The molecular and electronic structure of [Fe$^{III}_2$($^{t-bu}$L^{ISQ})$_4$(μ-O)]— a dinuclear ferric complex containing four, *O,N*-coordinated *o*-iminobenzosemiquinonate(1−) π radical anions

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The synthesis and crystal structure of a dinuclear complex containing a μ-oxo(diferric) core and four *O,N*-coordinated *o*-iminobenzosemiquinonate(1−) π radical anions, [Fe$^{III}_2$-(μ-O)($^{t-bu}$L^{ISQ})$_4$], is described; its electronic structure is best described as comprising two Fe^{III}(L^{ISQ})$_2$ halves with $S^* = 3/2$ ($S_{Fe} = 5/2$ coupled to two organic radicals) which are then intramolecularly antiferromagnetically coupled *via* the oxo group yielding the observed $S = 0$ ground state.

In a series of recent papers[1–11] we have been able to show that *o*-aminophenolate ligands *O,N*-coordinated to transition metal ions form in the presence of air *O,N*-coordinated *o*-iminobenzosemiquinonate π radical monoanions, (L^{ISQ})$^{1−}$. We have shown that the spin of such a ligand π radical interacts intramolecularly with the spins of unpaired d electrons at the transition metal ion.[3] In accordance with the Goodenough–Kanamori rules[12] for spin exchange coupling the interaction of a π radical anion with an unpaired electron in an e$_g$ orbital of an octahedral nickel(II) ion is strongly ferromagnetic yielding an $S_t = 3/2$ ground state. Coupling with an electron in a t$_{2g}$ orbital is, in general, antiferromagnetic.[13] Thus, octahedral [Cr^{III}(L^{ISQ})$_3$] is diamagnetic at ambient temperature and possesses a singlet ground state.[3]

We have also shown that the octahedral complex [Fe^{III}(L^{ISQ})$_3$] (**1**) possesses an $S_t = 1$ ground state[3] where a high spin ferric ion ($S_{Fe} = 5/2$) is intramolecularly antiferromagnetically coupled to three (L^{ISQ})$^{1−}$ radical anions. Similarly, [Fe^{III}(L^{ISQ})$_2$Cl] (**2**) has an $S_t = 3/2$ ground state[8,10] comprising a high spin ferric ion and two antiferromagnetically coupled radical anions. The complexes are shown in Scheme 1

It is interesting that variable temperature (3–300 K) magnetic susceptibility measurements of **2** revealed a temperature-independent magnetic moment of 3.8 μ_B in the range 50–300 K indicating an $S_t = 3/2$ ground state[8] and no population of excited states. In contrast, similar measurements of **1** show that in the range 30–120 K a magnetic moment of ~2.9 μ_B ($S_t = 1$) prevails but above 120 K a monotonic increase to 3.3 μ_B at 300 K is observed.[3] From this behaviour an antiferromagnetic coupling constant of $J_{12} = J_{13} = J_{14} = -120$ cm^{-1}, $g = 2.04$ has been deduced by using the spin Hamiltonian $J = -2JS_{Fe}S_{rad}$ ($S_{Fe} = 5/2$; $S_{rad} = 1/2$). Apparently, the spin coupling in **1** is weaker than in **2**. This is due to the fact that the average Fe–O and Fe–N bond distances are significantly shorter in **2** at 2.041 and 1.963 Å,[8] respectively, than those in **1** at 2.099 and 2.015 Å,[3] respectively.

The presence of *O,N*-coordinated *o*-iminobenzosemiquinonate radicals in **1** and **2** has been clearly established by single crystal X-ray crystallography at cryogenic temperature (100(2) K). The C–C, C–N, C–O distances of the (L^{ISQ})$^{1−}$ ligands in **1** and **2** are identical within 3σ (±0.015 Å) (see Fig. 1). As shown previously, the aromatic ligand dianion which is the one-electron reduced form of (L^{ISQ})$^{1−}$ [7] and the neutral one-electron oxidized quinone form of (L^{ISQ})$^{1−}$ display significantly different C–C, C–O, and C–N distances.[9]


error: ±0.015 Å (3σ)
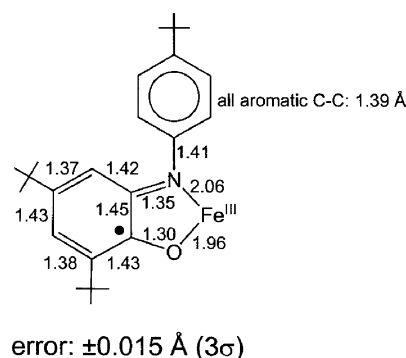
Fig. 1 Average C–C, C–N, C–O bond distances (Å) of the four *O,N*-coordinated *o*-iminobenzosemiquinonate(1-) π radical anions in **3**. The same bond lengths have been reported for **1** and **2** in ref. 3 and 8, respectively.

Here we report the synthesis, the electronic and molecular structure of the first dinuclear μ-oxo bridged ferric complex [Fe$^{III}_2$(μ-O)($^{t-bu}$L^{ISQ})$_4$] (**3**) which contains four *O,N*-coordinated *o*-iminobenzosemiquinonate(1−) π radical anions (see Scheme 2).

The ligand 2-(*p-tert*-butyl)anilino-4,6-di-*tert*-butylphenol, H[$^{t-bu}$L^{AP}], has been obtained from the reaction 4-*tert*-butylaniline, triethylamine and 3,5-di-*tert*-butylcatechol in n-heptane.†[2] A solution of the ligand in methanol reacts with [Fe^{II}(OH$_2$)$_6$](ClO$_4$)$_2$ and NEt$_3$ in the presence of air at 60 °C to give a deep green solution from which green–black crystals of **3** were obtained. ‡ Recrystallization from CH$_2$Cl$_2$/CH$_3$CN (3 : 1 vol) mixture produced single crystals of **3**·2.75CH$_2$Cl$_2$ suitable for X-ray crystallography. §
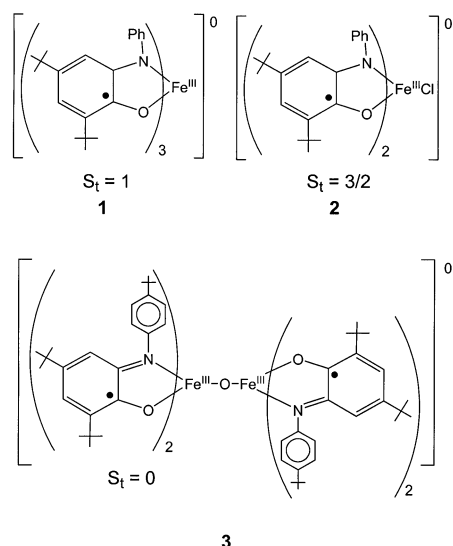
Scheme 1 Complexes.
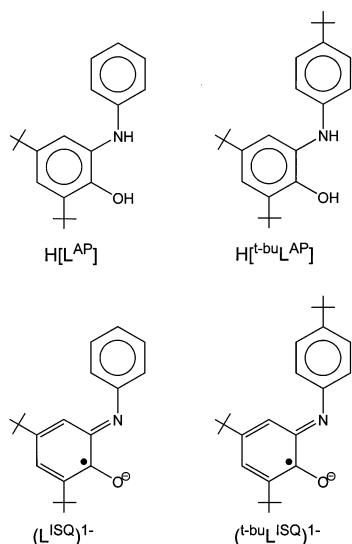
Scheme 2 Ligands and abbreviations.

Fig. 2 shows the structure of a neutral dinuclear molecule of the complex in crystals of $3 \cdot 2.75CH_2Cl_2$. Both ferric ions are coordinated to two *o*-iminobenzosemiquinonate(1−) π radical anions. This is conclusively deduced from the average C–N, C–C, and C–O distances which are identical within experimental error in each of the four ligands (Fig. 1). They are the same as those reported previously for **1**,[3] **2**,[8] and [Cr^{III}(L^{ISQ})$_3$],[3] [Co^{III}(L^{ISQ})$_3$],[1] and [Pt^{II}(bpy)(L^{ISQ})](PF$_6$).[7]
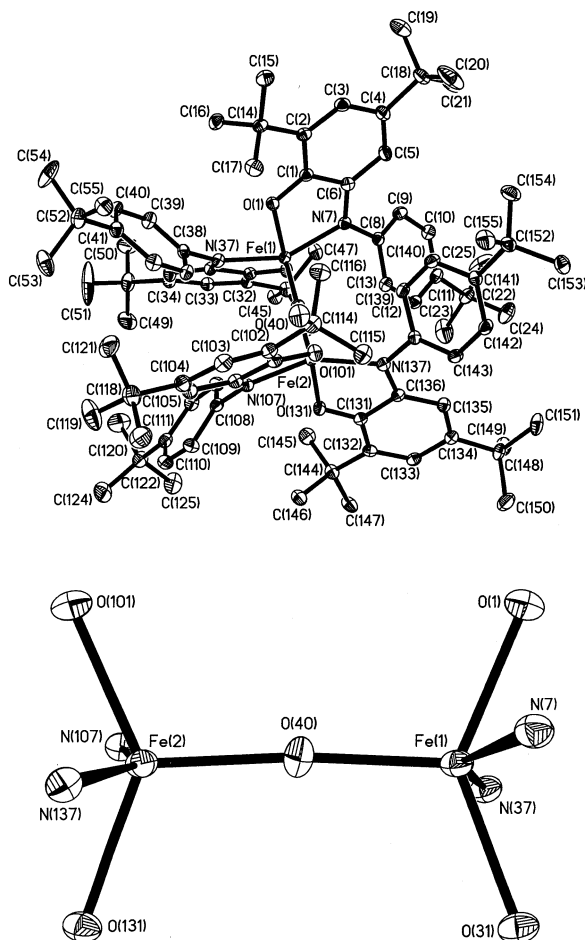
Fig. 2 Structure of the neutral molecule [Fe$^{III}_2$(μ-O)($^{t-bu}$L^{ISQ})$_4$] in crystals of $3 \cdot 2.75CH_2Cl_2$ (top) and of the [(Fe^{III}N$_2$O$_2$)$_2$(μ-O)] core (bottom).

Table 1 Selected bond lengths (Å)[a] and angles (°) for $3 \cdot 2.75CH_2Cl_2$

Fe(1)–O(40)	1.776(2)	Fe(2)–O(40)	1.775(2)
Fe(1)–O(31)	1.968(2)	Fe(2)–O(131)	1.958(2)
Fe(1)–O(1)	1.970(2)	Fe(2)–O(101)	1.961(2)
Fe(1)–N(37)	2.051(3)	Fe(2)–N(107)	2.066(3)
Fe(1)–N(7)	2.057(3)	Fe(2)–N(137)	2.069(3)
Fe(1)–O(40)–Fe(2)	175.2(2)		

[a] See Fig. 1 for average C–C, C–O, C–N distances of the (L^{ISQ})$^{1-}$ anions.

Table 2 Zero-field Mössbauer data of complexes **1**–**3** at 80 K

Compound	S_t[a]	δ/mm s^{-1}[b]	ΔE_Q/mm s^{-1}[c]	Ref.
1	1	0.54	1.035	3
2	3/2	0.45	1.26	8
3	0	0.38	1.105	This work

[a] Ground state. [b] Isomer shift *vs.* α-Fe at 298 K. [c] Quadrupole splitting.

The two halves Fe^{III}(L^{ISQ})$_2$ in dinuclear **3** are bridged by a nearly linear oxo group (Fe–O–Fe 175.2(2)°). The two Fe–O$_{oxo}$ distances are short at 1.775(2) Å and indicative of a strongly covalent bond with double bond character. This bonding situation has been observed in many dinuclear μ-oxo bridged complexes containing two high spin ferric ions (S_{Fe} = 5/2).[14]

Table 1 summarizes Fe–O and Fe–N bond lengths in **3**. The average Fe–O$_{rad}$ distance is 1.964 Å whereas the average Fe–N bond length is 2.061 Å. They are both nearly identical in five-coordinate [Fe^{III}Cl(L^{ISQ})$_2$][8] but significantly longer at 2.014 Å (Fe–O) and 2.099 (Fe–N) Å, respectively, in six-coordinate [Fe^{III}-(L^{ISQ})$_3$].[3] These data are in excellent agreement with the notion that complexes **1**, **2**, and **3** contain high spin ferric ions. In [Fe^{III}(L^{ISQ})$_2$I][8] which possesses an S_t = 1/2 ground state these Fe–N and Fe–O$_{rad}$ bonds are much shorter at 1.885 Å and 1.875 Å, respectively; they indicate the presence of an intermediate spin ferric ion (S_{Fe} = 3/2) with two antiferromagnetically coupled *O,N*-coordinated π radicals.

The electronic spectrum of **3** has been measured in CH$_2$Cl$_2$ solution: $\lambda_{max}(\varepsilon$/L mol^{-1} cm^{-1}): 305(3.8 × 10^4), 350sh(3.1 × 10^4), 430(2.2 × 10^4), 540sh(1.1 × 10^4), 690(0.9 × 10^4). Interestingly, the spectra of **1** and **2** are very similar[3,8] and indicate the presence of Fe^{III}(L^{ISQ})$_x$ units (x = 1, 2, or 3).

The notion of the presence of high spin ferric ions in **1**, **2**, and **3** is corroborated by their Mössbauer spectra. Table 2 gives isomer shift, δ, and quadrupole splitting, ΔE_Q, parameters at 80 K and Fig. 3 exhibits the zero-field Mössbauer spectrum of **3** at 80 K. The fact that the isomer shift decreases from 0.54 mm s^{-1} for octahedral **1** to 0.45 mm s^{-1} for five-coordinate **2** and to 0.38 mm s^{-1} for five-coordinate **3** is rationalized by an increasingly covalent character of the iron-to-ligand bonds; in **3** it is dominated by the covalently bound oxo bridge.[14]
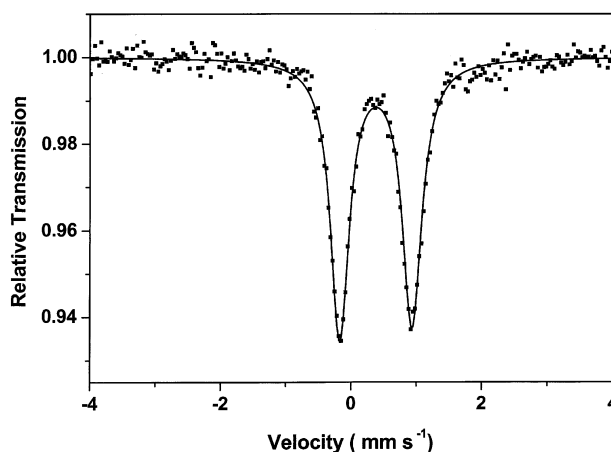
Fig. 3 Zero-field Mössbauer spectrum of **3** at 80 K.

Finally, Fig. 4 exhibits the temperature dependence of the magnetic moment of dinuclear **3** in the range 3–300 K. It has been possible to fit the behaviour successfully by using a model which invokes very strong intramolecular antiferromagnetic coupling between high spin ferric ions (S_{Fe} = 5/2) and—in each case—two o-iminosemiquinonate π radicals yielding a fictitious S^* = 3/2 state at each iron ion. This is fully in accord with the magnetism of mononuclear **2** which possesses an S_t = 3/2 ground state with no population of higher excited states up to 300 K.[8] The two halves of **3** are then coupled through the μ-oxo group. Thus, using the spin Hamiltonian $H = -2JS_1S_2$ ($S_1 = S_2$ = 3/2) yields the following parameters: J = −123(5) cm^{-1}, g = 2.0 (fixed). A mononuclear paramagnetic impurity of 0.6% (S = 5/2) was included. Thus, a strong antiferromagnetic coupling between the two halves in **3** prevails yielding the observed singlet ground state.
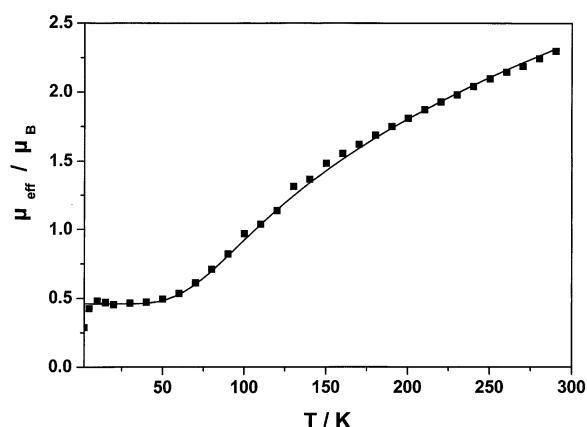

Fig. 4 Temperature dependence of the magnetic moment of **3** (per dinuclear unit): experimental values; the solid line represents a best fit of the data by using parameters given in the text.

Complex **3** provides the first example of a structurally characterized μ-oxo(diferric) complex containing four organic ligand radicals.

Notes and references

† The ligand 2-(p-*tert*-butyl)anilino-4,6-di-*tert*-butylphenol, H[$^{t-bu}$L^{AP}], has been prepared as follows. 3,5-Di-*tert*-butylcatechol (11.1 g; 50 mmol) and 4-*tert*-butylaniline (7.5 g; 50 mmol) were dissolved in n-heptane (60 mL) and triethylamine (0.5 mL). The solution was heated to reflux for 3 h in the presence of air. After cooling and reduction of the reaction volume by evaporation of the solvent (~30 mL) a colorless microcrystalline solid precipitated (yield: 12 g; 68%) which was collected by filtration and washed with n-pentane. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.33 (s, 9H), 1.38 (s, 9H), 1.56 (s, 9H), 4.95 (s, 1H), 6.70 (d, 2H), 7.14 (d, 1H), 7.33 (1H), 7.34 (2H).
‡ [Fe$^{III}_2$(μ-O)($^{t-bu}$L^{ISQ})$_4$] **3**: the ligand H[$^{t-bu}$L^{AP}] (0.36 g; 1.0 mmol) and [Fe^{II}(H$_2$O)$_6$](ClO$_4$)$_2$ (0.06 g; 0.25 mmol) were dissolved in methanol (25 mL). Upon addition of NEt$_3$ (0.5 mL) the color of the solution

turned deep red. The solution was heated to reflux for 1 h in the presence of air whereupon a color change to deep green was observed. From the cooled and filtered solution black microcrystals crystallized upon slow evaporation of the solvent within 2 d. The crude material was recrystallized from a CH$_2$Cl$_2$/CH$_3$CN (3 : 1) mixture. Yield: 0.12 g (63%). Anal. calcd. for (C$_{24}$H$_{33}$NO)$_4$OFe$_2$: C, 75.15; H, 8.68; N, 3.65; Fe, 7.30. Found: C, 75.0; H, 8.6; N, 3.5; Fe, 7.4.
§ *X-Ray crystallography*: diffraction data were collected at 100(2) K with Mo-Kα radiation (λ = 0.71073 Å) on a Nonius Kappa-CCD diffractometer equipped with a Mo-target rotating-anode X-ray source and a graphite monochromator ($2\theta_{max}$ = 55°). Data collection was performed by a full-sphere run taking frames at 1.0° in ω up to a data completeness of 90.6% (R(int) = 0.0482). Crystal faces were determined and the intensity data were corrected for absorption effects by using the Gaussian-type routine embedded in XPREP[15] giving min/max transmission factors of 0.927 and 0.953, respectively. The Siemens ShelXTL[15] software package was used for solution and artwork of the structure; ShelXL97[16] was used for refinement. The structure was solved by Patterson and subsequent difference Fourier techniques. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. The CH$_2$Cl$_2$ solvent molecules were found to be poorly defined. A split atom model with occupation factors of 0.8 (C(80)) and 0.2 (C(85)) was employed to account for disorder of one CH$_2$Cl$_2$ molecule. Another solvent molecule was found to be fully occupied (C(70)) and two more positions were refined with occupation factors of 0.5 (C(60)) and 0.25 (Cl(91) and Cl(92)). It has not been possible to locate the corresponding carbon atom. C–Cl and Cl–Cl distances were restrained to be equal within certain error limits using the SADI option of ShelXL97.
Crystal data for **3**·2.75CH$_2$Cl$_2$: C$_{96}$H$_{132}$Fe$_2$N$_4$O$_5$·2.75CH$_2$Cl$_2$, M = 1767.3, triclinic, space group $P\bar{1}$, a = 11.9826(6), b = 15.9612(9), c = 27.532(2) Å, α = 84.48(1), β = 82.47(1), γ = 77.64(1)°, V = 5086.7(5) Å^3, Z = 2, D_c = 1.154 g cm^{-1}, μ = 0.479 mm^{-1}. Full-matrix least squares refinement on F^2 (21829 unique data, 1065 variables) converged to $R1$ = 0.068, $wR2$ = 0.180 for all data. CCDC reference number 211465. See http://www.rsc.org/suppdata/dt/b3/b306764p/ for crystallographic data in CIF or other electronic format.

1 C. N. Verani, S. Gallert, E. Bill, T. Weyhermüller, K. Wieghardt and P. Chaudhuri, *Chem. Commun.*, 1999, 1747.
2 P. Chaudhuri, C. N. Verani, E. Bill, E. Bothe, T. Weyhermüller and K. Wieghardt, *J. Am. Chem. Soc.*, 2001, **123**, 2213.
3 H. Chun, C. N. Verani, P. Chaudhuri, E. Bothe, E. Bill, T. Weyhermüller and K. Wieghardt, *Inorg. Chem.*, 2001, **40**, 4157.
4 D. Herebian, P. Ghosh, H. Chun, E. Bothe, T. Weyhermüller and K. Wieghardt, *Eur. J. Inorg. Chem.*, 2002, 1957.
5 H. Chun, P. Chaudhuri, T. Weyhermüller and K. Wieghardt, *Inorg. Chem.*, 2002, **41**, 790.
6 H. Chun, E. Bill, E. Bothe, T. Weyhermüller and K. Wieghardt, *Inorg. Chem.*, 2002, **41**, 5091.
7 X. Sun, H. Chun, K. Hildenbrand, E. Bothe, T. Weyhermüller, F. Neese and K. Wieghardt, *Inorg. Chem.*, 2002, **41**, 4295.
8 H. Chun, T. Weyhermüller, E. Bill and K. Wieghardt, *Angew. Chem. Int. Ed.*, 2001, **40**, 2489.
9 K. S. Min, T. Weyhermüller and K. Wieghardt, *Dalton Trans.*, 2003, 1126.
10 H. Chun, E. Bill, T. Weyhermüller and K. Wieghardt, *Inorg. Chem.*, in press.
11 S. Mukherjee, E. Rentschler, T. Weyhermüller, K. Wieghardt and P. Chaudhuri, *Chem. Commun.*, 2003, 1828.
12 (*a*) O. Kahn, *Molecular Magnetism*, Wiley-VCH, New York, 1993; (*b*) A. P. Ginsberg, *Inorg. Chim. Acta Rev.*, 1971, **5**, 45.
13 (*a*) C. G. Pierpont and C. W. Lange, *Prog. Inorg. Chem.*, 1994, **41**, 331; (*b*) A. Dei and D. Gatteschi, *Inorg. Chim. Acta*, 1992, **198–200**, 813.
14 D. M. Kurtz Jr., *Chem. Rev.*, 1990, **90**, 585.
15 ShelXTL V.5, Siemens Analytical X-Ray Instruments, Inc.1994 .
16 ShelXL97 G. M. Sheldrick, University of Göttingen, 1997 .