Trinuclear Oxo-Centered Iron and Iron/Nickel Clusters – Ligand-Controlled Homo/Hetero Valency[‡]

Rolf W. Saalfrank,*[a] Andreas Scheurer,[a] Klaus Pokorny,[a] Harald Maid,[a] Uwe Reimann,[a] Frank Hampel,[a] Frank W. Heinemann,[b] Volker Schünemann,[c] and Alfred X. Trautwein[d]

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Cleavage of the all-iron(III) μ_2-O^{2-}-linked dimer $[Fe^{III}_3O(L)_2(OAc)_4]_2O$ (**3**) with lithium chloride yields $[Fe^{III}_3O(L)_2(OAc)_4]Cl$ (**4**) and with sodium benzoate, in combination with complete acetate-to-benzoate coligand exchange, gives $[Fe^{III}_3O(L)_2(OBz)_4]OBz$ (**5**). Reduction of the all-Fe^{III} complex **5** [Fe/L/OBz = 3:2:(4+1)] with sodium iodide affords the homonuclear mixed-valent cluster $[Fe^{II}Fe^{III}_2O(L)_3(OBz)_3]$ (**6**) (Fe/L/OBz = 1:1:1) and requires fundamental coligand-to-ligand exchange. Likewise, when the all-Fe^{III} dimer $[Fe^{III}_3O(L)_2(OAc)_4]_2O$ (**3**) (Fe/L/OAc = 3:2:4) is cleaved with nickel acetate, the mixed-valent heteronuclear complex $[Ni^{II}Fe^{III}_2O(L)_3(OAc)_3]$ (**7**) (M/L/OAc = 1:1:1) is formed.

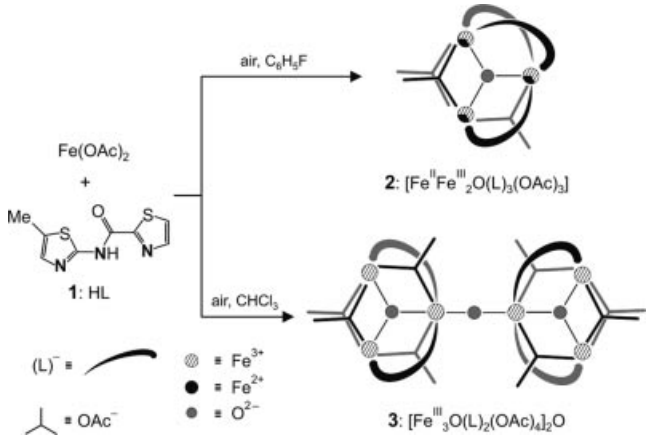
Introduction

Recently, we reported that the reaction of *N*-(5-methylthiazol-2-yl)thiazole-2-carboxamide HL (**1**) with fresh iron(II) acetate in fluorobenzene under aerobic conditions yields the deeply violet μ_3-O^{2-}-centered mixed-valent complex $[Fe^{II}Fe^{III}_2O(L)_3(OAc)_3]$ (**2**), whereas aged $Fe(OAc)_2$ in chloroform under aerobic conditions leads to homovalent dimer $[Fe^{III}_3O(L)_2(OAc)_4]_2O$ (**3**) (Scheme 1).[1–4] Most notably, the metal/ligand/coligand ratio (Fe/L/OAc) in mixed-valent **2** is 1:1:1, whereas the ratio in homo-valent **3** is 3:2:4.

Results and Discussion

All-Iron(III) Complexes

Herein we describe the cleavage of the μ_2-O^{2-}-linked dimer $[Fe^{III}_3O(L)_2(OAc)_4]_2O$ (**3**) in chloroform with lithium chloride or sodium benzoate to give $[Fe^{III}_3O(L)_2(OAc)_4]Cl$ (**4**) or $[Fe^{III}_3O(L)_2(OBz)_4]OBz$ (**5**) (Scheme 2). The cleavage of **3** with benzoate ions to give **5** obviously proceeds with complete acetate-to-benzoate coligand exchange.

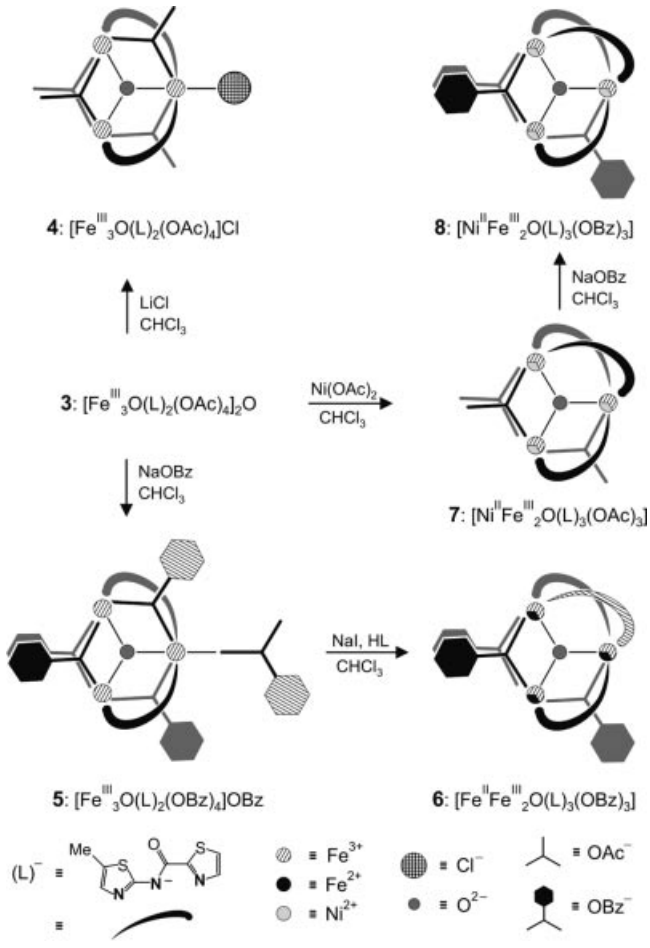


Scheme 1. Synthesis of heteroleptic **2** and **3**. In **2**, the mixed valency and its statistical distribution is highlighted by differently marked segments.

The all-iron(III) character of **4** and **5** was confirmed by Mössbauer spectra of their powder samples recorded at 77 K. The spectra exhibit quadrupolar doublets and isomeric shifts consistent with high-spin iron(III) (**4**: ΔE_Q = 0.77 mm s^{-1}, δ = 0.48 mm s^{-1}, and Γ = 0.36 mm s^{-1}; **5**: ΔE_Q = 0.77 mm s^{-1}, δ = 0.51 mm s^{-1}, and Γ = 0.45 mm s^{-1}). The Mössbauer spectrum of **5** is displayed in Figure 1 as an example.

The structure of **4** was unequivocally determined by single-crystal X-ray analysis.[5–7] According to these data, heteroleptic $[Fe^{III}_3O(L)_2(OAc)_4]Cl$ (**4**) is made up of two ditopic, tridentate ligands $(L)^-$ and four bridging acetate coligands, fixing the three Fe^{III} ions in the corners of a triangle with a μ_3-O^{2-} ion in the center. Fe1/2 are linked by

[‡] Chelate Complexes, 30. Part 29: Ref.[1]
[a] Institut für Organische Chemie der Universität Erlangen-Nürnberg,
Henkestrasse 42, 91054 Erlangen, Germany
Fax: +49-9131-852-1165
E-mail: saalfrank@chemie.uni-erlangen.de
[b] Institut für Anorganische Chemie der Universität Erlangen-Nürnberg,
91058 Erlangen, Germany
[c] Fachbereich Physik, Technische Universität Kaiserslautern,
67663 Kaiserslautern, Germany
[d] Institut für Physik der Medizinischen Universität Lübeck,
23538 Lübeck, Germany
[‡] Chelate Complexes, 30. Part 29: Ref.[1]



Scheme 2. Synthesis of **4**–**8**. In **5** the monodentate and bidentate $(OBz)^-$ coligands substituted in **6** by ditopic, tridentate $(L)^-$ are highlighted (diagonal). In **6**–**8**, the mixed valency and its statistical distribution are emphasised by differently marked segments.

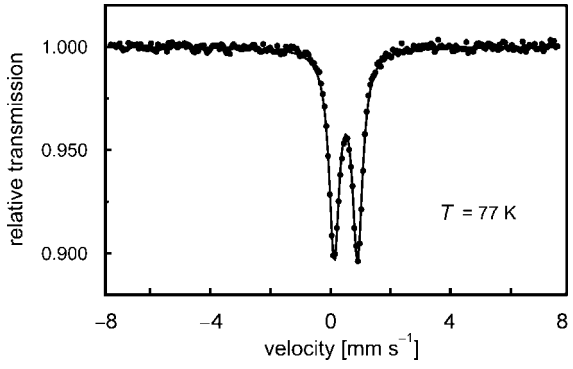


Figure 1. Mössbauer spectrum of **5**.

one ligand $(L)^-$ head-to-tail and Fe2/3 by one ligand $(L)^-$ tail-to-head. Furthermore, Fe1/2 and Fe2/3 are linked by one μ_2-$(OAc)^-$ bridge, each, and Fe1/3 by two μ_2-$(OAc)^-$ bridges. As a consequence, in the all-iron(III) compound **4**, Fe1 and Fe3 are identically octahedrally coordinated. The extra coordination site at Fe2 is occupied by a chloride ion, leading to charge compensation (Figure 2). As with **4**, complexes **2**–**10** were obtained as racemic mixtures.

Since we were not successful in growing single crystals suitable for an X-ray analysis of $[Fe^{III}_3O(L)_2(OBz)_4]OBz$ (**5**), we prepared $[Fe^{III}_3O(L)_2(OBzBr)_4]OBzBr$ (**9**). The all-iron(III) complex **9** was synthesised from iron(II) acetate with an excess of sodium 4-bromobenzoate and *N*-(5-methylthiazol-2-yl)thiazole-2-carboxamide HL (**1**) in chloroform under aerobic conditions, and separated from mixed-valent $[Fe^{II}Fe^{III}_2O(L)_3(OBzBr)_3]$ (**10**) by fractionising crystallization (Scheme 3). According to the X-ray analysis, **9** is isostructural with $[Fe^{III}_3O(L)_2(OAc)_4]Cl$ (**4**) with one μ_1-$(OBzBr)^-$ coligand bound to Fe, necessary for coordination and charge compensation (**9**: $\Delta E_Q = 0.81\ mm\,s^{-1}$, $\delta = 0.48\ mm\,s^{-1}$, and $\Gamma = 0.35\ mm\,s^{-1}$).[6–8]

Mixed-Valent Homonuclear and Mixed-Valent Heteronuclear Complexes

The reversible cyclic voltammograms of redox-active $[Fe^{II}Fe^{III}_2O(L)_3(OAc)_3]$ (**2**) and $[Fe^{II}Fe^{III}_2O(L)_3(OBz)_3]$ (**6**) displayed basically two processes attributable to the reduction of **2** and **6** from $Fe^{II}Fe^{III}_2$ to $Fe^{II}_2Fe^{III}$ and oxidation to the all-Fe^{III} species.[1] The number of electrons transferred at different potentials during this process was determined in acetonitrile vs. Fc/Fc^+ and turned out to be one for the reduction of all-Fe^{III} to $Fe^{II}Fe^{III}_2$ and one for the second reduction to $Fe^{II}_2Fe^{III}$. Further reduction of $Fe^{II}_2Fe^{III}$ to the all-Fe^{II} species is irreversible. Consequently, the cyclic voltammograms of redox-active $[Ni^{II}Fe^{III}_2O(L)_3(OAc)_3]$ (**7**) and $[Ni^{II}Fe^{III}_3O(L)_3(OBz)_3]$ (**8**) represent the reduction of $Ni^{II}Fe^{III}_2$ to $Ni^{II}Fe^{II}Fe^{III}$ and reoxidation to $Ni^{II}Fe^{III}_2$.[1] As determined in acetonitrile vs. Fc/Fc^+, one electron is transferred during this redox process. Further reduction of $Ni^{II}Fe^{II}Fe^{III}$ to the $Ni^{II}Fe^{II}_2$ species is irreversible.

Reduction of the all-iron(III) complex $[Fe^{III}_3O(L)_2(OBz)_4]$-OBz (**5**) in chloroform with 5 equiv. of sodium iodide[9] yields homonuclear mixed-valent cluster $[Fe^{II}Fe^{III}_2O(L)_3(OBz)_3]$ (**6**) (Scheme 2). Worth noting is that reduction of **5** does not simply occur by a one-electron reduction, but rather affords fundamental coligand-to-ligand exchange to give **6**. In order to generate **6** (Fe/L/OBz = 1:1:1), the mono- and bidentate $(OBz)^-$ coligands in **5** [Fe/L/OBz = 3:2:(4+1)] have to be substituted by the ditopic, tridentate ligand $(L)^-$ (Scheme 2). Furthermore, these findings coherently explain the irreversibility of the cyclic voltammograms of **4**, **5**, and **9**.

Likewise, when the all-iron(III) dimer $[Fe^{III}_3O(L)_2(OAc)_4]_2O$ (**3**) (Fe/L/OAc = 3:2:4) is cleaved with nickel acetate in chloroform, the mixed-valent heteronuclear $[Ni^{II}Fe^{III}_2O(L)_3(OAc)_3]$ (**7**) (M/L/OAc = 1:1:1) is formed. This again is a complex reaction and requires the exchange of Fe^{III}-to-Ni^{II} and of $(OAc)^-$ coligand-to-$(L)^-$. Since it was not possible to grow single crystals of acetate **7** suitable for X-ray structure determination, $[Ni^{II}Fe^{III}_2O(L)_3(OBz)_3]$ (**8**) was generated from **7** by exchange of the $(OAc)^-$ coligands with $(OBz)^-$ ions (Scheme 2).

The chelate complexes **6**–**8** are also accessible starting from complex **2**.[1] For example, **6** and **7** were prepared from

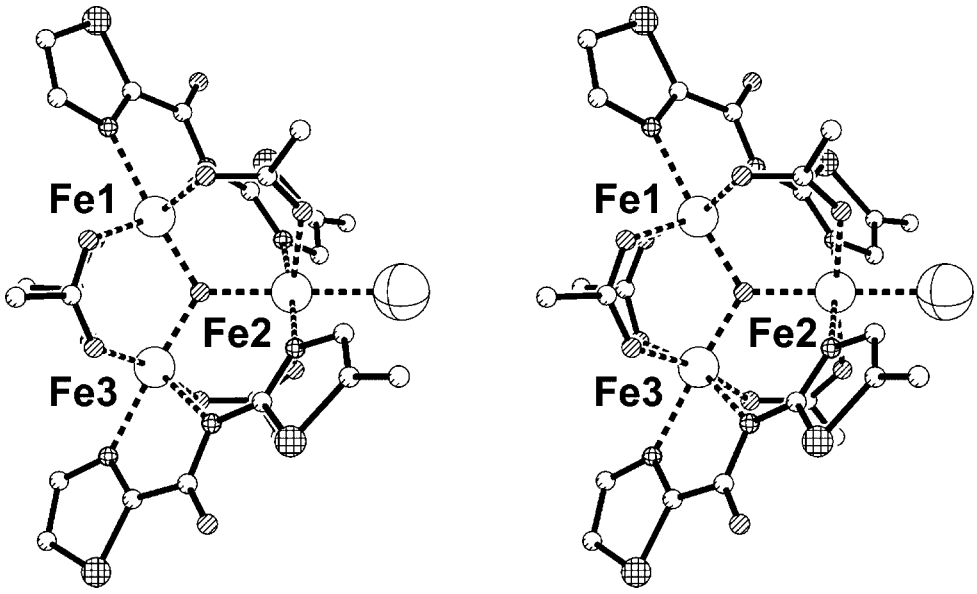
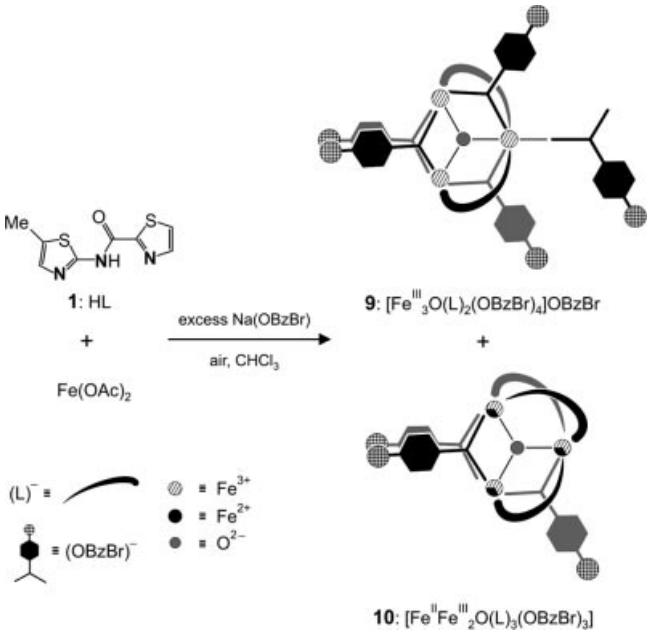


Figure 2. Molecular structure of **4** in the crystal (stereoview, PLUTON presentation, with the numbering of the iron ions, only one stereoisomer shown). H atoms omitted for clarity. C: shaded; N: net; O: diagonal; S: mesh; Fe: void; Cl: cross. Selected bond lengths [Å] and angles [°]: Fe1–μ_3-O 1.87, Fe2–μ_3-O 1.95; Fe1–μ_3-O–Fe2 121.1, Fe1–μ_3-O–Fe3 117.7.



Scheme 3. Synthesis of all-iron(III) complex **9** and mixed-valent species **10**. In **10**, the mixed valency is marked by segments.

mixed-valent homonuclear $[Fe^{II}Fe^{III}_2O(L)_3(OAc)_3]$ (**2**) by mere exchange of the $(OAc)^-$ coligands by $(OBz)^-$ ions and by Fe^{II}-to-Ni^{II} exchange, respectively.

Conclusions

In summary, we have presented the cleavage of dimer **3** into **4**, **5**, and **7** and the interconversion of **5** into **6** and **7** into **8**. Most interestingly, in mixed-valent homonuclear **2** and **6** and in mixed-valent heteronuclear **7** and **8** the metal/ligand/coligand ratio M/L/co-L is 1:1:1, whereas, in homovalent **3**–**5** the ratio is 3:2:4. This result indicates ligand-controlled stabilization of the all-Fe^{III} and mixed-valent species.

Experimental Section

General Methods: IR spectra were recorded from $CHBr_3$ triturations with a Bruker IFS 25 spectrometer. FAB-MS spectra were recorded with a Micromass ZAB-Spec spectrometer. Elemental analyses were performed with an EA 1110 CHNS-Microautomat. The microanalytical data for **4**–**9** deviate from theory due to varying crystal solvents and are not recorded here.

Materials: All reagents and solvents employed were commercially available high-grade purity materials (Fluka, Aldrich), used as supplied without further purification. Ligand HL (**1**) was prepared according to ref.[2] Sodium 4-bromobenzoate was generated by reaction of 4-bromobenzoic acid (1.1 equiv.) with NaH (1.0 equiv.) in dry THF. The precipitate was filtered off, washed with THF and dried in vacuo.

General Procedure: The metal salt (LiCl, NaOBz, $Ni(OAc)_2$, NaI) was added, in one portion, to a solution of complexes **3** or **5** in chloroform. The initially pale violet suspension was stirred at 20 °C for 48 h. After removal of the excess metal salt by filtration through a pad of Celite, the remaining solution was concentrated to dryness.

Compound $[Fe^{III}_3O(L)_2(OAc)_4]Cl$ (4): 3 (131 mg, 0.075 mmol), anhydrous lithium chloride (509 mg, 12 mmol), and chloroform (60 mL). Yield: 110 mg (81%) dark-violet crystals from $CHCl_3$ by vapor diffusion of diethyl ether; m.p. >250 °C (decomp.). IR ($CHBr_3$): $\tilde{\nu}$ = 3137, 3109, 2995, 2923, 1615, 1575, 1556, 1505 cm^{-1}. FAB-MS (*m*-NBA): *m*/*z* (%) = 902 (6) $[M]^+$, 868 (100) $[M - Cl]^+$, 809 (59) $[M - Cl - OAc]^+$, 750 (22) $[M - Cl - 2\ OAc]^+$, 691 (11) $[M - Cl - 3\ OAc]^+$, 644 (33) $[M - Cl - L]^+$, 585 (32) $[M - Cl - OAc - L]^+$, 526 (25) $[M - Cl - 2\ OAc - L]^+$, 470 (21) $[M - Cl - 2\ OAc - L - Fe]^+$, 411 (21) $[M - Cl - 3\ OAc - L - Fe]^+$, 352 (16) $[M - Cl - 4\ OAc - L - Fe]^+$.

Compound $[Fe^{III}_3O(L)_2(OBz)_4]OBz$ (5): 3 (175 mg, 0.1 mmol), sodium benzoate (2.30 g, 16 mmol), and chloroform (80 mL). Yield: 178 mg (72%) dark-violet microcrystalline solid from $CHCl_3$ by vapor diffusion of diethyl ether; m.p. >250 °C (decomp.). IR ($CHBr_3$): $\tilde{\nu}$ = 3127, 3111, 2922, 1615, 1596, 1557, 1539, 1504 cm^{-1}. FAB-MS (*m*-NBA): *m*/*z* (%) = 1237 (3) $[M]^+$, 1116 (91) $[M – OBz]^+$, 1013 (32) $[M – L]^+$, 995 (100) $[M – 2\ OBz]^+$, 892 (60) $[M – OBz – L]^+$, 874 (41) $[M – 3\ OBz]^+$, 771 (73) $[M – 2\ OBz – L]^+$, 650 (76) $[M – 3\ OBz – L]^+$, 529 (35) $[M – 4\ OBz – L]^+$.

Compound $[Fe^{II}Fe^{III}_2O(L)_3(OBz)_3]$ (6): 5 (247 mg, 0.2 mmol), **1** (45 mg, 0.2 mmol), sodium iodide (50 mg, 0.33 mmol), and chloroform (50 mL). Yield: 129 mg (53%) dark-violet crystals from $CHCl_3$ by vapor diffusion of diethyl ether. For analytical data see ref.[1]

Compound $[Ni^{II}Fe^{III}_2O(L)_3(OAc)_3]$ (7): 3 (123 mg, 0.07 mmol), nickel acetate tetrahydrate (174 mg, 0.7 mmol), and chloroform (30 mL). Yield: 68 mg (47%) brown precipitate from $CHCl_3$/*n*-pentane (5 mL/30 mL; once repeated). For analytical data see ref.[1]

Compound $[Ni^{II}Fe^{III}_2O(L)_3(OBz)_3]$ (8): 7 (52 mg, 0.05 mmol), sodium benzoate (432 mg, 3 mmol), and chloroform (10 mL). Yield: 42 mg (68%) brown crystals from $CHCl_3$ by vapor diffusion of diethyl ether. For analytical data see ref.[1]

Compounds $[Fe^{III}_3O(L)_2(OBzBr)_4]OBzBr$ (9), $[Fe^{II}Fe^{III}_2O(L)_3(OBzBr)_3]$ (10): A suspension of iron(II) acetate (348 mg, 2 mmol) and sodium 4-bromobenzoate (6.70 g, 30 mmol) in chloroform (300 mL) was stirred under nitrogen for 2 h. After addition of HL (**1**) (534 mg, 2.4 mmol), the pale violet reaction mixture was stirred in air for a further 48 h. After removal of the excess metal salt by filtration through a pad of Celite, and concentration to dryness, the mixture of **9** and **10** (ratio of ca. 6:1) was purified by fractionizing crystallization from CH_2Cl_2/ether, yielding dark-violet crystals of **9**. Yield: 348 mg (32%); m.p. >250 °C (decomp.). IR ($CHBr_3$): $\tilde{\nu}$ = 3107, 2920, 1589, 1554, 1504, 1411 cm^{-1}. FAB-MS (*m*-NBA): *m*/*z* (%) = 1656 (2) $[M + Na]^+$, 1431 (80) $[M – OBzBr]^+$, 1408 (14) $[M – L]^+$, 1232 (100) $[M – 2\ OBzBr]^+$, 1207 (39) $[M – L – OBzBr]^+$, 1032 (51) $[M – 3\ OBzBr]^+$, 1008 (49) $[M – L – 2\ OBzBr]^+$, 831 (23) $[M – 4\ OBzBr]^+$, 808 (63) $[M – L – 3\ OBzBr]^+$, 752 (24) $[M – Fe – L – 3\ OBzBr]^+$. Complex **10** was characterized by FAB-MS and was not further purified: FAB-MS (*m*-NBA): *m*/*z* (%) = 1458 (65) $[M + H]^+$, 1256 (100) $[M – OBzBr]^+$, 1058 (31) $[M – OBzBr]^+$.

Acknowledgments

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[1] R. W. Saalfrank, A. Scheurer, U. Reimann, F. Hampel, C. Trieflinger, M. Büschel, J. Daub, A. X. Trautwein, V. Schünemann, V. Coropceanu, *Chem. Eur. J.*, submitted.

[2] R. W. Saalfrank, U. Reimann, M. Göritz, F. Hampel, A. Scheurer, F. W. Heinemann, M. Büschel, J. Daub, V. Schünemann, A. X. Trautwein, *Chem. Eur. J.* **2002**, *8*, 3614–3619.

[3] Fresh $Fe(OAc)_2$ (Supplier Aldrich 51,793-3; 99.995%); aged $Fe(OAc)_2$ (kept under nitrogen in a Schlenk tube for 6–9 months with occasional opening). We suspect that aging of $Fe(OAc)_2$ leads to the formation of oligonuclear iron species. This assumption is supported by the fact that reaction of ten-membered iron wheel $[Fe^{III}_{10}(OAc)_{10}(OMe)_{20}]$ with HL (**1**) yields a mixture of $[Fe^{II}Fe^{III}_2O(L)_3(OAc)_3]$ (**2**), and $[Fe^{III}_3O(L)_2(OAc)_4]_2O$ (**3**, main product). The Fe^{II} ions in **2** are generated by reduction of Fe^{III} by methanol. We generated $[Fe^{III}_{10}(OAc)_{10}(OMe)_{20}]$ in ≥80% yield simply by stirring $Fe(OAc)_2$ or $FeCl_2$ together with NaOAc in air at 20 °C in methanol for 10 h. The X-ray crystallographic data matched those reported in ref.[10]

[4] For further iron acetate complexes, see: a) C. T. Dziobkowski, J. T. Wrobleski, D. B. Brown, *Inorg. Chem.* **1981**, *20*, 671–678; b) C. J. Harding, R. K. Henderson, A. K. Powell, *Angew. Chem.* **1993**, *105*, 583–585, *Angew. Chem. Int. Ed.* **1993**, *32*, 570–572; c) C. A. Christmas, H.-L. Tsai, L. Pardi, J. M. Kesselman, P. K. Gantzel, R. K. Chadha, D. Gatteschi, D. F. Harvey, D. N. Hendrickson, *J. Am. Chem. Soc.* **1993**, *115*, 12483–12490; d) I. Shweky, L. E. Pence, G. C. Papaefthymiou, R. Sessoli, J. W. Yun, A. Bino, S. J. Lippard, *J. Am. Chem. Soc.* **1997**, *119*, 1037–1042; e) S. J. Lippard, *Angew. Chem.* **1988**, *100*, 353–371; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 344–361.

[5] Crystal data for $[Fe^{III}_3O(L)_2(OAc)_4]Cl$ (**4**): $C_{24}H_{24}ClFe_3N_6O_{11}S_4{\cdot}3CHCl_3{\cdot}(C_2H_5)_2O$, M = 1335.96; crystal dimensions 0.30 × 0.10 × 0.10 mm; monoclinic, space group $C2/c$, a = 17.961(4) Å, b = 15.158(3) Å, c = 19.875(4) Å, β = 99.57(3)°, V = 5336(2) $Å^3$; Z = 4; $F(000)$ = 1828, $\rho_{calcd.}$ = 1.663 g/cm^3; Nonius KappaCCD diffractometer, Mo-K_α radiation (λ = 0.71073 Å); T = 173(2) K; graphite monochromator; θ range 2.30° < θ < 27.47°; section of the reciprocal lattice: $-23 \le h \le 23$, $-18 \le k \le 19$, $-25 \le l \le 25$; of 11363 measured reflections, 6097 were independent and 4434 with $I > 2\sigma(I)$; linear absorption coefficient 1.053 mm^{-1}. The structure was solved by direct methods using SHELXS-97 and refinement with all data (309 parameters) by full-matrix least squares on F^2 using SHELXL97; all non-hydrogen atoms were refined anisotropically; $R1$ = 0.0541 for $I > 2\sigma(I)$ and $wR2$ = 0.1651 (all data); largest peak (0.748 e $Å^{-3}$) and hole (–1.226 e $Å^{-3}$).[6,7]

[6] a) G. M. Sheldrick, C. Krüger, P. Goddard, *Crystallographic Computing 3*, Oxford University Press, Oxford **1985**, p. 175; b) G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen **1997**.

[7] CCDC-213507 (**4**), -250374 (**9**), and -213506 $[Fe^{III}_3O(L)_3(OBz)_3]I_3$[9] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[8] Crystal data for $[Fe^{III}_3O(L)_2(OBzBr)_4]OBzBr$ (**9**): $C_{51}H_{32}Br_5Fe_3N_6O_{13}S_4{\cdot}2.5CH_2Cl_2$, M = 1844.48; crystal dimensions 0.25 × 0.20 × 0.20 mm; monoclinic, space group $P2_1/c$, a = 19.506(4) Å, b = 16.882(3) Å, c = 21.112(4) Å, β = 105.74(3)°, V = 6691(2) $Å^3$; Z = 4; $F(000)$= 3624, $\rho_{calcd.}$ = 1.831 g/cm^3; Nonius KappaCCD diffractometer, Mo-K_α radiation (λ = 0.71073 Å); T = 173(2) K; graphite monochromator; θ range 2.89° < θ < 25.05°; section of the reciprocal lattice: $-23 \le h \le 23$, $-18 \le k \le 20$, $-25 \le l \le 25$; of 21421 measured reflections, 11780 were independent and 8118 with $I > 2\sigma(I)$; linear absorption coefficient 4.015 mm^{-1}. The structure was solved by direct methods using SHELXS-97 and refinement with all data (842 parameters) by full-matrix least squares on F^2 using SHELXL97; all non-hydrogen atoms were refined anisotropically; $R1$ = 0.0983 for $I > 2\sigma(I)$ and $wR2$ = 0.2856 (all data); largest peak (2.954 e $Å^{-3}$) and hole (–1.966 e $Å^{-3}$).[6,7]

[9] When **5** was treated with a fortyfold excess of sodium iodide in the presence of air after workup some crystals of all-iron(III) complex $[Fe^{III}_3O(L)_3(OBz)_3]I_3$ were isolated.[7] Crystal data for $[Fe^{III}_3O(L)_3(OBz)_3]I_3$: $C_{45}H_{33}Fe_3I_3N_9O_{10}S_6{\cdot}3CHCl_3$, M = 1958.52; crystal dimensions 0.38 × 0.15 × 0.06 mm; triclinic, space group $P\bar{1}$, a = 14.2184(3) Å, b = 16.2989(3) Å, c = 16.6062(5) Å, α = 97.223(2)°, β = 106.855(2)°, γ = 110.318(2)°,

V = 3342.2(2) Å^3; Z = 2; F(000)= 1906, $\rho_{calcd.}$ = 1.946 g/cm^3; Nonius KappaCCD diffractometer, Mo-K_α radiation (λ = 0.71073 Å); T = 100(2) K; graphite monochromator; θ range 3.31° < θ < 27.00°; section of the reciprocal lattice: –18 ≤ h ≤ 18, –20 ≤ k ≤ 20, –21 ≤ l ≤ 21; of 61686 measured reflections, 14561 were independent and 9683 with $I > 2\sigma(I)$; linear absorption coefficient 2.635 mm^{-1}. A numerical absorption correction has been performed[11] (T_{min} = 0.744, T_{max} = 0.916). The structure was solved by direct methods and refined with all data (822 parameters) by full-matrix least squares on F^2 using SHELXLTL NT 5.10.[12] With the exception of C301 (representing the minor component of a disordered $CHCl_3$ solvate molecule) all non-hydrogen atoms were refined anisotropically; $R1$ = 0.0574 for $I > 2\sigma(I)$ and $wR2$ = 0.1613 (all data); largest peak (2.653 e Å^{-3}) and hole (–2.052 e Å^{-3}).[6,7] All significant residual electron density maxima can be found in close proximity of either the I_3 anion positions or the disordered solvate molecule.

[10] C. Benelli, S. Parsons, G. A. Solan, R. E. P. Winpenny, *Angew. Chem.* **1996**, *108*, 1967–1970; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1825–1828.
[11] P. Coppens, *Crystallographic Computing*, Munksgaard, Copenhagen, **1970**, p. 255.
[12] *SHELXTL NT 5.10*, Bruker AXS, Inc., Madison WI, USA, **1998**.

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