

The Novel Mixed-valence, Exchange-coupled, Class III Dimer $[\text{L}_2\text{Fe}_2(\mu\text{-OH})_3]^{2+}$ (L = *N,N',N''*-Trimethyl-1,4,7-triazacyclononane)

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The reaction of $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with *N,N',N''*-trimethyl-1,4,7-triazacyclononane (L) in methanol affords, in the presence of a small amount of oxygen, the deep blue binuclear complex $[\text{L}_2\text{Fe}_2(\mu\text{-OH})_3](\text{ClO}_4)_2 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$ which was characterized by EXAFS, e.s.r., u.v.-visible, and Mössbauer spectroscopy to be a mixed valence iron (II/III) species of class III with an $S_{\text{tot}} = 9/2$ ground state.

Recently Münck *et al.*¹ reported a Mössbauer study on the reduced form of the electron transport protein ferredoxin (II) from *Desulfovibrio gigas* containing the Fe_3S_4 cluster with one trapped valence Fe^{3+} site and one electronically delocalized $\text{Fe}^{2+}\text{-Fe}^{3+}$ pair. The two Fe atoms of the delocalized pair were shown to be indistinguishable on the Mössbauer time scale. This pair has a dimer spin $S_{12} = 9/2$. Electron delocalization together with ferromagnetic spin alignment suggested that the spin coupling of the mixed-valent dimer was dominated by double exchange.²

Here we report on a novel, genuine dimer which exhibits the above electronic properties. The cofacial bioctahedral dimer $[\text{L}_2\text{Fe}_2(\mu\text{-OH})_3]^{2+}$ (L = *N,N',N''*-trimethyl-1,4,7-triazacyclononane) represents the first example of this kind.

To a stirred, argon-purged solution of L (1 mmol) in methanol (10 cm³) was added $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.4 mmol). Within 2.5 h at room temperature a deep blue solution was obtained to which NaClO_4 (0.6 mmol) was added. After 2 days at 5 °C deep blue crystals of $[\text{L}_2\text{Fe}_2(\mu\text{-OH})_3]\text{-}$

$(\text{ClO}_4)_2 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$ precipitated in 65% yield (based on Fe). Addition of NaBPh_4 instead of NaClO_4 to the solution initiated the immediate precipitation of blue $[\text{L}_2\text{Fe}_2(\mu\text{-OH})_3][\text{BPh}_4]_2 \cdot 2\text{MeOH}$.

The structure of the dication in the perchlorate salt has been established by a preliminary single crystal X-ray analysis[†] and by X-ray absorption measurements (EXAFS) and is shown in Figure 1. The latter experiments were performed on a powdered sample at room temperature at the Synchrotron

[†] The complete X-ray crystal structure determination of $[\text{L}_2\text{Fe}_2(\mu\text{-OH})_3](\text{ClO}_4)_2 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$ at ambient temperature has been hampered owing to severe disorder of the cation and ClO_4^- anions.

Preliminary crystal data: trigonal space group $P3_121$ (No. 152), $a = 14.439(1)$, $c = 18.810(3)$ Å, $U = 3396(1)$ Å³. The positions of the Fe and Cl atoms were located and a reliable Fe...Fe distance of 2.509(6) Å has been established. Data collection at -80 °C is underway. We thank Professor W. S. Sheldrick (Universität Kaiserslautern) for this information.

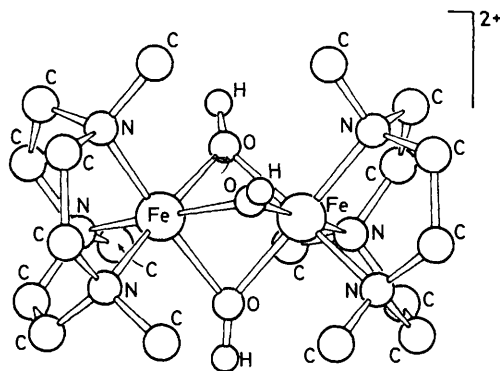


Figure 1. Ball and stick representation for the proposed structure of the dication $[L_2Fe_2(\mu-OH)_3]^{2+}$.

Table 1. EXAFS results of four-shells fit in the energy range 15–740 eV. $E_0 = 13.2$ eV and FI = 3.06.

Ligand	Co-ordination number ^a	Distance/Å	Debye-Waller factor/Å ²
O	3	2.00 ± 0.01	0.012 (2)
N	3	2.25 ± 0.02	0.023 (5)
Fe	1	2.50 ± 0.01	0.008 (1)
C	3	3.05 ± 0.01	0.007 (3)

^a Held constant.

Radiation Source, Daresbury Laboratory. The background-corrected and k^3 -weighted experimental EXAFS spectrum is shown in Figure 2 (solid line) together with a calculated spectrum (dashed line) which was derived by the least-squares curve-fitting program EXCURV.³ A full analysis yields the structural results summarized in Table 1. The Fe...Fe distance of 2.50 ± 0.01 Å is in agreement with the preliminary X-ray structure determination [$2.509(6)$ Å][†] and indicates a cofacial bioctahedral structure.⁴ The Fe–O and Fe–N distances of 2.00 ± 0.01 and 2.25 ± 0.02 Å also agree very well with those found in other hydroxo bridged Fe_2^{III} (d^5 high spin) and Fe_2^{II} (d^6 high spin) complexes containing tridentate N-donor ligands.⁵ Of specific interest is also the environment of the iron centres by carbon atoms in a distant shell. Keeping the numbers of different carbon atoms at 6 (methylene C-atoms) and 9 (methylene plus methyl C-atoms), the fit index (FI) increases to 3.21 and 3.25, respectively, compared to FI = 3.06 for only three methyl carbon atoms. This result would indicate (in agreement with the proposed structure) that three methyl carbon atoms are located closer to the metal sites than the ring carbon atoms.

In the electronic spectrum of the perchlorate salt in acetonitrile solution a strong absorption maximum at 758 nm ($\epsilon = 2.4 \times 10^3$ dm³ mol⁻¹ cm⁻¹ per dimer) is observed. The position and intensity (line width at half-height $\Delta\nu_{1/2}$) does not vary in a variety of solvents (H₂O, MeOH, MeCN, dimethylformamide, and dimethyl sulphoxide). The experimental value of $\Delta\nu_{1/2}$ is 3800 cm⁻¹ which is narrower than predicted by Hush's relation for a class II mixed valence species ($\Delta\nu_{1/2} = [2310 \bar{\nu}_{max}]^{1/2} = 5500$ cm⁻¹). These observations clearly indicate that the new mixed valence dimer exhibits class III behaviour with two equivalent iron sites at the 2.5 oxidation level.⁶ Variable-temperature magnetic susceptibility measurements on a powdered sample of the $[BPh_4]^-$ salt in the range 4–300 K using the Faraday method yielded a temperature

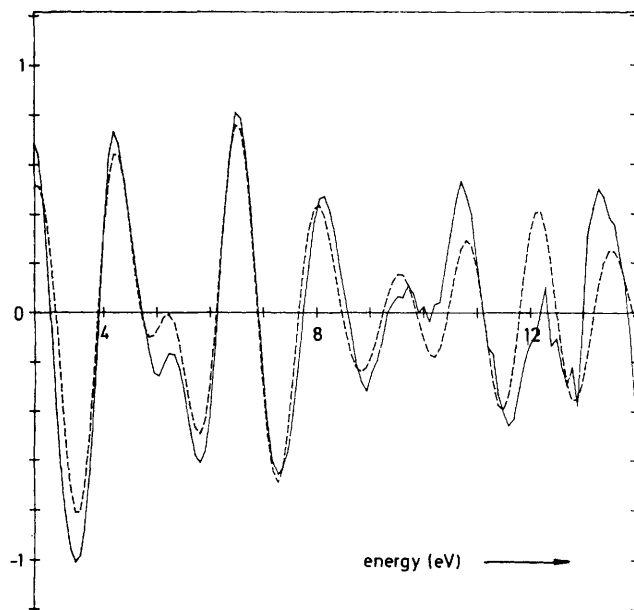


Figure 2. Background-corrected and k^3 -weighted EXAFS spectrum of $[L_2Fe_2(\mu-OH)_3](ClO_4)_2 \cdot 2MeOH \cdot 2H_2O$. Solid line: experimental spectrum; dashed line: curve-fit (see text).

independent magnetic moment of $10.5 \mu_B$ per dimer above 30 K which suggests intramolecular ferromagnetic coupling.⁷

The ^{57}Fe Mössbauer spectrum of the $[LFe(\mu-OH)_3FeL]^{2+}$ cation at 4.2 K in zero field exhibits a single quadrupole doublet (Figure 3A) indicating that the valence states and chemical structures of the two iron sites are identical. The isomer shift of $\delta = 0.74$ mm s⁻¹ at 4.2 K is between the values expected for ferric and ferrous high spin iron co-ordinated by six oxygen or nitrogen ligands (δ 0.35–0.60 mm s⁻¹ for Fe^{3+} and 0.9–1.3 mm s⁻¹ for Fe^{2+}).^{8,9} We therefore conclude that, within the Mössbauer time window of ca. 10^{-7} s, both metal sites form a mixed valence pair with one electron being delocalized over the $\{Fe^{2.5+}(\mu-OH)_3Fe^{2.5+}\}^{2+}$ core.

From a series of Mössbauer measurements recorded in the temperature range 1.5–300 K with applied magnetic field we selected two representative spectra shown in Figure 3B, 3C. The complete series was analysed on the basis of a spin Hamiltonian which, besides the usual zero field splitting, Zeeman [$g\mu_B \vec{B}^{ext}(\vec{S}_1 + \vec{S}_2)$] and exchange ($\vec{S}_1 \vec{S}_2$) terms,¹⁰ additionally includes the term $T_{12}B(S_{tot} + 1/2)$ to account for double exchange² [equation (1)].

$$H_{el} = D_1 \left[S_{1z}^2 - \frac{S_1(S_1 + 1)}{3} + \frac{E_1}{D_1} (S_{1x}^2 - S_{1y}^2) \right] + D_2 \left[S_{2z}^2 - \frac{S_2(S_2 + 1)}{3} + \frac{E_2}{D_2} (S_{2x}^2 - S_{2y}^2) \right] + g\mu_B \vec{B}^{ext}(\vec{S}_1 + \vec{S}_2) - \vec{S}_1 \vec{S}_2 + T_{12}B(S_{tot} + 1/2) \quad (1)$$

The transfer operator T_{12} and the transfer integral B represent electron transfer between the two metal sites. It is intuitively obvious that double exchange lowers the energy of spin multiplets with large total spin ($S_{tot} = S_1 + S_2$), i.e. electron transfer favours parallel spin coupling. On the other hand, antiparallel spin coupling is favoured by a large and negative J . Altogether, it depends on the relative magnitudes of $|J|$ and B , whether a dinuclear system acquires high or low spin multiplicity in its ground state. Zero field splitting D and

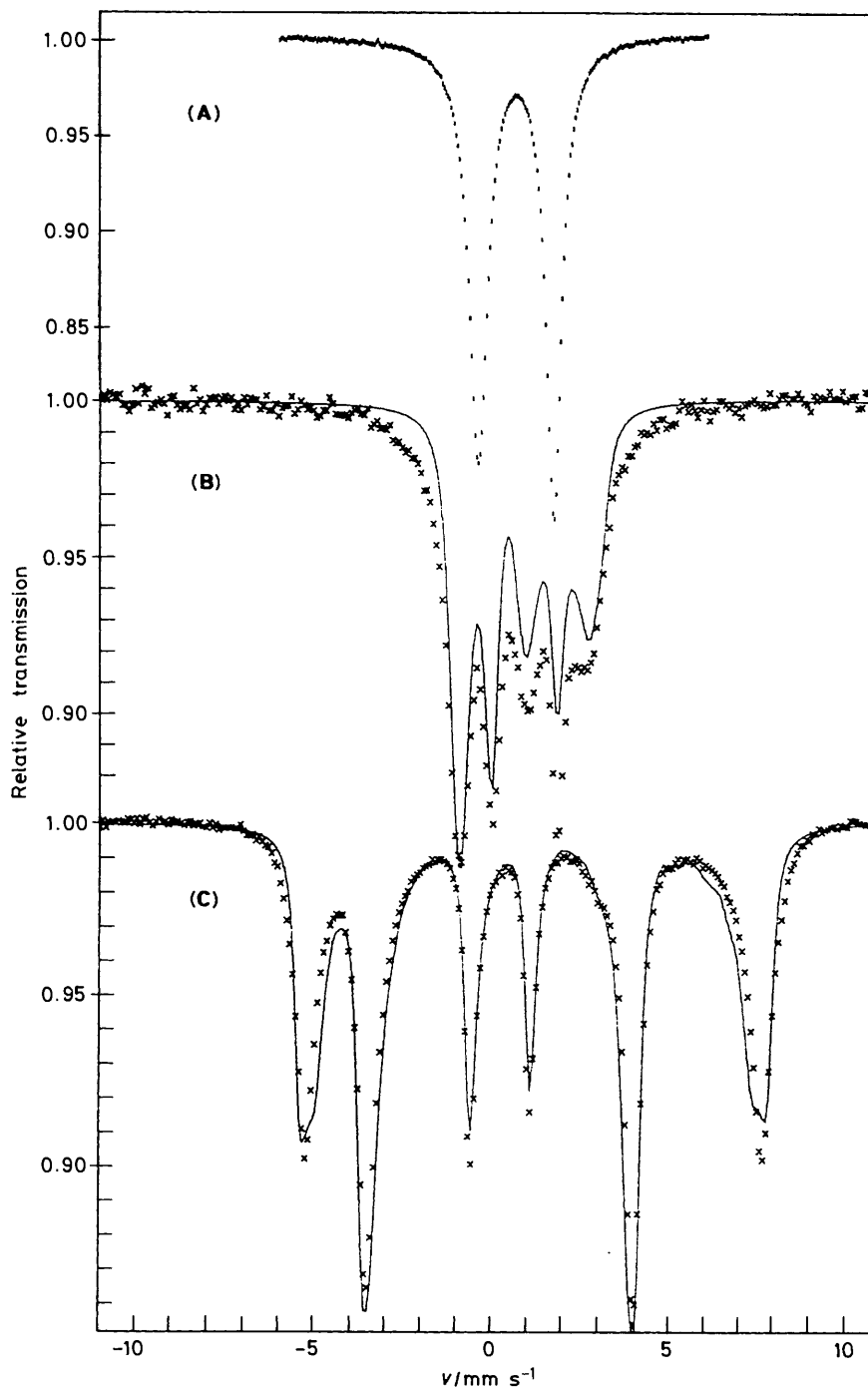


Figure 3. Mössbauer spectra of $[\text{L}_2\text{Fe}_2(\mu\text{-OH})_3](\text{ClO}_4)_2 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$ recorded at 4.2 K with an external field \vec{B}^{ext} of (A) 0 T, (B) 0.25 T, and (C) 2.47 T, applied perpendicular to the γ -beam. Solid lines were simulated with the spin-Hamiltonian of equation (1), using parameters $S_1 = 5/2$, $S_2 = 2$, $S_{\text{tot}} = 9/2$, $D_1 = D_2 = 2 \text{ cm}^{-1}$, $E_1/D_1 = E_2/D_2 = 0$; $J = -16 \text{ cm}^{-1}$, and $B = 100 \text{ cm}^{-1}$.

rhombicity E/D describe separation and ordering of Kramers doublets within the spin multiplets. Spin expectation values $\langle \vec{S} \rangle$ of the various spin states give rise to internal magnetic fields acting on the nuclear spin I . Nuclear Zeeman and quadrupole interactions were calculated as usual.¹⁰

The wide magnetic splitting of the spectrum measured at 4.2 K, 2.47 T (Figure 3C) is due to a strong internal field and indicates large total spin for the ground state of $[\text{LFe}(\mu\text{-OH})_3\text{FeL}]^{2+}$, *i.e.* $S_{\text{tot}} = 9/2$. This is consistent with the magnetic moment derived from susceptibility measurements. The intensity ratio of the Mössbauer absorption lines depends

on the direction of the external field \vec{B}^{ext} (*ca.* 3:4:1 for $\vec{B}^{\text{ext}} \perp \gamma$ in Figure 3C). It reveals either complete magnetic isotropy or at least an easy plane of magnetization in the present case. The latter is characteristic for a low lying $S_2 = \pm 1/2$ Kramers doublet belonging to $S_{\text{tot}} = 9/2$, which has spin expectation values larger than 2 in x - and y -direction, yielding an easy plane of magnetization. In particular, this finding implies a large transfer integral B (*i.e.* $B > 5|J|$), positive zero field splitting D , and small rhombicity E/D . This picture is supported by e.s.r. spectra recorded in the temperature range 2.5–50 K. They exhibit strong resonances at large effective

g -values, $g_{x,y} \approx 10$, and broad features at $g_z \approx 2-2.5$, and their temperature dependence is typical for ground state resonances.

The collapse of magnetic splitting in the Mössbauer spectra recorded in weak fields (Figure 3B) reveals fast spin relaxation. In this relaxation limit spin expectation values of populated spin states yield a thermal average $\langle \vec{S} \rangle_T$ and therefore contribute with a single internal field to the Mössbauer spectrum only.

From simulations of Mössbauer spectra in various fields at low temperature the values of B and J could not be identified uniquely, because the energy separations within the $S_{\text{tot}} = 9/2$ multiplet hardly depends on B and J . However, from spectra recorded at elevated temperatures up to 250 K, where also excited spin multiplets contribute to the internal field, these parameters could be derived. Details of this investigation will be published elsewhere.

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