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Five-coordinate M^{II}-semiquinonate (M = Fe, Mn, Co) complexes: reactivity models of the catechol dioxygenases†

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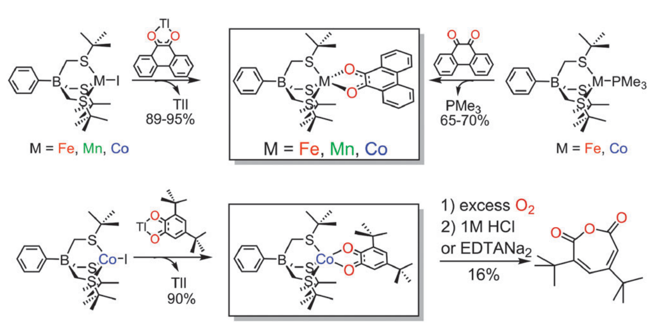
A series of five-coordinate M^{II}-semiquinonate (M = Fe, Mn, Co) complexes were synthesized and characterized, including the first example of a mononuclear Fe^{II}-semiquinonate. Intermediates were observed in the reactions of M^{II}-phenSQ (M = Fe, Co) with O_2. Evidence for the relevance of these intermediates to the intradiol catechol dioxygenases was obtained by characterization of the oxidized semiquinone-derived product, muconic anhydride, resulting from the reaction of $[PhTt^{tBu}]Co^{II}(3,5\text{-DBSQ})$ with O_2.

Intradiol catechol dioxygenases are non-heme iron enzymes that catalyze the oxidative cleavage of the C1–C2 bond of catechols.[1] The state of the enzyme that reacts with O_2 contains a five-coordinate metal site. The activity of the enzyme and its synthetic analogs has been attributed to the partial Fe^{II}-semiquinonate (SQ) character within the Fe^{III}-catecholate species,[2] which results in the formation of a Fe^{III}-alkylperoxy intermediate upon addition of O_2. The extradiol catechol dioxygenases contain iron or manganese active sites and catalyze the oxidative cleavage of C2–C3 bond of catechols.[1,3] During catalytic turnover, superoxo-Fe^{II}-semiquinonate and Fe^{II}-alkylperoxy intermediates have been detected.[4] Interestingly, comparable extradiol-cleaving activities were obtained by substituting the native iron with manganese or cobalt suggesting the intermediacy of superoxo-M^{II}-semiquinonate species (M = Fe, Mn, Co) in the catalytic cycles.[5] Moreover, reactions of redox-active ligand complexes with dioxygen have received recent attention due to their potential utility in stoichiometric and catalytic transformations.[6]

In spite of the implications of the Fe^{II}-semiquinonate species in both intradiol and extradiol dioxygenases, to the best of our knowledge, well characterized mononuclear Fe^{II}-semiquinonate complexes are unknown. Related complexes were reported recently by Fiedler and co-workers, including a mononuclear Fe^{II}-(imino)-semiquinonate complex[7] and a semiquinonate-bridged diiron(II) complex.[8] Herein, we report the first well characterized mononuclear Fe^{II}-semiquinonate complex and its Mn^{II} and Co^{II} analogues – $[PhTt^{tBu}]M(phenSQ)$ (M = Fe, Mn, Co, $PhTt^{tBu}$ = phenyltris((*tert*-butylthio)methyl)borate, phenSQ = 9,10-phenanthrene-semiquinonate). The suitability of these complexes in modelling catalytic intermediates of the intradiol dioxygenases was evaluated by O_2 reactivity studies. A related complex, $[PhTt^{tBu}]Co(3,5\text{-DBSQ})$ (3,5-DBSQ = 3,5-di-*tert*-butyl-1,2-semiquinonate) exhibited the intradiol reactivity, suggesting the relevance of the observed intermediates to the intradiol catechol dioxygenases.

$[PhTt^{tBu}]M(phenSQ)$ were synthesized using two complementary preparative routes, Scheme 1. Metathesis of $[PhTt^{tBu}]MI$ (M = Fe, Mn, Co) with Tl(phenSQ) yielded $[PhTt^{tBu}]M(phenSQ)$ in excellent yields (89–95%). A similar method was applied to the synthesis of $[PhTt^{tBu}]Co(3,5\text{-DBSQ})$ by replacing Tl(phenSQ) with Tl(3,5-DBSQ). Alternatively, the oxidative addition of phenQ to monovalent metal precursors, $[PhTt^{tBu}]M(PMe_3)$ (M = Fe, Co)[9] afforded $[PhTt^{tBu}]M(phenSQ)$ (M = Fe, Co) in good yields (65–70%). High resolution mass spectroscopy (HRMS) data combined with ^1H NMR spectral analyses confirmed the composition and purity of the $[PhTt^{tBu}]M^{II}$-(SQ) complexes (Fig. S4–S7, S11–S14, ESI†).



Scheme 1 Synthetic routes to $[PhTt^{tBu}]M(SQ)$ complexes (M = Fe, Mn, Co) and O_2 reactivity of $[PhTt^{tBu}]Co(3,5\text{-DBSQ})$.

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† Electronic supplementary information (ESI) available: Experimental details, new compound characterization data and crystallographic data, *etc.* CCDC 969713 ($[PhTt^{tBu}]Fe(phenSQ)$), 969714 ($[PhTt^{tBu}]Co(phenSQ)$), 969715 ($[PhTt^{tBu}]CoI$), 969716 ($[PhTt^{tBu}]MnI$), 969717 ($[PhTt^{tBu}]Mn(phenSQ)$) and 992704 ($[PhTt^{tBu}]Co(3,5\text{-DBSQ})$). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc49143a

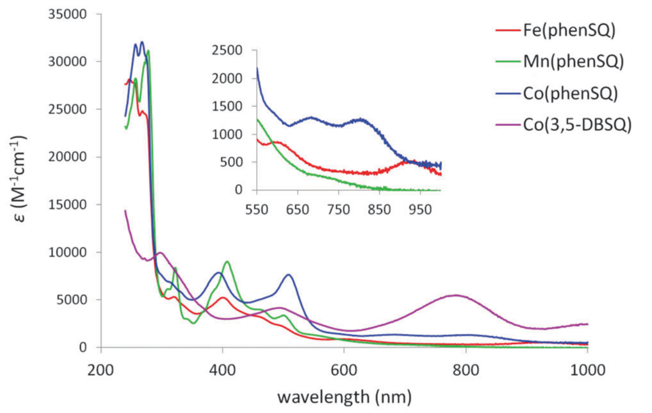
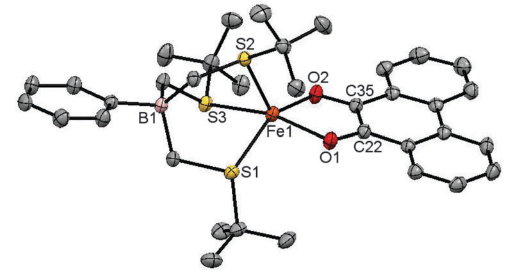


Fig. 1 Electronic spectra of the [PhTt^{tBu}]M(SQ) complexes. The insert highlights ligand field transitions.

Table 1 Molecular structure of [PhTt^{tBu}]Fe(phenSQ) and selected metric parameters of the [PhTt^{tBu}]M(phenSQ) complexes. Hydrogen atoms are omitted for clarity. (Structures of the other new complexes are available in the ESI)



	Fe(phenSQ)	Mn(phenSQ)	Co(phenSQ)
M1–O1	2.064(2)	2.109(2)	1.922(1)
M1–O2	2.015(2)	2.080(2)	1.912(1)
O1–C22	1.285(2)	1.282(4)	1.301(2)
O2–C35	1.285(2)	1.280(4)	1.297(2)
C35–C22	1.435(3)	1.436(5)	1.411(2)
τ-value	0.14	0.58	0.01

The electronic spectra of the [PhTt^{tBu}]M(SQ) complexes are contained in Fig. 1. [PhTt^{tBu}]Fe(phenSQ) shows two features of low intensity at 600 nm (ε = 868 M^{-1} cm^{-1}) and 935 nm (ε = 539 M^{-1} cm^{-1}), the latter being consistent with a typical ligand field transition for five-coordinate, high-spin Fe^{II} complexes.[10] No apparent ligand field transition was observed for [PhTt^{tBu}]Mn(phenSQ), indicating a high-spin Mn^{II} center. [PhTt^{tBu}]Co(phenSQ) exhibits two features at 683 (ε = 1310 M^{-1} cm^{-1}) and 803 (ε = 1290 M^{-1} cm^{-1}), both of which agree well with the ligand field transitions of five-coordinate, high-spin Co^{II}.[11] Unlike the previously reported [Tp^{Cum,Me}]-Co(3,5-DBSQ),[12] the ligand field transitions of [PhTt^{tBu}]Co(3,5-DBSQ) were not observed in the spectrum presumably due to the overlap with the intense band at 784 nm (ε = 5470 M^{-1} cm^{-1}).[13]

The description of the metal complex electronic structures as M^{II}-SQ is supported by their infrared spectra. In contrast to the IR spectra of the respective [PhTt^{tBu}]MI complexes, [PhTt^{tBu}]M(phenSQ) exhibit intense bands between 1500 cm^{-1} and 1600 cm^{-1}, which are consistent with the C═O stretches of phenSQ (Fig. S15–S17, ESI†).[14] Although [PhTt^{tBu}]CoI also shows two bands in the 1400–1450 cm^{-1} range, the much more intense band at 1462 cm^{-1} of [PhTt^{tBu}]Co(3,5-DBSQ) is tentatively assigned to the ν(C═O) of 3,5-DBSQ (Fig. S18, ESI†).[15]

All the complexes are five-coordinate as deduced by X-ray diffraction analyses (Fig. S20, ESI†). The coordination geometry of the [PhTt^{tBu}]Mn(phenSQ) lies between trigonal-bipyramidal and square pyramidal (τ_5 = 0.58),[16] whereas the geometries of [PhTt^{tBu}]Fe(phenSQ) (τ_5 = 0.14), [PhTt^{tBu}]Co(phenSQ) (τ_5 = 0.01) and [PhTt^{tBu}]Co(3,5-DBSQ) (τ_5 = 0.17) are best described as distorted square pyramids. Key bond lengths support the redox state assignment of the bidentate ligand as semiquinonate, Table 1 and Fig. S20 (ESI†). For the M^{II}-phenSQ complexes, the C–O distances are in the range of 1.28–1.30 Å and C–C distances are in the range of 1.41–1.44 Å. These bond distances are characteristic of a bound phenSQ ligand.[14a,17] For [PhTt^{tBu}]Co(3,5-DBSQ), the average C–O distance is 1.314(2) Å. This distance is certainly among the longest C–O distances for 3,5-DBSQ, but is not unprecedented.[18] Furthermore, the "four long/two short" quinoid distortion in the semiquinonate ring further supports its electronic structure description. All complexes are air-sensitive in solution as demonstrated by O$_2$ reactivity studies, *vide infra*, which can be rationalized by the M^{II}-SQ charge distribution.[2a–c] Space filling models (Fig. S21, ESI†) indicate O$_2$ accessibility to both the metal centers and the semiquinonate ligands.

The M^{II}-SQ complexes showed paramagnetic ^{1}H NMR spectra. Their effective magnetic moments measured in solution by the Evans method are [PhTt^{tBu}]Mn(phenSQ) and [PhTt^{tBu}]Co(3,5-DBSQ) μ_{eff} = 5.01(6) μ_B and 2.91(2) μ_B, respectively. These values are very close to the spin-only values for S = 2 and S = 1 systems, indicating strong antiferromagnetic coupling between high-spin divalent metal centers and the SQ radicals. [PhTt^{tBu}]Fe(phenSQ) and [PhTt^{tBu}]Co(phenSQ) display μ_{eff} = 4.65(2) μ_B and 3.43(3) μ_B, respectively. These values are higher than the spin-only values for S = 3/2 and S = 1 systems, but lower than expected for non-spin coupled systems,[12] suggesting either weaker antiferromagnetic coupling or more likely, non-negligible spin–orbit coupling.

The cyclic voltammograms (CV) were measured in THF to evaluate the redox characteristics of the M^{II}-SQ complexes (Fig. S22, ESI†). [PhTt^{tBu}]Co(phenSQ) and [PhTt^{tBu}]Co(3,5-DBSQ) exhibit reversible reduction events at −0.97 V and −0.82 V (*vs.* Fc$^{+/0}$) which are assigned as ligand-centered reductions, phenSQ/phenCat and 3,5-DBSQ/DBCat, respectively. These redox potentials match very well with the values reported for Me$_4$cyclam supported Co^{II}-semiquinonate complexes (−1.00 V for phenSQ/phenCat and −0.85 V for 3,5-DBSQ/DBCat).[19] The redox events for [PhTt^{tBu}]M-(phenSQ) (M = Mn, Fe) are irreversible on the electrochemical timescale, exhibiting E_c values of −1.17 V for [PhTt^{tBu}]Fe(phenSQ) and −1.11 V for [PhTt^{tBu}]Mn(phenSQ), assigned as phenSQ/phenCat reductions. The trend in reduction potentials among the [PhTt^{tBu}]M(phenSQ) species, Fe < Mn < Co, indicates the Co complex is most readily reduced. The oxidations of [PhTt^{tBu}]-Co(phenSQ) and [PhTt^{tBu}]Co(3,5-DBSQ) at 0.26 V and 0.47 V, respectively are also irreversible.

To evaluate the utility of five-coordinate M^{II}-SQ complexes to model putative intermediates in catechol dioxygenase catalysis,

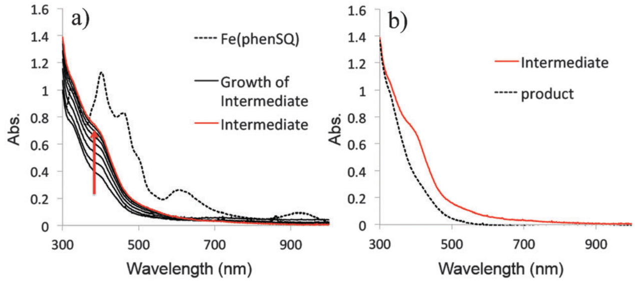


Fig. 2 Electronic spectral changes during the oxygenation of [PhTt^{tBu}]-Fe(phenSQ) at −90 °C in toluene. (a) Spectral changes after exposing [PhTt^{tBu}]Fe(phenSQ) to O_2. Intermediate growth indicated by red arrow. Spectra were recorded at 2 min intervals. (b) Spectra of intermediate and product collected at −90 °C. The spectrum of the product was obtained by warming the sample to 0 °C for 5 min to allow the decay of the intermediate and cooling back to −90 °C for 15 min.

electronic spectroscopy was employed to monitor the reaction of [PhTt^{tBu}]M(phenSQ) with O_2.[20] Even at very low temperature (−90 °C) rapid spectroscopic changes were observed upon addition of O_2 to [PhTt^{tBu}]M(phenSQ) (M = Fe, Co), producing intermediates which decay to the thermodynamic products in 5–10 minutes upon warming to higher temperatures (Fig. 2 and Fig. S28, ESI†).[21] Indirect evidence for the relevance of these synthetic intermediates to the intradiol dioxygenases was obtained using [PhTt^{tBu}]Co(3,5-DBSQ). Upon reaction with O_2 in THF for 16 hours, [PhTt^{tBu}]Co(3,5-DBSQ) produced the intradiol cleavage product, muconic anhydride in 16% yield, Scheme 1 (see ESI† for details). This result, together with a previous discovery that the five coordinate complex [Tp^{iPr_2}]Mn(3,5-DBSQ) also produces the intradiol product,[22] suggests that the semiquinonate character of the ligand may contribute to the intradiol cleaving reactivity, even for different metals. To the best of our knowledge, this is the first example of intradiol reactivity of a Co^{II}(3,5-DBSQ) complex.[23]

In summary, a series of five-coordinate M^{II}-semiquinonate (M = Fe, Mn, Co) complexes supported by the tris(thioether) ligand [PhTt^{tBu}] were synthesized and characterized, including the first example of a mononuclear Fe^{II}-semiquinonate complex. While [PhTt^{tBu}]Co(3,5-DBSQ) was found to be a reactivity model for the intradiol catechol dioxygenases, [PhTt^{tBu}]M(phenSQ) (M = Fe, Co) serve as potential precursors to model the putative intermediates in intradiol dioxygenase catalysis. Our current efforts are focused on additional spectroscopic and structural characterization of the intermediates produced from the low temperature reactions of [PhTt^{tBu}]M(phenSQ) with O_2. Also under investigation are the reactions of [PhTt^{tBu}]M(phenSQ) with superoxide to model intermediate(s) of relevance in extradiol dioxygenase catalysis.

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Notes and references

1 (*a*) T. D. H. Bugg and S. Ramaswamy, *Curr. Opin. Chem. Biol.*, 2008, **12**, 134–140; (*b*) M. Costas, M. P. Mehn, M. P. Jensen and L. Que, Jr., *Chem. Rev.*, 2004, **104**, 939–986.
2 For experimental work, see: (*a*) D. D. Cox and L. Que, Jr., *J. Am. Chem. Soc.*, 1988, **110**, 8085–8092; (*b*) H. G. Jang, D. D. Cox and L. Que, Jr., *J. Am. Chem. Soc.*, 1991, **113**, 9200–9204; (*c*) T. Funabiki, A. Fukui, Y. Hitomia, M. Higuchia, T. Yamamotoa, T. Tanaka, F. Tani and Y. Naruta, *J. Inorg. Biochem.*, 2002, **91**, 151–158. For theoretical work, see: (*d*) T. Funabiki and T. Yamazaki, *J. Mol. Catal. A: Chem.*, 1999, **150**, 37–47; (*e*) N. Nakatani, Y. Hitomi and S. Sakaki, *J. Phys. Chem. B*, 2011, **115**, 4781–4789.
3 J. D. Lipscomb, *Curr. Opin. Struct. Biol.*, 2008, **18**, 644–649.
4 E. G. Kovaleva and J. D. Lipscomb, *Science*, 2007, **316**, 453–457.
5 (*a*) J. P. Emerson, E. G. Kovaleva, E. R. Farquhar, J. D. Lipscomb and L. Que, Jr., *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 7347–7352; (*b*) A. J. Fielding, E. G. Kovaleva, E. R. Farquhar, J. D. Lipscomb and L. Que, Jr., *JBIC, J. Biol. Inorg. Chem.*, 2011, **16**, 341–355.
6 (*a*) S. Mukherjee, T. Weyhermuller, E. Bothe, K. Wieghardt and P. Chaudhuri, *Dalton Trans.*, 2004, 3842–3853; (*b*) C. A. Lippert, S. A. Arnstein, C. D. Sherrill and J. D. Soper, *J. Am. Chem. Soc.*, 2010, **132**, 3879–3892; (*c*) C. J. Rolle, III, K. I. Hardcastle and J. D. Soper, *Inorg. Chem.*, 2008, **47**, 1892–1894.
7 M. M. Bittner, S. V. Lindeman and A. T. Fiedler, *J. Am. Chem. Soc.*, 2012, **134**, 5460–5463.
8 A. E. Baum, S. V. Lindeman and A. T. Fiedler, *Chem. Commun.*, 2013, **49**, 6531–6533.
9 (*a*) M. T. Mock, C. V. Popescu, G. P. A. Yap, W. G. Dougherty and C. G. Riordan, *Inorg. Chem.*, 2008, **47**, 1889–1891; (*b*) J. A. Dupont, G. P. A. Yap and C. G. Riordan, *Inorg. Chem.*, 2008, **47**, 10700–10707.
10 E. I. Solomon, T. C. Brunold, M. I. Davis, J. N. Kemsley, S. K. Lee, N. Lehnert, F. Neese, A. J. Skulan, Y. S. Yang and J. Zhou, *Chem. Rev.*, 2000, **100**, 235–349.
11 (*a*) M. Ciampolini, N. Nardi and G. P. Speroni, *Coord. Chem. Rev.*, 1966, **1**, 222–233; (*b*) Z. Dori and H. B. Gray, *Inorg. Chem.*, 1968, **7**, 889–892.
12 M. Ruf, B. C. Noll, M. D. Groner, G. T. Yee and C. G. Pierpont, *Inorg. Chem.*, 1997, **36**, 4860–4865.
13 Analogous to [PhTt^{tBu}]Co(3,5-DBSQ), an intense band at 818 nm was observed for [PhTt^{tBu}]Co(phenSQ) at −90 °C.
14 (*a*) A. Caneschi, A. Dei, F. Fabrizi de Biani, P. Gutlich, V. Ksenofontov, G. Levchenko, A. Hoefer and F. Renz, *Chem. – Eur. J.*, 2001, **7**, 3926–3930; (*b*) S. Roy, B. Sarkar, D. Bubrin, M. Niemeyer, S. Zalis, G. K. Lahiri and W. Kaim, *J. Am. Chem. Soc.*, 2008, **130**, 15230–15231.
15 (*a*) F. Hartl and A. Vlcek, Jr., *Inorg. Chem.*, 1996, **35**, 1257–1265; (*b*) P. A. Wicklund, L. S. Beckmann and D. G. Brown, *Inorg. Chem.*, 1976, **15**, 1996–1997.
16 A. W. Addison, T. N. Rao, J. Reedijk, J. Vanrijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349–1356.
17 C. G. Pierpont and R. M. Buchanan, *Coord. Chem. Rev.*, 1981, **38**, 45–87.
18 M. Graf, G. Wolmershäser, H. Kelm, S. Demeschko, F. Meyer and H.-J. Krüger, *Angew. Chem., Int. Ed.*, 2010, **49**, 950–953.
19 A. Caneschi, A. Dei, D. Gatteschi and V. Tangoulis, *Inorg. Chem.*, 2002, **41**, 3508–3512.
20 A (triphos)Ir(O_2)(phenSQ) complex modeling the intradiol dioxygenase intermediate was formed from the reaction of [(triphos)Ir(phenCat)]-BPh_4 with O_2. See: P. Barbaro, C. Bianchini, C. Mealli and A. Meli, *J. Am. Chem. Soc.*, 1991, **113**, 3181–3183.
21 No intermediate was observed upon reaction of [PhTt^{tBu}]Mn-(phenSQ) with O_2 at −90 °C.
22 H. Komatsuzaki, A. Shiota, S. Hazawa, M. Itoh, N. Miyamura, N. Miki, Y. Takano, J. Nakazawa, A. Inagaki, M. Akita and S. Hikichi, *Chem. – Asian J.*, 2013, **8**, 1115–1119.
23 A tetramine-Co^{II}(3,5-DBSQ) complex reacted with O_2, leading to the ring cleavage of the catechol. However, the organic products were not unambiguously characterized as intradiol or extradiol products. See: S. Nakashima, H. Ohya-Nishiguchi, N. Hirota, S. Tsuboyama and T. Chijimatsu, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 1225–1232.