$,[6] although its Ni–C bond lengths are shorter (2.060–2.087 vs. 2.115–2.132 Å for $[Ni(cod)_2]$) owing to the oxidized nickel center. These parameters are very similar to those seen for the previously isolated

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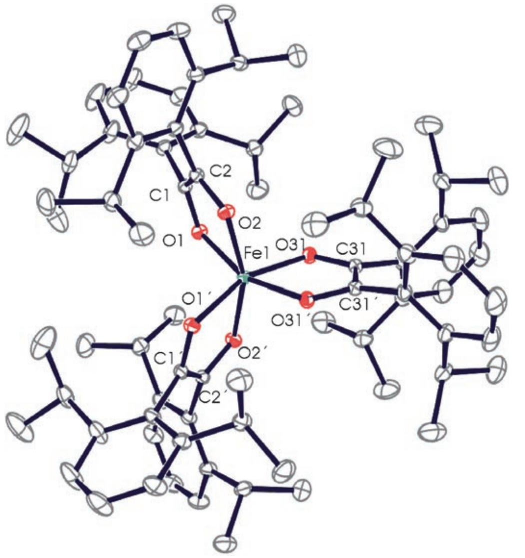

Figure 2. Thermal ellipsoid (50% probability) plot of [$Fe^{III}L^{\bullet}_3$]. H atoms are not shown. Selected bond lengths [Å]: Fe1–O1 2.0313(5), Fe1–O2 2.0094(5), Fe1–O31 2.0275(3), O1–C1 1.285(1), O2–C2 1.286(1), O31–C31 1.285(1), C1–C2 1.445(1), C31–C31′ 1.441(1).

diazabutadiene system [$Ni(cod)(DAB^{Me})$],[7] which should also be formulated as Ni^{I} and $(DAB^{Me})^{\bullet-}$.[8] The values for the Fe–O bond lengths in [$Fe^{III}L^{\bullet}_3$] are typical for octahedral high-spin Fe^{III}.

[$Ni^{I}L^{\bullet}(cod)$] is diamagnetic (see the Supporting Information). Its electronic spectrum recorded in C_6H_6 displays a broad charge-transfer band in the visible region at about 795 nm ($\varepsilon = 1440\ \text{M}^{-1}\text{cm}^{-1}$) which can be assigned to a ligand-to-metal charge-transfer (LMCT) transition. [$Fe^{III}L^{\bullet}_3$] in THF displays two broad overlapping charge-transfer bands in the visible to near IR region at approximately 740 ($\varepsilon = 2500$) and 1000 nm ($\varepsilon = 2000\ \text{M}^{-1}\text{cm}^{-1}$) which are assigned to LMCT and ligand-to-ligand charge-transfer (LLCT) bands, respectively.

Temperature-dependent magnetic susceptibility measurements on [$Fe^{III}L^{\bullet}_3$] (Figure 3) display a plateau at $\mu_{\text{eff}} = 2.82\ \mu_B$, which is indicative of an $S_t = 1$ ground state consistent with a high-spin Fe^{III} center strongly antiferromagnetically coupled to three ligand radicals. The increase of μ_{eff} at temperatures above 200 K can be simulated in a symmetric coupling scheme by applying a strong exchange interaction of $-J = 211\ \text{cm}^{-1}$ between a high-spin Fe^{III} center ($S_{\text{Fe}} = {}^5\!/_2$) and three π-radical anions ($S_{\text{Rad}} = {}^1\!/_2$). Previous attempts to simulate the temperature-dependent magnetism of tris(benzosemiquinone)iron complexes led to $-J$ values of 60–140 cm^{-1}.[1b,9] These lower values are probably due to a greater delocalization of the unpaired spin on the ligands,[10] although the quality of the fit was poor and required the introduction of semiquinone–semiquinone exchange.[9]

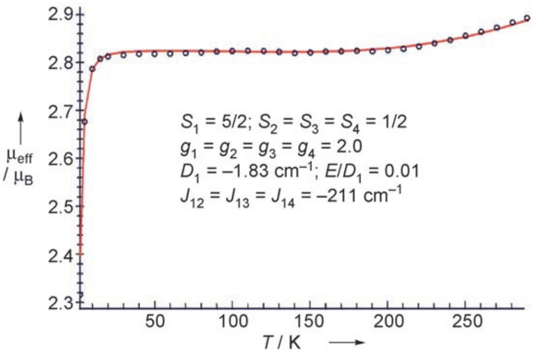

Figure 3. Temperature-dependence of the magnetic moment of [$Fe^{III}L^{\bullet}_3$]. The solid (red) line represents a spin Hamiltonian simulation based on:

$$\hat{H} = -2J\,\hat{\vec{S}}_1 \cdot \hat{\vec{S}}_2 + g\beta(\hat{\vec{S}}_1 + \hat{\vec{S}}) \cdot \vec{\mathrm{B}} + D\,[\hat{S}_{1,z}{}^2 - 2]$$

The zero-field Mössbauer spectrum of [$Fe^{III}L^{\bullet}_3$] recorded at 80 K shows a quadrupole doublet with an isomer shift (δ) and quadrupole splitting (ΔE_Q) of 0.63 and 0.87 $\text{mm}\,\text{s}^{-1}$, respectively. The Mössbauer spectra with applied fields (Figure 4) show magnetic high-field splittings of about 10 $\text{mm}\,\text{s}^{-1}$, which correspond to an internal field of about 33 T. This value is significantly lower than what would be expected for a magnetically isolated high-spin Fe^{III} ion. The magnetic spectra for [$Fe^{III}L^{\bullet}_3$] were simulated with an isotropic effective hyperfine constant for the ground state ($S_t = 1$) of $A_t/g_N\mu_N = -31.3$ T, which yields $A_{\text{Fe}}/g_N\mu_N = -17.9$ T with respect to the local spin ($S_{\text{Fe}} = {}^5\!/_2$) when converted into the intrinsic value with $A_{\text{Fe}} = {}^7\!/_4 A_t$.[11]

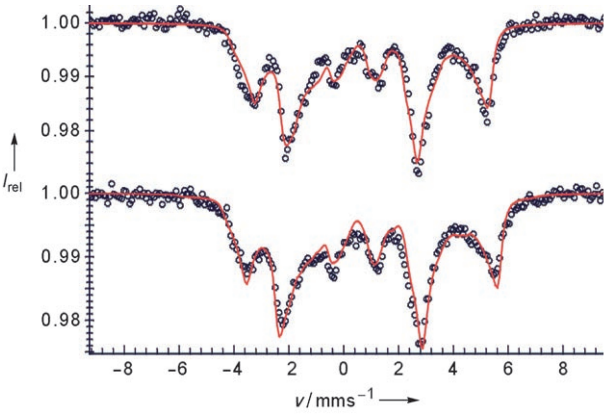

Figure 4. Applied field Mössbauer spectra of [$Fe^{III}L^{\bullet}_3$] at 4.2 K with fields of 5 (bottom) and 7 T (top) applied perpendicular to the γ-beam. The solid (red) lines are fitted Lorentzian line shapes.

The unusually high isomer shift, which is dependent on the occupation of Fe d and s orbitals, is indicative of a relatively high electron density at the metal center.[12] Similar shifts have also been observed for the previous benzosemiquinone systems (0.53–0.60 $\text{mm}\,\text{s}^{-1}$)[1a,13] although only a few high-spin Fe^{III} systems have been isolated with isomer shifts greater than 0.6 $\text{mm}\,\text{s}^{-1}$.[14–16] The intrinsic hyperfine coupling constant $A_{\text{Fe}}/g_N\mu_N$ for [$Fe^{III}L^{\bullet}_3$] is comparatively small (−20 to −22 T for ionic complexes). This low coupling constant can be reconciled with the high isomer shift, by the effect of the antiferromagnetic coupling to the β-spin of the ligand, which means that the *unpaired*-electron density at the Fe center is low. This spin-coupled system can thus be properly described as containing a high-spin Fe^{III} cation and three π-radical ligand anions.

It has been found previously that the presence of benzosemiquinone ligands offers the possibility for significant ligand-based redox activity.[2] For instance, there is the potential for stepwise oxidation to coordinated benzoquinone and stepwise reductions to catecholate ligands as well as reduction of the metal center. Owing to the extreme air- and moisture-sensitivity of these species some decomposition in solution was always observed. The cyclic voltammogram of $[Fe^{III}L^{\bullet}_3]$ demonstrates one reversible reduction in THF at −1.25 V vs. Fc/Fc^+ (Fc = ferrocene), which can be assigned to the Fe^{III}/Fe^{II} reduction couple, and a series of irreversible oxidation steps at −0.55, −0.11, and +0.02 V, which can be assigned to successive ligand oxidations. No reversible features were observed in the cyclic voltammogram of $[Ni^{I}L^{\bullet}(cod)]$.

The structure of $[Ni^{I}L^{\bullet}(cod)]$ was also optimized using a broken-symmetry (BS(1,1)) density functional theoretical (DFT) approach at the B3LYP level of theory.[17] The agreement between the experimental and calculated C−O and C−C bond lengths is excellent. The calculated Ni−O and Ni−C bonds are longer than the corresponding experimental ones—this overestimation is typical for the B3LYP functional.[18]

The qualitative molecular-orbital (MO) scheme for $[Ni^{I}L^{\bullet}(cod)]$ is shown in Figure 5 (top). Four metal-centered orbitals are doubly occupied and a singly occupied ligand π* orbital, which is antiferromagnetically coupled to a singly occupied metal d-type orbital, is also identified. Interestingly ,a Mulliken spin-population analysis (Figure 5 (bottom)) showed no significant unpaired-electron density on the cyclooctadiene ligand but a single electron on the $(L^{\bullet})^-$ ligand and another on the metal center (Ni^{I}). The same result was found when $[Ni(cod)(DAB^{Me})]$[7] was optimized using the same BS(1,1) B3LYP method (see Figure 6 and the Supporting Information).

A truncated model of $[Fe^{III}L^{\bullet}_3]$, with the isopropyl groups removed, was optimized using the BS(5,3) B3LYP method. The agreement between the experimental and calculated C−O and C−C bond lengths is again excellent. All three ligands are clearly open-shell π-radical monoanions.

The molecular-orbital (MO) scheme for $[Fe^{III}L^{\bullet}_3]$ is shown in Figure 7 (top). Five singly occupied metal d orbitals can be identified, with the three lowest energy orbitals spin-coupled to three singly occupied ligand orbitals.[19] These are exactly the features expected for a high-spin Fe^{III} ion ($S_{Fe} = 5/2$) coupled to three ligand radical anions. This notion is further confirmed by the Mulliken spin-population analysis shown in Figure 7 (bottom), which clearly shows that the α spin density is localized on the central iron ion with the β spin delocalized over the ligands.

It is possible to calculate Mössbauer parameters, namely the isomer shift (δ) and the quadrupole splitting (ΔE_Q) of the central iron ion, for the truncated DFT model.[20] The calculated values of δ and ΔE_Q for $[Fe^{III}L^{\bullet}_3]$ are 0.63 and +1.38 mm s^{-1}, respectively, which are in excellent agreement with the experimental data at 80 K. Both the Mössbauer isomer shift and the quadrupole splitting parameters are sensitive reporters of the physical oxidation state as well as the intrinsic spin-state of the iron ion, hence the excellent agreement between theory and experiment confirms the oxidation-state assignment for $[Fe^{III}L^{\bullet}_3]$.

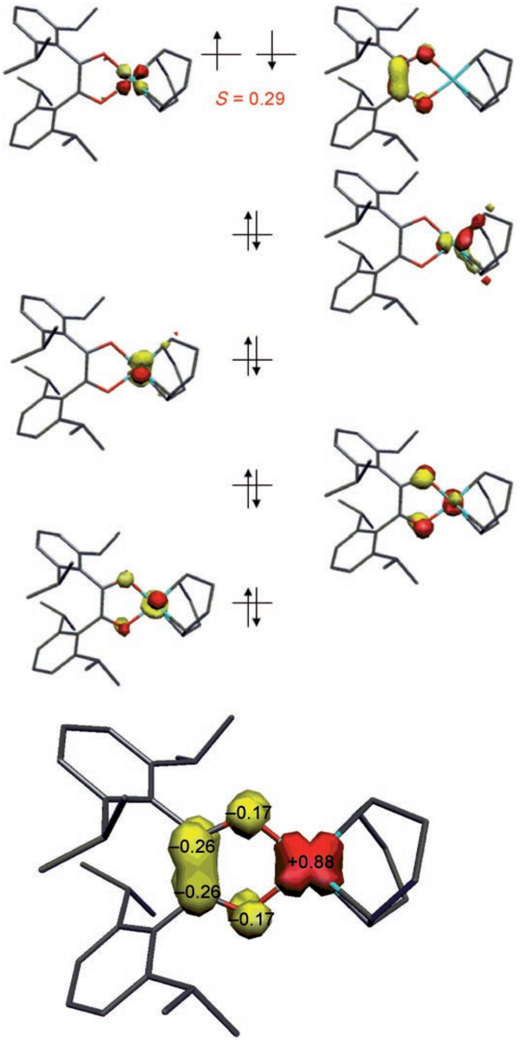

Figure 5. Qualitative MO scheme of the corresponding orbitals of magnetic pairs of $[Ni^{I}L^{\bullet}(cod)]$ as derived from BS(1,1) DFT calculations (top) and spin-density plots with values for the spin density obtained from a Mulliken spin-population analysis (bottom). Calculated/experimental C−O and ligand backbone C−C bond lengths: 1.289/1.293 and 1.449/1.432 Å, respectively.

Very little is known about the coordination chemistry of acyclic 1,2-diketones or their one- and two-electron-reduced forms. Indeed, until recently only 1,2-diketone complexes containing the ligand in its two-electron-reduced diolate form with an early transition metal or main-group element had been isolated.[21] Complexes of bis(1-methylimidazol-2-yl)glyoxal with late transition metals have been shown by EPR spectroscopy, to undergo reduction at the ligand, although these intermediates have not been isolated and are thought to be coordinated through the imidazolyl moiety.[22]The one-electron-reduced form has been implicated by EPR spectroscopy in the adducts formed by the reaction of 1,2-diketones with in situ photolyzed manganese carbonyl

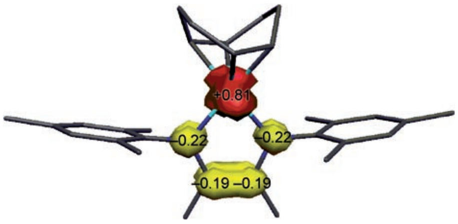

Figure 6. Spin-density plot for [Ni(cod)(DAB^{Me})] together with values for the spin density obtained from a Mulliken spin-population analysis. Calculated/experimental C–N and ligand backbone C–C bond lengths: 1.338/1.332–1.348 and 1.431/1.404 Å, respectively.

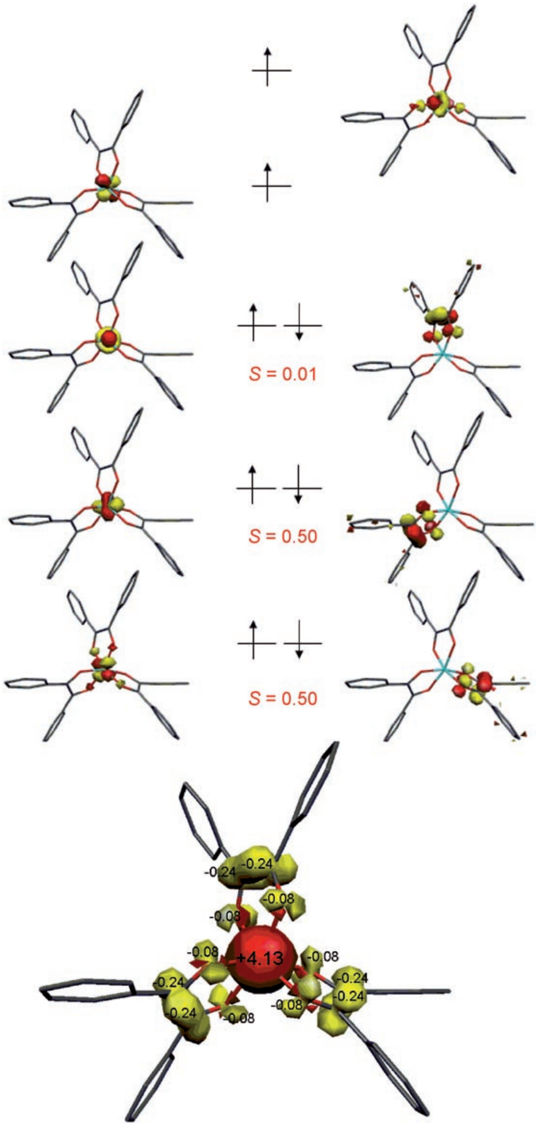

Figure 7. Qualitative MO scheme of the corresponding orbitals of magnetic pairs of [Fe^{III}L$^{\bullet}_3$] as derived from BS(5,3) DFT calculations (top) and spin-density plots with values for the spin density obtained from a Mulliken spin-population analysis (bottom). Calculated/experimental C–O and ligand backbone C–C bond lengths: 1.281–1.283/1.285–1.286 and 1.457/1.445 Å respectively.

compounds,[23,24] although again these products were not isolated and the unpaired electron was assigned as ligand-based only by comparing the observed g value with that expected for an organic radical.

In summary, two examples of complexes with singly reduced 1,2-diketone radical ligands have been isolated and fully characterized, thereby demonstrating that these ligands can reproduce the rich chemistry of their semiquinone equivalents.

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