Inorganic Chemistry
Communication
pubs.acs.org/IC

Synthesis and Characterization of a Neutral Titanium Tris(iminosemiquinone) Complex Featuring Redox-Active Ligands

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Ⓢ *Supporting Information*

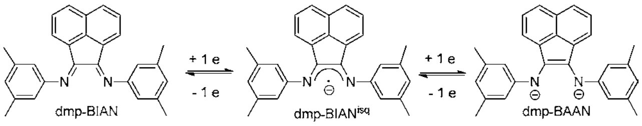
ABSTRACT: The neutral tris(semiquinonate) complex [Ti(dmp-BIAN^{isq})$_3$] [dmp-BIAN^{isq} = *N*,*N*′-bis(3,5-dimethylphenylimino)acenaphthenesemiquinonate] was structurally, spectroscopically, and electrochemically characterized. Solid-state magnetism experiments reveal field-quenchable, enhanced temperature-independent paramagnetism (TIP). Density functional theory calculations employing the experimental geometry predicts a strong antiferromagnetic coupling, leading to an $S = 0$ ground state, but they also hint at spin frustration and concomitant close-lying, excited states, which cause the observed large TIP by admixture into the ground state. The dmp-BIAN^{isq} ligand, which facilitates intramolecular electron transfer, was shown to undergo four quasi-reversible redox processes, demonstrating the ability of the ligand to act as an electron reservoir in complexes of early metals.

Transition-metal complexes supported by redox-active ligands have recently garnered much attention because of their singular electronic and magnetic properties,[1,2] as well as their applications to catalysis,[3] pharmaceuticals,[4] and electronic materials.[5] In these complexes, the ligand acts as electron reservoir by facilitating inner-sphere charge redistribution with the metal center. This noninnocent behavior arises from strong mixing between energetically similar metal d(π) and ligand p(π) frontier orbitals,[6] which in some cases can result in intramolecular electron transfer (IET) to generate changes in the formal oxidation states of metal and ligand.[7]

Homoleptic complexes of transition metals have become ubiquitous with the study of IET between metal centers and redox-active ligands.[8] The high inherent symmetry of these complexes simplifies electronic and structure treatments, making them reference systems of choice for elucidation of the frontier orbital interactions of metals and their coordinated ligands. Whereas IET has been explored with a variety of homoleptic complexes, tris(semiquinonate) complexes of dithiolene,[9] dioxolene,[10] and diimine[11] ligands are among the most information-rich systems, providing considerable insight regarding ligand-tunable electronic structures for noninnocent metal complexes.

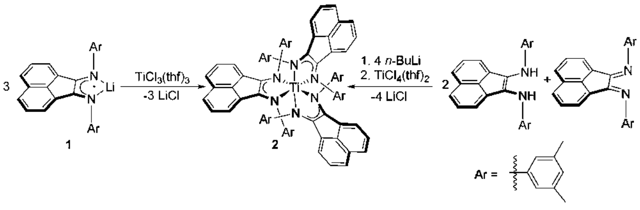
Bis(arylimino)acenaphthylenes (BIANs) represent a class of α-diimine ligands that is gaining increased prominence because of their easily tuned steric and electronic properties.[12] Similar to their dithiolene and dioxolene counterparts, these redox-active ligands are able to coordinate to metal centers in multiple oxidation states (Scheme 1)[13] and have even been shown to facilitate IET.[14] This feature makes complexes supported by BIAN ligands particularly attractive candidates for use in diverse applications, which include catalysis[15] and potentially optics and electronics.[14,16] Despite numerous reports of complexes that employ BIAN as ancillary ligands, the number of early-transition-metal complexes remains quite limited,[17] and, consequently, an understanding of the electronic and magnetic interactions of early transition metals and this ligand class remains limited. In pursuit of our interest in the redox properties of BIAN-equipped group IV metal complexes, we herein report the synthesis and characterization of the first isolated neutral titanium tris(semiquinonate) complex, supported by *N*,*N*′-bis(3,5-dimethylphenylimino)acenaphthenesemiquinonate (dmp-BIAN^{isq}). This complex can be obtained from different ligand oxidation states, which is in line with the capability of this ligand system to engage in IET.

Scheme 1. First Three Oxidation Levels of the BIAN Ligand



The neutral complex [Ti(dmp-BIAN^{isq})$_3$] (**2**) was readily synthesized from treatment of the titanium(IV) starting material $TiCl_4(THF)_2$ (THF = tetrahydrofuran) with 2 equiv of H_2[dmp-BAAN] and 1 equiv of dmp-BIAN in the presence of *n*-BuLi (Scheme 2). By this method, **2** was isolated as a turquoise microcrystalline solid in 66% yield. Alternatively, **2** was isolated in 72% yield from the reaction of the complex $TiCl_3(THF)_3$ and 3 equiv of the monoionic ligand as its Li^+ salt, Li[dmp-BIAN^{isq}]

Scheme 2. Synthesis of 2



Received: May 21, 2012
Published: July 2, 2012

dx.doi.org/10.1021/ic301059p | *Inorg. Chem.* 2012, 51, 7457−7459

(**1**) (Scheme 2). **1** was generated in situ via comproportionation of a 1:1 mixture of the neutral dmp-BIAN ligand and the protonated dianionic ligand H_2[dmp-BAAN] in the presence of *n*-BuLi. A THF solution of the titanium(III) precursor was then added by cannula transfer into the ligand solution. The composition of **2** was confirmed by elemental analysis, APCI mass spectrometry, and single-crystal X-ray diffraction.

The molecular structure of **2** was determined by X-ray diffraction at 163 K (Figure 1). The complex was shown to possess D_3 symmetry. The six-coordinate titanium center is pseudooctahedral because of a trigonal twist angle of 42°.[18] The BIAN ligand has a small N−Ti−N ligand bite angle of 77.23(6)° enforced by the five-membered chelate ring (Ti−N−C−C−N), which is formed upon coordination to the metal center. As a result of crystallographically imposed 6-fold symmetry, metrical parameters for the three ligands about the metal center are averaged. The average C−NAr bond length (~1.33 Å), however, is consistent with the values reported for the semiquinonate Na[dpp-BIAN^{isq}] (~1.32 Å; dpp = 2,6-diisopropylphenyl).[13] Another key diagnostic value, the C(1)−C(2) bond length, has been reported as ~1.47 and ~1.39 Å for the BIAN and BAAN forms of the ligand, respectively.[13] In complex **2**, it was determined to be 1.420(3) Å, a value intermediate between the two oxidation levels. These parameters corroborate the presence of the semiquinonate ligand form.

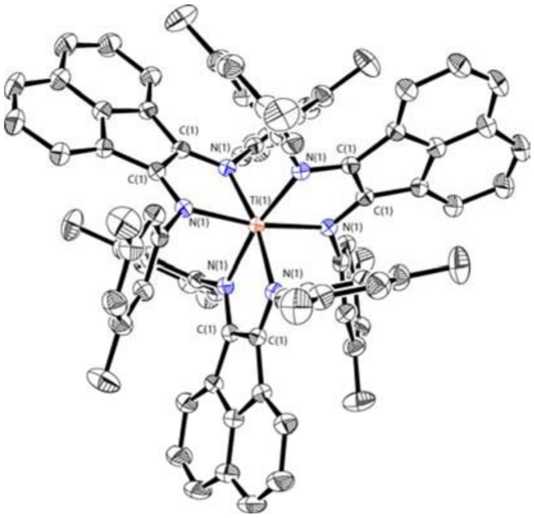


Figure 1. ORTEP of **2**·C_6H_6 ($R\bar{3}c$). Thermal ellipsoids are shown at 50% probability. Hydrogen atoms and solvent molecules have been omitted for clarity. Select bond lengths (Å): Ti(1)−N(1) 2.0940(11), C(1)−N(1) 1.3386(18), C(1)−C(1) 1.420(3) (see the Supporting Information for more details).

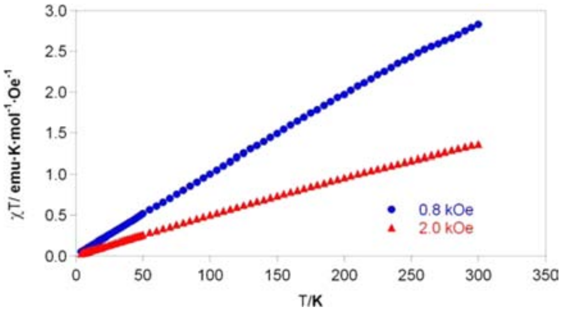


Figure 2. Plot of χT versus temperature, T, at 0.8 and 2.0 kOe for **2**.

Solid-state magnetism data collected for **2** display a strong temperature dependence in the range of 4−300 K (Figure 2). In this temperature range, χT varies linearly with temperature corresponding to temperature-independent paramagnetism (TIP); however, at $\approx 10^{-2}$ emu mol^{-1}Oe^{-1} (0.8 kOe), it is approximately 2 orders of magnitude larger than that in normally observed TIP in 3d systems.[19] A similarly enhanced TIP was recently observed in a dinuclear cobalt(II) compound by Rohmer et al.[20] and subsequently thoroughly analyzed by Van den Heuvel and Chibotaru.[21] It was found that, for systems with unquenched or partially unquenched orbital angular momenta, modeling based on spin-only Hamiltonians was insufficient for understanding the magnetic properties. In the present case, the trigonal symmetry further complicates the situation compared to the approximately tetragonal system by Rohmer: the 3-fold symmetry makes the system spin-frustrated, and accordingly the effects of both vibronic and interligand coupling need to be taken into consideration in a complete analysis of the magnetism. For **2**, the temperature variation of the susceptibility was determined at two different fields (Figure 2) and found to be approximately inversely proportional to the field in the range 0.8−2 kOe. The field dependence was not experimentally determined or analyzed in the theoretical modeling of the aforementioned dinuclear cobalt(II) system. It should, however, be pointed out that quenching of the susceptibility by the field observed here makes the behavior radically different from that of classical TIP, which as a perturbative effect is independent of the magnetic field strength. The magnetic behavior is thus quite complex, but antiferromagnetic coupling between the metal and ligated radicals as well as between the radicals are prerequisites for the observed behavior, leading to a $S = 0$ ground state with close-lying excited states. It is also notable that the high-temperature values of χT significantly exceed that of two unpaired electrons, effectively eliminating the formulation [Ti^{IV}(BAAN)(BIAN^{isq})$_2$].

Despite the availability of close-lying excited states, complex **2** displays well-resolved ^{1}H NMR signals in C_6D_6 that are in agreement with the expected structure (Figure SI1, Supporting Information). At room temperature, the peak intensities of the proton resonances are consistent with only ~70% of the sample, and upon increasing temperature, the resonances broaden, with less than 45% of the sample detected at 343 K. This observed broadening is fully reversible and in agreement with the aforementioned magnetism data, offering further support for an $S = 0$ ground state with close-lying excited states.

The electronic spectrum of **2** in THF reveals intense absorption bands in the near-IR (NIR) and visible regions at 1450 nm ($\varepsilon = 6690$ M^{-1} cm^{-1}), 910 nm ($\varepsilon = 8000$ M^{-1} cm^{-1}), 731 nm ($\varepsilon = 4730$ M^{-1} cm^{-1}), and 634 nm ($\varepsilon = 4520$ M^{-1} cm^{-1}) (Figure SI2, Supporting Information). The intervalence charge-transfer transition observed at 1450 nm indicates that there is a high degree of electronic delocalization in this complex,[1,9] while the ligand-to-ligand charge-transfer bands observed in the region between 700 and 1000 nm are characteristic of both transition-metal semiquinone complexes and systems with symmetrical dispositions of ligand oxidation states.[9,22] In the ultraviolet region, two charge-transfer transitions (likely ligand-to-metal charge transfer) at 393 nm ($\varepsilon = 9000$ M^{-1} cm^{-1}) and 282 nm ($\varepsilon = 31500$ M^{-1} cm^{-1}) were also observed.

Density functional theory calculations employing the experimental coordination geometry yield a singlet ground state with the $S = 2$ state ca. 4000 cm^{-1} higher in energy. This large energy difference reflects a quite strong antiferromagnetic interaction between the metal center and the coordinated radicals in the $[Ti^{III}(dmp\text{-}BIAN^{isq})_3]$ formulation suggested by the structural data. It is worth noting that it was impossible to converge the electron distribution in the $S = 1$ state with the experimental geometry. This is not surprising because the $[Ti^{III}(dmp\text{-}BIAN^{isq})_3]$ electronic structure suffers both from spin frustration and from an orbital degeneracy, which render it Jahn−Teller unstable. The experimentally determined magnetism of the compound (vide supra) makes it likely that vibronically coupled components of the $S = 1$ state are low in energy.

The cyclic voltammogram of **2** recorded in a THF solution reveals four one-electron redox processes within the solvent window. Two quasi-reversible oxidations occur at −0.84 V ($[\mathbf{2}]^+/[\mathbf{2}]^0$) and −0.20 V ($[\mathbf{2}]^{2+}/[\mathbf{2}]^+$) versus the Fc^+/Fc couple, while the two remaining waves at −1.81 V ($[\mathbf{2}]^0/[\mathbf{2}]^-$) and −2.38 V ($[\mathbf{2}]^-/[\mathbf{2}]^{2-}$) correspond with reductions (Figure 3).[23]

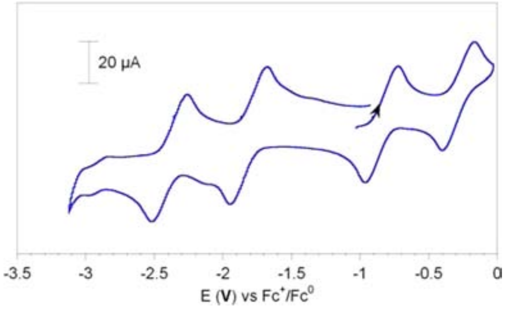


Figure 3. Cyclic voltammogram in THF (0.10 M $[n\text{-}Bu_4N][PF_6]$) of **2** with a glassy carbon working electrode and a scan rate of 200 mV s^{-1}.

Considering the electronic delocalization observed in the electronic spectrum of **2**, it is likely that these four processes involve molecular orbitals with significant ligand character. These data demonstrate the ability of the BIAN ligand to act as an electron reservoir, providing stability and electronic flexibility in this early metal complex.

In summary, the first known neutral tris(semiquinonate) complex of titanium, **2**, was isolated and characterized. Formally, the electronic structure can be written in the Enemark−Feltham notation as $\{Ti(BIAN)_3\}^4$, with the four valence electrons leaving possibilities for $S = 0$, 1, and 2 states. This pseudooctahedral complex displays enhanced TIP arising from the mixing of close-lying excited states with an $S = 0$ ground state. The observed magnetic behavior is consistent with the formulation of a titanium(III) metal center ligated by three ligand radicals, while the electronic spectrum of **2** further supports this conclusion. Moreover, transitions in the NIR region suggest strong electronic delocalization, such that the metal and ligand redox sites are nondiscrete. The ability to synthesize **2** from either the reaction of the open-shell radical dmp-BIAN^{isq} ligand and a Ti^{III} complex or the reaction of the closed-shell dmp-BAAN and dmp-BIAN ligands with a titanium(IV) complex shows that the ligand allows for IET to yield $Ti^{III}(dmp\text{-}BIAN^{isq})_3$ as the presumably thermodynamically preferred arrangement. Last, cyclic voltammetry experiments reveal that this complex undergoes four quasi-reversible processes, demonstrating both the stability of the complex over five oxidation states and the ability of the ligand to serve as an electron reservoir when coordinated to early metals. Further studies are currently underway to determine the nature of the unusual magnetic behavior observed for this complex.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, experimental procedures, and NMR and electronic spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was funded by grants from the NSF (NSF-CAREER Grant CHE-0645685). K.M.C. thanks the American−Scandinavian Foundation for financial support.

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