Inorganic Chemistry
Communication
pubs.acs.org/IC

Synthesis and Characterization of Iron Trisphenolate Complexes with Hydrogen-Bonding Cavities

Mario Adelhardt, Matthew J. Chalkley, Frank W. Heinemann, Jörg Sutter, Andreas Scheurer, and Karsten Meyer*

Department of Chemistry and Pharmacy, Inorganic Chemistry, Friedrich-Alexander University Erlangen−Nürnberg (FAU), Egerlandstraße 1, 91058 Erlangen, Germany

Supporting Information

ABSTRACT: A new family of C_3-symmetric ligands, featuring phenolate donors and a secondary coordination sphere, have been synthesized. We report the synthesis and subsequent coordination chemistry of these new tripodal N-anchored tris(phenolate) chelates, [tris(5-*tert*-butyl-3-*N*-carboxamide-2-hydroxybenzyl)amines] ($H_3{}^R$SalAmi), to iron(II), iron(III), and zinc(II). These electron-rich complexes have intramolecular hydrogen bonds, and therefore the potential to stabilize biologically relevant substrates in small-molecule activation chemistry.

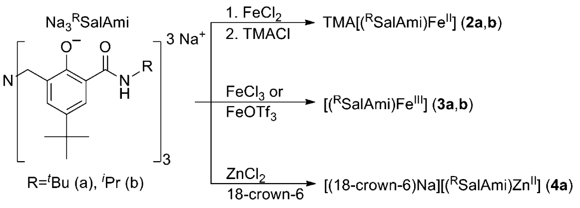
The use of C_3-symmetric ligands has become more widespread because ligands of this type have repeatedly shown the ability to stabilize fleeting intermediates and previously inaccessible species.[1] It has been shown that these ligands, by lowering the symmetry around the metal from octahedral or tetrahedral to trigonal, make additional nonbonding orbitals available that, in turn, stabilize these highly reactive terminal ligands.[2] On iron in particular, C_3-symmetric ligands have provided access to both terminal nitride[1,3−5] and oxo ligands.[6−8]

Much of this work has been pursued because such species are believed to be models of important intermediates in biological transformations. In biological systems, these transformations are almost always made more energetically favorable by the utilization of hydrogen-bonding interactions between the enzyme and substrate or intermediates. The hydrogen bonds provide both a means of stabilization and a means of directing the reactivity. Accordingly, there has been a growing interest in developing ligands that incorporate hydrogen-bond donors into the secondary coordination sphere in a biomimetic fashion. This attempt to synthetically mimic nature has led to some impressive successes, such as Tolman et al.'s copper hydroxide,[9] Masuda et al.'s copper hydroperoxo,[10] Nocera et al.'s iron hydroxide,[11] Berreau et al.'s zinc alkoxide,[12] and Goldberg et al.'s iron peroxide.[13]

Borovik et al. have applied both of these approaches through their use of tris[(*N*′-*tert*-butylureaylato)-*N*-ethyl)]aminato (H_6buea), a C_3-symmetric ligand with a secondary coordination sphere.[14] By using ligands with varying numbers of hydrogen-bond donors from 0 to 3, Borovik et al. have demonstrated how the secondary coordination sphere is essential to stabilizing a variety of terminal ligands of biological interest.[15] Furthermore, his studies of the electronic structure of these complexes have shown that hydrogen bonding reduces the M−E bond order and stabilizes high-spin species, making these species more similar to what is spectroscopically observed in metalloproteins.[16]

Our group has recently worked to develop a series of C_3-symmetric N-anchored tripodal ligands with donors from tris(carbenes) to tris(phenolates), including mixed-donor species, for first-row transition metals.[17] Subsequently, we believed there was an opportunity to combine the biologically relevant phenolate system[18,19] with a biologically relevant secondary coordination sphere. To this end, we developed a new family of C_3-symmetric N-anchored tris(phenolate) ligands with amide moieties in the secondary coordination sphere ($H_3{}^R$SalAmi). The synthetic pathway (see the Supporting Information, SI) allows for a large-scale synthesis from inexpensive precursors with convenient control of the sterics of the binding cavity in the last step by changing the primary amine used. The ligands are selectively deprotonated at the phenol position by reaction with NaOMe and, as seen in Scheme 1, subsequently metalated with both iron(II) and iron(III) chloride or iron(III) triflate salts to generate the monoanionic and neutral complexes, respectively. Additionally, as expected, the iron(III) species could be generated through chemical oxidation of the iron(II) species. Tris(phenolate) amine complexes of iron are relatively rare,[17,20−23] and to this point, none has introduced a secondary coordination sphere. For structural, spectroscopic, and electrochemical comparison, a zinc(II) species was also synthesized.

Scheme 1. Synthesis of Metal Complexes from the Deprotonated SalAmi Ligand and Metal Salts



The divalent iron complex TMA[(^{tBu}SalAmi)Fe^{II}] (**1a**; TMA = tetramethylammonium) was fully characterized by means of single-crystal X-ray crystallography, ^{1}H NMR, Mößbauer, IR, UV−vis spectroscopy, and variable-temperature (VT)/variable

Received: January 29, 2014
Published: March 3, 2014

dx.doi.org/10.1021/ic5002286 | *Inorg. Chem.* 2014, 53, 2763−2765

field (VF) SQUID magnetization. The isopropyl derivative TMA[(^{iPr}SalAmi)Fe^{II}] (**1b**) was characterized by analogous ^{1}H NMR and IR. The molecular and crystal structure of **1a** (see Figure 1) was determined by X-ray crystallography. The molecule crystallizes in the $Pa\overline{3}$ space group, so the expected C_3 geometry around the metal is crystallographically enforced. However, the ^{1}H NMR spectra of **1a** and **1b** suggest that the 3-fold geometry is maintained in solution as well. The iron center in **1a** is five-coordinate (trigonal-bipyramidal, tbp), with the tetradentate chelate and an axially bound pyridine. The three phenolate moieties coordinate the iron center with a small out-of-plane shift, d_{oop}, of 0.026(3) Å [distance of the iron atom above the plane formed by the three phenolate oxygen (O_{Ar}) atoms] and therefore nearly ideal O_{Ar}−Fe−O_{Ar} angles of 119.6(2)°. The Fe−O_{Ar} distance in **1a** is 2.056(3) Å, which is 0.1 Å longer than that in our recently reported iron(II) tris(phenolate) amine, PNP[((^{Ad,Me}ArO)$_3$N)Fe^{II}] [d(Fe−O_{Ar})$_{avg}$ = 1.952(2) Å].[17] The anchoring amine is located at a distance of 2.184(4) Å, again longer than that in our previous complex, but is still coordinated to the metal center.[17] As expected, the amide protons are oriented toward the metal center and theoretically available to interact with (and stabilize) a donor atom of an appropriate terminal ligand. In this complex, the amide protons are hydrogen-bonded to form a six-membered ring with the phenolate oxygen atoms. The N(H)−O_{Ar} distance is 2.756(4) Å, and the N−H−O_{Ar} angle is 133.0°.

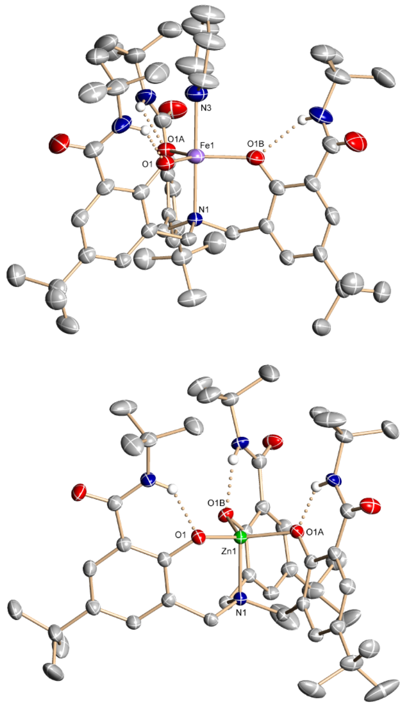


Figure 1. Molecular structure of the complex anions of **1a** in crystals of TMA[(^{tBu}SalAmi)Fe^{II}(pyridine)]·3pyridine and of **3a** in crystals of TMA[(^{tBu}SalAmi)Zn^{II}]·3.5pyridine (50% probability ellipsoids; hydrogen atoms except for amide protons, counterions, and solvent molecules omitted for clarity).

The zero-field ^{57}Fe Mößbauer spectrum of **1a**, seen in Figure 2 along with the VT/VF SQUID data, was recorded in solution, using a 30% ^{57}Fe-enriched sample synthesized from $^{57}FeCl_2$ in acetonitrile.[24] Both the isomer shift, δ, of 1.19(1) mm/s and the quadrupole splitting, ΔE_Q, of 2.84(1) mm/s are larger than those for the iron(II) tris(phenolate) amine complex, PNP[((^{Ad,Me}ArO)$_3$N)Fe^{II}] [δ = 1.04(1) mm/s and ΔE_Q = 2.24(1) mm/s].[17] The observed trend in the isomer shift is in good agreement with the Fe−O_{Ar} bond distances in these iron(II) tris(phenolate) complexes. Only recently, Neese and Petrenko stated that "the most decisive factor for the isomer shift is the metal ligand bond".[25] Thus, for the series of complexes, the shorter the Fe−O_{Ar} bond, the lower the isomer shift.

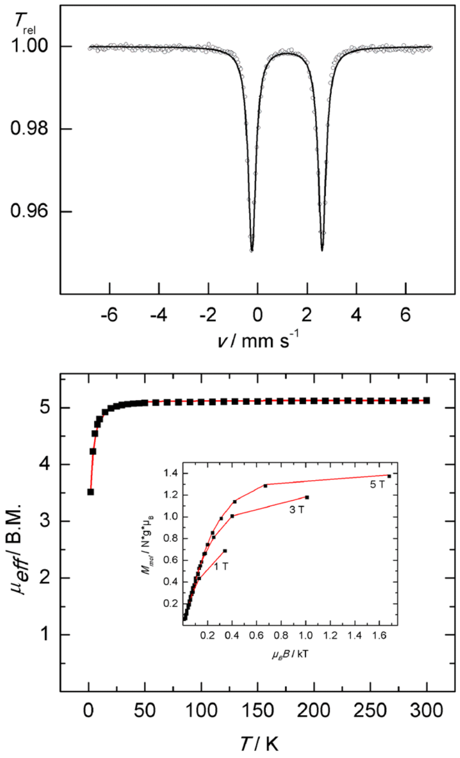


Figure 2. Zero-field Mößbauer spectrum of ^{57}Fe-enriched **1a** in solution at 77 K [top; fit results of δ = 1.19(1) mm/s and ΔE_Q = 2.84(1) mm/s]. VT/VT SQUID data for **1a** in the solid state (bottom; fit results of $\mu_{eff,RT}$ = 5.1 μ_B) and VF SQUID data (inset: H = 1, 3, and 5 T; fit results of D = 6.472 cm^{-1} and E/D = 0.282).

For **1a**, the magnetic moment, μ_{eff}, of 5.1 μ_B, obtained by VT SQUID, is slightly higher than the spin-only value of 4.9 μ_B but reproducible and well within the normal range for iron(II) complexes.

In order to better understand the coordination and electrochemistry of iron(II) complex **1a**, the corresponding zinc(II) complex was synthesized by reaction of the deprotonated ligand with $ZnCl_2$. To ensure that this was a reasonable comparison, the molecular and crystal structure of TMA[(^{tBu}SalAmi)Zn^{II}] (TMA-**3a**; Figure 2) was determined, and it revealed a coordination geometry very similar to that of **1a**. In contrast to five-coordinate tbp **1a**, the zinc complex, TMA-**3a**, is four-coordinate trigonal-pyramidal, with an empty axial coordination site trans to the chelates' N anchor. The Zn−O_{Ar} bond lengths are 1.916(2) Å with a Zn−N_{anchor} distance of 2.040(3) Å. The slight contractions in bond distances are likely due to the smaller zinc radius and lower coordination number in TMA-**3a**. Hydrogen bonding between the amide and phenolate is again present in this complex.

The electrochemistry of Na(18 crown 6)-**3a** was then studied and revealed several irreversible, presumably phenolate-based oxidation events between 0.4 and 1 V, referenced to Fc$^+$/Fc (see the SI for all electrochemistry). As expected, the redox chemistry of **1a** revealed similar, irreversible ligand-based redox events between 0.6 and 1 V. Two additional redox events were present: The first event at −1.25 V we assign to an iron(II)/iron(III) couple that is quasi-reversible at scan rates from 50 to 1600 mV/s, whereas the origin of the second event at −0.38 V remains as of yet unknown. As expected, the electrochemistry of the independently synthesized iron(III) complex, **2a**, demonstrated similar features when investigated.

Because of the quasi-reversible nature of the iron(II)/iron(III) couple, we believed that the iron(III) species could be synthesized by chemical oxidation. Chemical oxidation of the sodium salt of the iron(II) complexes did indeed lead to a characteristic color change and the isolation of analytically pure $[(^{R}\text{SalAmi})\text{Fe}^{\text{III}}]$ (**2a**, R = ^{t}Bu, and **2b**, R = ^{i}Pr).

Further investigation will include a detailed analysis of the electronic structure of **2a**, because initial experiments indicate that the high-spin Fe^{III} d^5 system is unexpectedly complicated [see the SI for preliminary SQUID, X-band electron paramagnetic resonance (EPR), and ^{57}Fe Mößbauer data]. In addition, iron(II) complexes will be studied for their ability to reductively activate small molecules, in particular O_2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic details, CHN elemental analyses, ^{1}H/^{13}C NMR, UV−vis, IR, EPR, magnetization, and ^{57}Fe Mößbauer data, as well as X-ray crystallographic details and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: karsten.meyer@fau.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Friedrich-Alexander University Erlangen−Nürnberg (FAU) and DFG. We thank the Bavarian California Technology Center (BaCaTeC) for generous funding. M.J.C. thanks the Fulbright Commission for a fellowship. The authors gratefully acknowledge Dr. Eckhard Bill (MPI CEC, Mülheim/Ruhr, Germany) for his magnetochemical expertise and discussions.

■ REFERENCES

(1) Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 6252−6254.

(2) Saouma, C. T.; Peters, J. C. *Coord. Chem. Rev.* **2011**, *255*, 920−937.

(3) Scepaniak, J. J.; Fulton, M. D.; Bontchev, R. P.; Duesler, E. N.; Kirk, M. L.; Smith, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 10515−10517.

(4) Vogel, C.; Heinemann, F. W.; Sutter, J.; Anthon, C.; Meyer, K. *Angew. Chem.* **2008**, *47*, 2681−2684.

(5) Scepaniak, J. J.; Vogel, C. S.; Khusniyarov, M. M.; Heinemann, F. W.; Meyer, K.; Smith, J. M. *Science* **2011**, *331*, 1049−1052.

(6) England, J.; Martinho, M.; Farquhar, E. R.; Frisch, J. R.; Bominaar, E. L.; Munck, E.; Que, L., Jr. *Angew. Chem. Int. Ed.* **2009**, *48*, 3622−3626.

(7) Smith, J. M.; Mayberry, D. E.; Margarit, C. G.; Sutter, J.; Wang, H.; Meyer, K.; Bontchev, R. P. *J. Am. Chem. Soc.* **2012**, *134*, 6516−6519.

(8) Bigi, J. P.; Harman, W. H.; Lassalle-Kaiser, B.; Robles, D. M.; Stich, T. A.; Yano, J.; Britt, R. D.; Chang, C. J. *J. Am. Chem. Soc.* **2012**, *134*, 1536−1542.

(9) Berreau, L. M.; Mahapatra, S.; Halfen, J. A.; Young, V. G., Jr.; Tolman, W. B. *Inorg. Chem.* **1996**, *35*, 6339−6342.

(10) Wada, A.; Harata, M.; Hasegawa, K.; Jitsukawa, K.; Masuda, H.; Mukai, M.; Kitagawa, T.; Einaga, H. *Angew. Chem. Int. Ed.* **1998**, *37*, 798−799.

(11) Yeh, C.-Y.; Chang, C. J.; Nocera, D. G. *J. Am. Chem. Soc.* **2001**, *123*, 1513−1514.

(12) Garner, D. K.; Fitch, S. B.; McAlexander, L. H.; Bezold, L. M.; Arif, A. M.; Berreau, L. M. *J. Am. Chem. Soc.* **2002**, *124*, 9970−9971.

(13) Sahu, S.; Widger, L. R.; Quesne, M. G.; de Visser, S. P.; Matsumura, H.; Moënne-Loccoz, P.; Siegler, M. A.; Goldberg, D. P. *J. Am. Chem. Soc.* **2013**, *135*, 10590−10593.

(14) Hammes, B. S.; Young, V. G., Jr.; Borovik, A. S. *Angew. Chem. Int. Ed.* **1999**, *38*, 666−669.

(15) Lucas, R. L.; Zart, M. K.; Murkerjee, J.; Sorrell, T. N.; Powell, D. R.; Borovik, A. S. *J. Am. Chem. Soc.* **2006**, *128*, 15476−15489.

(16) MacBeth, C. E.; Gupta, R.; Mitchell-Koch, K. R.; Young, V. G., Jr.; Lushington, G. H.; Thompson, W. H.; Hendrich, M. P.; Borovik, A. S. *J. Am. Chem. Soc.* **2004**, *126*, 2556−2567.

(17) Käß, M.; Hohenberger, J.; Adelhardt, M.; Zolnhofer, E. M.; Mossin, S.; Heinemann, F. W.; Sutter, J.; Meyer, K., *Inorg. Chem.* **2013**.ASAP. 10.1021/ic4024053

(18) Davis, M. I.; Orville, A. M.; Neese, F.; Zaleski, J. M.; Lipscomb, J. D.; Solomon, E. I. *J. Am. Chem. Soc.* **2002**, *124*, 602−614.

(19) Bandara, D. M. I.; Sono, M.; Bruce, G. S.; Brash, A. R.; Dawson, J. H. *J. Inorg. Biochem.* **2011**, *105*, 1786−1794.

(20) Hwang, J.; Govindaswamy, K.; Koch, S. A. *Chem. Commun.* **1998**, 1667−1668.

(21) Whiteoak, C. J.; Martin, E.; Belmonte, M. M.; Benet-Buchholz, J.; Kleij, A. W. *Adv. Synth. Catal.* **2012**, *354*, 469−476.

(22) Whiteoak, C. J.; Gjoka, B.; Martin, E.; Belmonte, M. M.; Escudero-Adán, E. C.; Zonta, C.; Licini, G.; Kleij, A. W. *Inorg. Chem.* **2012**, *51*, 10639−10649.

(23) Licini, G.; Mba, M.; Zonta, C. *Dalton Trans.* **2009**, 5265−5277.

(24) Solution-state Mößbauer was necessary; otherwise, difficulty in completely removing the coordinated solvent from the samples led to the observation of multiple species.

(25) Neese, F.; Petrenko, T. Quantum Chemistry and Mößbauer Spectroscopy. In *Mößbauer Spectroscopy and Transition Metal Chemistry*; Gütlich, P., Bill, E., Trautwein, A., Eds.; Springer: Berlin, 2011; pp 137−199.