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

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Cleavage of the all-iron(III) μ_2 -O²⁻-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^{III}₂O(L)₃(OBz)₃] (**6**) $\begin{array}{l} ({\rm Fe/L/OBz}=1{:}1{:}1) \mbox{ and requires fundamental coligand-to-ligand exchange. Likewise, when the all-Fe^{III} dimer <math display="inline">[{\rm Fe^{III}}_{3}{\rm O}{-}({\rm L})_{2}({\rm OAc})_{4}]_{2}{\rm O}$ (3) (Fe/L/OAc = 3:2:4) is cleaved with nickel acetate, the mixed-valent heteronuclear complex $[{\rm Ni^{II}Fe^{III}}_{2}{-}{\rm O(L)_{3}({\rm OAc})_{3}}]$ (7) (M/L/OAc = 1:1:1) is formed.

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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 -O²⁻-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 mixedvalent 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 -O²⁻-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.

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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**: $\Delta E_Q =$ 0.77 mm s⁻¹, $\delta = 0.48$ mm s⁻¹, and $\Gamma = 0.36$ mm s⁻¹; **5**: ΔE_Q = 0.77 mm s⁻¹, $\delta = 0.51$ mm s⁻¹, and $\Gamma = 0.45$ 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]



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 $[Fe^{III}_{3}O(L)_{2}(OBz)_{4}]OBz$ (5), we prepared $[Fe^{III}_{3}O(L)_{2}(OBzBr)_{4}]OBzBr$ (9). The alliron(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 $[Fe^{II}Fe^{III}_{2}O(L)_{3}(OBzBr)_{3}]$ (10) by fractionising crystallization (Scheme 3). According to the X-ray analysis, 9 is isostructural with $[Fe^{III}_{3}O(L)_{2}(OAc)_{4}]Cl$ (4) with one μ_{1} -(OBzBr)⁻ coligand bound to Fe, necessary for coordination and charge compensation (9: $\Delta E_{Q} = 0.81 \text{ mm s}^{-1}$, $\delta =$ 0.48 mm s⁻¹, and $\Gamma = 0.35 \text{ mm s}^{-1}$).^[6–8]

Mixed-Valent Homonuclear and Mixed-Valent Heteronuclear Complexes

The reversible cyclic voltammograms of redox-active $[Fe^{II}Fe^{III}{}_{2}O(L)_{3}(OAc)_{3}]$ (2) and $[Fe^{II}Fe^{III}{}_{2}O(L)_{3}(OBz)_{3}]$ (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 $[Fe^{III}_{3}O(L)_{2}(OBz)_{4}]$ -OBz (5) in chloroform with 5 equiv. of sodium iodide^[9] yields homonuclear mixed-valent cluster $[Fe^{II}Fe^{III}_{2}O(L)_{3}$ - $(OBz)_{3}]$ (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 monoand 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 $[Fe^{III}_{3}O(L)_{2}$ -(OAc)_{4]2}O (3) (Fe/L/OAc = 3:2:4) is cleaved with nickel acetate in chloroform, the mixed-valent heteronuclear $[Ni^{II}Fe^{III}_{2}O(L)_{3}(OAc)_{3}]$ (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, $[Ni^{II}Fe^{III}_{2}O(L)_{3}(OBz)_{3}]$ (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 CHCl₃ by vapor diffusion of diethyl ether; m.p. >250 °C (decomp.). IR (CHBr₃): $\tilde{v} = 3137$, 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 CHCl₃ by vapor diffusion of diethyl ether; m.p. >250 °C (decomp.). IR (CHBr₃): $\tilde{v} = 3127$, 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 CHCl₃ 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 CHCl₃/*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 CHCl₃ 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 CH2Cl2/ether, yielding dark-violet crystals of **9**. Yield: 348 mg (32%); m.p. >250 °C (decomp.). IR (CHBr₃): \tilde{v} = 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) $[M - OBzBr]^+$.

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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 tenmembered iron wheel $[Fe^{III}_{10}(OAc)_{10}(OMe)_{20}]$ with HL (1) yields a mixture of $[Fe^{III}Fe^{III}_2O(L)_3(OAc)_3]$ (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 $\geq 80\%$ 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]

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- [Fe^{III}₃O(L)₂(OAc)₄]Cl [5] Crystal for data (4): $C_{24}H_{24}ClFe_3N_6O_{11}S_4 \cdot 3CHCl_3 \cdot (C_2H_5)_2O, M = 1335.96; crystal$ dimensions $0.30 \times 0.10 \times 0.10$ mm; monoclinic, space group C2/ c, a = 17.961(4) Å, b = 15.158(3) Å, c = 19.875(4) Å, $\beta =$ 99.57(3)°, $V = 5336(2) \text{ Å}^3$; Z = 4; F(000) = 1828, $\rho_{calcd.} =$ 1.663 g/cm³; Nonius KappaCCD diffractometer, Mo- K_{α} radiation ($\lambda = 0.71073$ 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 $e^{A^{-3}}$) and hole (-1.226 $e^{A^{-3}}$).^[6,7]
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- [7] CCDC-213507 (4), -250374 (9), and -213506 [Fe^{III}₃O(L)₃-(OBz)₃]I₃^[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.
- [Fe^{III}₃O(L)₂(OBzBr)₄]OBzBr [8] Crystal data for (9): $C_{51}H_{32}Br_5Fe_3N_6O_{13}S_4 \cdot 2.5CH_2Cl_2$, M = 1844.48; crystal dimensions $0.25 \times 0.20 \times 0.20$ mm; monoclinic, space group $P2_1/c$, a = 19.506(4) Å, b = 16.882(3) Å, c = 21.112(4) Å, $\beta =$ $105.74(3)^{\circ}$, $V = 6691(2) \text{ Å}^3$; Z = 4; F(000) = 3624, $\rho_{\text{calcd.}} =$ 1.831 g/cm³; Nonius KappaCCD diffractometer, Mo- K_{α} radiation ($\lambda = 0.71073$ 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 eÅ⁻³) and hole (-1.966 eÅ⁻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]I₃ were isolated.^[7] Crystal data for [Fe^{III}₃O(L)₃(OBz)₃]I₃: C₄₅H₃₃Fe₃I₃N₉O₁₀S₆·3CHCl₃, M =1958.52; crystal dimensions $0.38 \times 0.15 \times 0.06$ mm; triclinic, space group $P\bar{1}$, a = 14.2184(3) Å, b = 16.2989(3) Å, c =16.6062(5) Å, $a = 97.223(2)^\circ$, $\beta = 106.855(2)^\circ$, $\gamma = 110.318(2)^\circ$,

V = 3342.2(2) Å³; Z = 2; F(000) = 1906, $\rho_{calcd.} = 1.946$ g/cm³; Nonius KappaCCD diffractometer, Mo- K_{α} radiation ($\lambda = 0.71073$ Å); T = 100(2) K; graphite monochromator; θ range $3.31^{\circ} < \theta < 27.00^{\circ}$; section of the reciprocal lattice: $-18 \le h \le 18$, $-20 \le k \le 20$, $-21 \le l \le 21$; 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^[111] ($T_{\min} = 0.744$, $T_{\max} = 0.916$). 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 CHCl₃ 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 eÅ⁻³) and hole (-2.052 eÅ⁻³).^[6,7] All significant residual electron density maxima can be found in close proximity of either the I₃ anion positions or the disordered solvate molecule.

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