Inorg. Chem. **2008**, *47*, 5549−5551

Inorganic Chemistry
Communication

Radical−Ligand-Derived C−N Coupling, Ga(III)−Radical vs Low-Spin Co(III)−Radical Reactivity

Phalguni Chaudhuri,* Eckhard Bill, Rita Wagner, Ulrich Pieper, Biplab Biswas, and Thomas Weyhermüller

Max-Planck-Institut für Bioanorganische Chemie, Stiftstraβe 34-36, Mülheim an der Ruhr, Germany

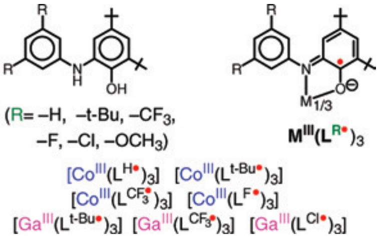
Received April 8, 2008

The redox-active ligand 2-(3,5-dimethoxyanilino)-4,6-di-*tert*-butylphenol, H_2L^{OCH3}, results in, as expected, a trisradical complex with a low-spin Co(III) center, $[Co^{III}(L^{OCH3\bullet})_3]$ (**1**), whereas the Ga(III) center yields a coordinated new hexadentate monoradical ligand, $[Ga^{III}L^{\bullet}{}_1]$ (**2**), presumably due to the ligand-derived redox activity involving C−H activation.

This work stems from our interest in redox-active ligands, based on 2-aminophenol,[1] which can coordinate to a metal ion not only in their deprotonated forms but also in their one-electron oxidized *o*-iminobenzosemiquinone $(L^{\bullet}{}_{SQ})^-$ radical and two-electron oxidized *o*-iminobenzoquinone $(L_{BQ})^0$ closed-shell forms (Scheme 1). In a recent communication, we reported[2] disparate properties with respect to exchange coupling between *o*-iminobenzosemiquinone radicals coordinated to diamagnetic metal centers, namely, low-spin Co(III) and Ga(III), depending on the nature of the meta substituents at the innocent aniline moieties (Scheme 1). Thus, we described Co(III)− and Ga(III)−tris-radical complexes (Scheme 1); irrespective of the nature of the substituents on the aniline-moiety, Ga(III) complexes are antiferromagnetically coupled, whereas spin-coupling in Co(III) complexes varies from ferromagnetic to moderate antiferromagnetic coupling.

For the sake of completion, we wanted to isolate the tris-radical complex Ga^{III} with the dimethoxy-substituted ligand, H_2L^{OCH3} (Scheme 1), in which case we discovered an unexpected C−N-coupling reaction mediated by the Ga(III) center, as reported here.

Scheme 1



The treatment of $Co(ClO_4)_2 \cdot 6H_2O$ in the presence of air and NEt_3 in acetonitrile with 3 equiv of the substituted N,O-chelating ligand H_2L^{OCH3} yields very dark crystals of **1**,[3] $[Co(L^{OCH3\bullet})_3] \cdot 0.5Et_2O$. The X-ray crystal structure and other spectroscopic data for **1** have been reported as Supporting Information in ref 2. The cobalt(III) center in **1** is d^6 low-spin, hexa-coordinated to three chelating *o*-iminobenzosemiquinone monoanion radicals $[L^{OCH3\bullet}]^-$, thus resulting in a Co(III)−tris-radical complex, which is also isostructural, as expected, to other Co(III) complexes[1a,2] listed in Scheme 1.

Magnetic data (SQUID)[2] for a polycrystalline sample of **1** are displayed in Figure 1 as μ_{eff} per molecule versus T. The effective magnetic moment for **1** remains practically constant at 3.01 μ_B ($\chi_M T = 1.114$ cm^3 mol^{-1} K), which is identical to the spin-only value for three uncoupled radicals with $S_R = {}^1/_2$, in the temperature range 290−50 K; it starts to decrease then with decreasing temperature to reach a value of 2.95 μ_B ($\chi_M T = 1.089$ cm^3 mol^{-1} K) at 40 K, below which it starts to decrease more rapidly, reaching a value of 1.67 μ_B ($\chi_M T = 0.350$ cm^3 mol^{-1} K) at 2 K. This arises from a dominating weak antiferromagnetic spin-coupling between three radical centers mediated by the filled 3dπ orbitals of a low-spin Co(III) center in **1**. The simulation based on the Hamiltonian

---

* Author to whom correspondence should be addressed. E-mail: Chaudh@mpi-muelheim.mpg.de.

(1) See, for example: (a) Verani, C. N.; Gallert, S.; Bill, E.; Weyhermüller, T.; Wieghardt, K.; Chaudhuri, P. *Chem. Commun.* **1999**, 1747. (b) Chun, H.; Chaudhuri, P.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **2002**, *41*, 790. (c) Mukherjee, S.; Weyhermüller, T.; Wieghardt, K.; Chaudhuri, P. *Dalton Trans.* **2003**, 3483. (d) Mukherjee, S.; Weyhermüller, T.; Bothe, E.; Wieghardt, K.; Chaudhuri, P. *Dalton Trans.* **2004**, 3842. (e) Kokatam, S.; Weyhermüller, T.; Bothe, E.; Chaudhuuri, P.; Wieghardt, K. *Inorg. Chem.* **2005**, *44*, 3709. (f) Mukherjee, S.; Weyhermüller, T.; Bill, E.; Wieghardt, K.; Chaudhuri, P. *Inorg. Chem.* **2005**, *44*, 7099. (g) Mukherjee, C.; Weyhermüller, T.; Bothe, E.; Chaudhuri, P. *C.R. Chim.* **2007**, *10*, 313. (h) Mukherjee, C.; Weyhermüller, T.; Bothe, E.; Rentschler, E.; Chaudhuri, P. *Inorg. Chem.* **2007**, *46*, 9895. (i) Mukherjee, C.; Weyhermüller, T.; Bothe, E.; Chaudhuri, P. *Inorg. Chem.* **2008**, *47*, 2740, and references cited therein.

(2) Chaudhuri, P.; Wagner, R.; Pieper, U.; Biswas, B.; Weyhermüller, T. *Dalton Trans.* **2008**, 1286.

(3) Details of characterization and crystallographic data for **1** are given in ref 2 as supplementary materials.

10.1021/ic8006348 CCC: $40.75

$$\hat{H} = -2J(\hat{S}_1\cdot\hat{S}_2+\hat{S}_2\cdot\hat{S}_3) - 2J_{13}(\hat{S}_1\cdot\hat{S}_3) + g\mu_{\mathrm{B}}\sum_i \hat{S}\cdot\vec{\mathrm{B}} \qquad (1)$$

with $S_1 = S_2 = S_3 = {}^1/_2$, shown as the solid line in Figure 1, yields $J = +11$ cm^{-1}, $J_{13} = -14$ cm^{-1}, and $g = 2.0$ (fixed). The magnetic data could not be fitted with only one "J" as satisfactorily as with "two J" values, as pointed out also earlier.[2] We do not claim that the values J and J_{13} represent a unique solution, but the results do demonstrate the presence of three radicals in **1** and indicate in a qualitative fashion dominating antiferromagnetic spin-coupling between the radical ligands, *o*-iminosemiquinones.

The reaction of H_2L^{OCH3} with Ga(III), possessing filled 3d^{10} orbitals, with 3 equiv of the ligand H_2L^{OCH3} in dry CH_3CN in the presence of NEt_3 (3 equiv) under argon yields a light-yellow solution, which on stirring in pressed air resulted in a dark-colored solid.[4] The solid was recrystallized from diethylether and acetonitrile (80:20) to obtain X-ray-quality violet crystals of **2**.[5] To our surprise, several features of **2**[4] differ remarkably from **1** and other similar tris-radical complexes[1a,2,6] of Ga(III) and Co(III) (Scheme 1): (i) mass spectrometry (EI and ESI-MS), (ii) electrochemistry, (iii) IR spectroscopy, and (iv) most notably μ_{eff} versus T behavior. In contrast to **1** and other tris(*o*-iminobenzosemiquinone)-M(III) complexes, a single peak with 100% abundance is observed for **2** in ESI(+)-MS (CH_2Cl_2) at *m*/*z* 1133.6 without any fragment at *m*/*z* corresponding to the $M(L^{R\bullet})_2$ atomic mass,[2] which is generally the fragment with a 100% abundance. Moreover, noticeably, the molecular mass of 1133.6 is smaller by two hydrogen atoms than that for putative tris-radical $Ga(L^{OCH3\bullet})_3$. Four strong IR bands at 1650, 1607, 1205, and 1155 cm^{-1} appear for **2**, which are absent in the corresponding complex **1**, $[Co^{III}(L^{OCH3\bullet})_3]$. Cyclic voltammetric experiments exhibit only two reversible one-electron redox waves for **2** in CH_2Cl_2: $E_{1/2}(\mathrm{ox}) = 0.215$ V and $E_{1/2}(\mathrm{red}) = -0.731$ V versus Fc$^+$/Fc, instead of at least four reversible redox processes observed for **1** and other $M^{III}(L^{R\bullet})_3$ complexes.[2] The temperature-independent (5−290 K) effective magnetic moment $\mu_{\mathrm{eff}} = 1.73 \pm 0.03$ μ_{B} for **2** (Figure 1) conspicuously indicates the presence of paramagnetism arising due to a value of $S = {}^1/_2$ throughout the temperature range. The solid line in Figure 1 represents the simulation with $g = 2.00$.

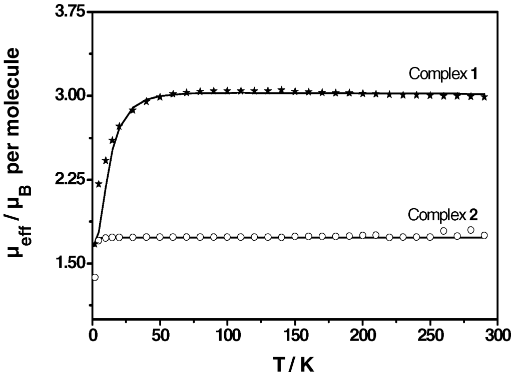


Figure 1. Plots of μ_{eff} vs T for complexes **1** and **2**. The solid lines represent the simulation of the experimental data.

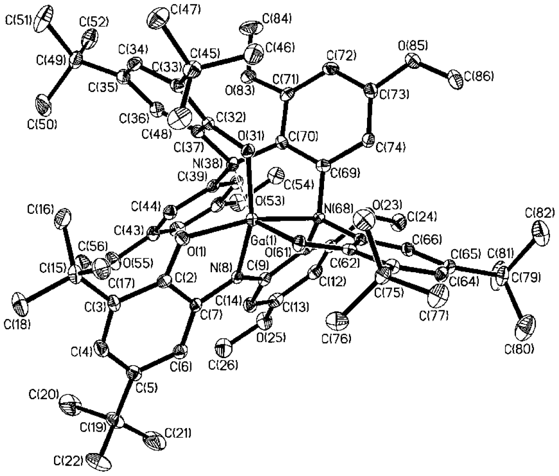


Figure 2. Molecular structure of complex **2**, $[Ga^{III}L_1{}^{\bullet}]$, with selected bond lengths (Å) and angles (deg): Ga(1)−O(1) 1.951(2), Ga(1)−N(8) 2.005(3), Ga(1)−O(31) 1.848(2), Ga(1)−N(38) 1.665(3), Ga(1)−O(61) 1.862(2), Ga(1)−N(68) 2.206(3), C(7)−N(8) 1.359(4), C(2)−O(1) 1.308(4), N(8)−C(9) 1.384(4), C(62)−O(61) 1.342(4), C(67)−N(68) 1.479(4), N(68)−C(69) 1.471(4), C(32)−O(31) 1.354(4), C(37)−N(38) 1.468(4), N(38)−C(39) 1.440(4), N(38)−C(70) 1.466(4), O(1)−Ga(1)−N(8) 81.12(10), N(8)−Ga(1)−O(61) 107.38(10), O(61)−Ga(1)−N(68) 84.80(10), N(68)−Ga(1)−O(31) 101.07(9), O(31)−Ga(1)−N(38) 70.66(9), N(38)−Ga(1)−O(1) 104.49(9).

The single-crystal X-ray structure[5] of **2** (Figure 2) unambiguously shows that three $[L^{OCH3}]$ units condense together to a new hexadentate noninnocent ligand H_4L_1, which coordinates to a Ga(III) center upon deprotonation and generates an iminosemiquinone monoradical in the presence of air. Thus, except the ring containing the carbon atoms C(2) to C(7), the C−C bond distances for each of the individual other rings, substituted with *t*-Bu and OCH_3, in complex **2** have been found to lie within the narrow range of 1.398 ± 0.030 Å, indicating that these C−C lengths are equidistant and the conjugation of the phenyl rings is retained.[1,2] In contrast, the six C−C distances in the ring with C(2) to C(7) are not equidistant: the typical pattern of

---

(4) Complex **2**: To an argon-scrubbed solution of 2-(3,5-dimethoxyaniline)-4,6-di-*tert*-butylphenol H_2L^{OCH3} (0.96 g; 3 mmol) in distilled acetonitrile (50 mL) was added dry Et_3N (2.02 mL) to yield a light-brown solution, which was charged with $GaCl_3$ (0.16 g; 1 mmol). The resulting solution was refluxed under argon for 1 h and stirred for a further 0.5 h in the presence of pressed air. The dark-colored solution upon concentration yielded a deep-violet microcrystalline solid. Yield: 0.480 g (∼ 42%). X-ray quality crystals were grown from a solution of Et_2O-CH_3CN (80:20). Anal. calcd for $C_{66}H_{85}N_3O_3Ga$: C, 69.90; H, 7.55; N, 3.71. Found: C, 69.6; H, 7.6; N, 3.8. ESI(pos.)-MS in CH_2Cl_2: *m*/*z* 1133.6 (100%) $[M]^+$. EI-MS (250 °C): *m*/*z* 1132 (95%), 1133 (94%), 1134 (100%), 1135 (66%), 1136 (27%) $[M]^+$, 641 (94%), 642 (38%), 643 (70.5%), 644 (26.4%) $[M-C_{22}H_{28}NO_3-C_4H_{12}O_4-CH_3]^+$. Cyclic voltammetry in CH_2Cl_2: E_{ox}, +0.697 V, $E_{1/2}{}^1(\mathrm{ox})$, +0.215 V; $E_{1/2}{}^1(\mathrm{red})$, −0.731 vs Fc$^+$/Fc. IR (KBr, cm^{-1}): 2954, 1650, 1607, 1478, 1443, 1420, 1301, 1252, 1205, 1155, 1122, 1092, 1062, 831, 776, 742. UV−vis in CH_2Cl_2 (λ, nm; ε, M^{-1} cm^{-1}): 918−1030 (∼3160), 576 (1960), 383 (15 040). The same product is not obtained under ambient conditions, and the product obtained under such conditions is diamagnetic and yet to be characterized fully.

(5) Crystal data for **2**: $C_{66}H_{85}N_3O_9Ga\cdot 0.25(C_2H_5)_2O$, $M_{\mathrm{f}} = 1152.62$, $T =$ 100(2) K, monoclinic, space group *P*2(1)/*n* (no. 14), $a = 10.9981(4)$ Å, $b = 20.6334(7)$ Å, $c = 28.9674(10)$ Å, $\beta = 95.440(3)°$, $Z = 4$, $D_{\mathrm{c}} = 1.170$ g cm^{-3}, $\mu = 0.476$ mm^{-1}, F(000) = 2462, λ (Mo Kα) = 0.710 73 Å, crystal size = 0.26 × 0.05 × 0.03 mm. A total of 11 488 independent reflections were used for solution and refinement (SHELXL 97) by full-matrix least-squares on F^2; semiempirical absorption correction. Final R indices: $R_1 = 0.0583$; R_1 (all data) = 0.0930.

(6) (a) Chaudhuri, P.; Verani, C. N.; Bill, E.; Bothe, E.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **2001**, *123*, 2213. (b) Chun, H.; Verani, C. N.; Chaudhuri, P.; Bothe, E.; Bill, E.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **2001**, *40*, 4157.

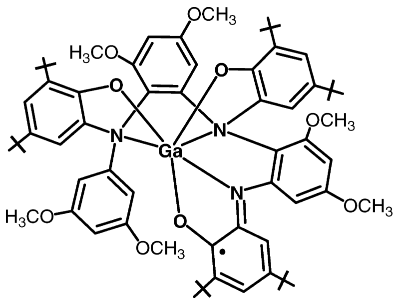


Figure 3. A schematic representation of complex **2**.

the iminobenzosemiquinone radicals of a short C(3)−C(4) = 1.376 Å, a long C(4)−C(5) = 1.426(5) Å, and again a short C(5)−C(6) = 1.377(5) Å and three adjacent long [C(6)−C(7) = 1.421(5), C(7)−C(2) = 1.450(5), and C(2)−C(3) = 1.435(4) Å] C−C bonds is found.[1,2] Additionally, these phenyl ring-related C(2)−O(1) and C(7)−N(8) bond lengths at 1.308(4) and 1.359(4) Å, respectively, are significantly shorter than the corresponding C−O and C−N bonds of order 1. Hence, this ring comprising C(2) to C(7) atoms adopts a quinoid-type structure and yields the most significant structural parameters for the assignment of the oxidation level of the ligand in **2**.[1,2,6] The same metrical parameters for the monoanionic radical ligands have been found in the complexes reported in the literature with different metal ions.[1,2,6] Thus, the new hexadentate in situ formed ligand $[L_I^{\bullet}]^{3-}$, shown schematically in Figure 3, yields the monoradical neutral complex $[Ga^{III}L_I^{\bullet}]$, **2**, and the physical properties described above are in accord with the description.

Moreover, complex **2** exhibits an electron paramagnetic resonance (EPR) spectrum (Figure 4) at 293 K corroborating with a value of $S = {}^1/_2$, arising from an iminobenzosemiquinone radical. The solution EPR spectrum consists of a complex hyperfine pattern centered at $g = 2.005$. We presume combined hyperfine coupling of the electron spin with probably two almost equivalent ^{14}N's ($I = 1$) arising from delocalization of the electron to explain the major five-line pattern and with ^{69}Ga ($I = {}^3/_2$, 60.2%) and ^{71}Ga ($I = {}^3/_2$, 39.8%) to assign the superhyperfine lines. This notion implicates a change in the electronic structure of **2** in solution. No "half-field" signals were observed which could be attributed to the transitions $\Delta M_S = 2$ and $\Delta M_S = 3$, which are further indications for the absence of three radicals[7] in **2**. Thus the EPR spectrum supports the monoradical nature of **2**, resulting also from X-ray diffraction, magnetic susceptibility, and spectroscopic measurements.

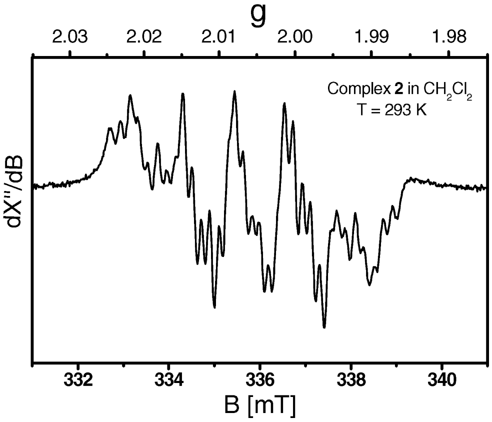


Figure 4. X-band EPR spectrum of **2**, 1×10^{-4} M in CH_2Cl_2 at 293 K. Experimental parameters: frequency 9.44 GHz, power 20 μW, modulation 5 mT, modulation frequency 100 MHz.

One may speculate about the mechanism to involve an intermediate bicyclic endoperoxide species[8] arising from the fully reduced form of the ligand, the amidophenolate dianion, Ga(III) and O_2; the hydrogen atoms of the aniline moieties generate hydrogen peroxide, which disproportionates in the strongly basic medium.

Summarily, the present work describes a hitherto unprecedented example of a Ga(III)−radical-mediated reaction that involves the activation of two C−H bonds, positioned ortho to the methoxy-substituted apparently "innocent" aniline moiety of the N-substituted 2-aminophenol. Such a double C−H activation leading to two C−N couplings is presumably due to a synergistic effect of the 3d^{10} metal and the ligand-derived redox event.

Acknowledgment. This work was supported by the DFG Priority Program "Molecular Magnetism (SPP1137)" Ch111/3-3.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC8006348

---

(7) (a) Ozarowski, A.; McGarvey, B. R.; El-Hadad, A.; Tian, Z.; Tuck, D. G. *Inorg. Chem.* **1993**, *32*, 841. (b) Lange, C. W.; Conklin, B. J.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 1276.

(8) Cherkasov, V. K.; Abakumov, G. A.; Grunova, E. V.; Poddel'sky, A. I.; Fukin, G. K.; Baranov, E. V.; Kurskii, Y. V.; Abakumov, L. G. *Chem.—Eur. J.* **2006**, *12*, 3916.