Cluster Compounds

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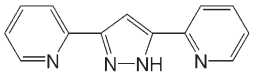
An $[Fe^{II}_3O]^{4+}$ Core Wrapped by Two $[Fe^{II}L_3]^-$ Units**

Ko Yoneda, Keiichi Adachi, Kyonosuke Nishio, Mikio Yamasaki, Akira Fuyuhiro, Motomi Katada, Sumio Kaizaki, and Satoshi Kawata**

The spontaneous self-organization of coordination compounds has been studied intensively over the last few decades.[1] One area of particular interest is the assembly of multistranded helicates.[2–5] As most strategies for the synthesis of helicates with high nuclearities make use of long and flexible organic ligands, many linear helicates have been prepared.[3,5] Because of their unique physical and chemical properties, helicates have been used as components of functional materials and devices.[6,7] These applications could experience remarkable development if clusters with novel properties were introduced into the helicates.

There are few examples of cluster helicates, in which metal clusters define the helical axis.[6] However, Saalfrank and co-workers have introduced $[M_3O]^{4+}$ ($M = Mn^{II}$, Zn^{II}, or Cd^{II}) clusters into helicates.[6c] This result prompted us to synthesize a cluster helicate with a similar cluster core. Herein, we report the first pentanuclear bis(triple-helical) complex, $[\{Fe^{II}(\mu\text{-}L)_3\}_2Fe^{II}_3(\mu\text{-}O)]^{2+}$ ($L^- = 3,5$-bis(pyridin-2-yl)pyrazolate), in which an $[Fe^{II}_3O]^{4+}$ core[8] is wrapped by two terminal $[Fe^{II}L_3]^-$ units.



HL

The reaction of HL with $FeCl_2{\cdot}4H_2O$ in the presence of NaNCS under an N_2 atmosphere led to $[\{Fe^{II}(\mu\text{-}L)_3\}_2Fe^{II}_3(\mu\text{-}O)](NCS)_2{\cdot}10H_2O$ (**1**) in 80% yield.[9] The Mössbauer spectrum of **1** at 78 K consists of three quadrupole doublets with relative peak areas of 2:1:2, which correspond to two types of high-spin iron(II) ions (isomer shift (IS) = 1.03 mm s^{-1}, quadrupole splitting (QS) = 3.34 mm s^{-1}; IS = 1.03 mm s^{-1}, QS = 2.81 mm s^{-1}) and one type of low-spin iron(II) ion (IS = 0.46 mm s^{-1}, QS = 0.26 mm s^{-1}), respectively (Figure 1).[10] These Mössbauer data are consistent with the structure determined by X-ray diffraction.

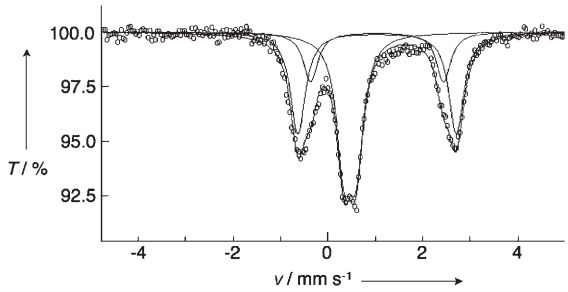


Figure 1. Mössbauer spectrum of a powder sample of **1** at 78 K; T = transmittance, v = velocity; experiment: circles, fit: lines; see text for details.

The structure of the cation of **1** at 93 K is shown in Figure 2.[11] Despite the helical configuration of the cation, which has C_2 point symmetry, the space group of **1** is $I\bar{4}$, and a pair of enantiomers is present in the crystal. The cation consists of six L^- ligands, two iron ions, and an $[Fe^{II}_3O]^{4+}$ core. The core consists of a triangle of three iron ions (Fe(1), Fe(2), and Fe(2*)) with a μ_3-oxygen atom in the center. The Fe-O-Fe angles of the core are 120.9(1) and 118.1(1)°. The remaining two iron ions (Fe(3) and Fe(3*)) take part in terminal triple-stranded $[Fe^{II}L_3]^-$ units. The Fe(3) and Fe(3*) ions, which are

[*] K. Yoneda, Dr. K. Adachi, K. Nishio, Dr. A. Fuyuhiro, Prof. Dr. S. Kaizaki, Prof. Dr. S. Kawata
Department of Chemistry, Graduate School of Science
Osaka University
Toyonaka, Osaka 560-0043 (Japan)
Fax: (+81) 6-6850-5473
E-mail: kaizaki@chem.sci.osaka-u.ac.jp
kawata@chem.sci.osaka-u.ac.jp
Homepage: http://www.chem.sci.osaka-u.ac.jp/lab/kaizaki/
http://www.chem.sci.osaka-u.ac.jp/%7ekawata/
Dr. M. Yamasaki
Single Crystal Structural Analysis Group
Application Laboratories, Rigaku Corporation
Akishima, Tokyo 196-8666 (Japan)
Prof. Dr. M. Katada
Department of Chemistry, Graduate School of Science
Tokyo Metropolitan University
Hachiouji, Tokyo 192-0397 (Japan)

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$L^- = 3,5$-bis(pyridin-2-yl)pyrazolate.

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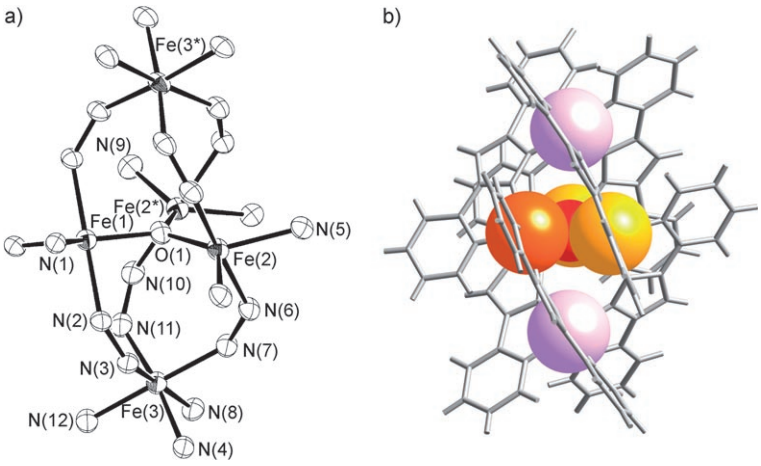

Figure 2. Structure of the $[\{Fe^{II}(\mu\text{-}L)_3\}_2Fe^{II}{}_3(\mu\text{-}O)]^{2+}$ cation of **1**. a) ORTEP representation; displacement ellipsoids set at 50% probability; noncoordinated atoms of the L^- ligands omitted for clarity. b) Ball-and-stick representation; Fe(1) orange, Fe(2)/Fe(2*) yellow, Fe(3)/Fe(3*) purple, O red; C, H, and N gray.

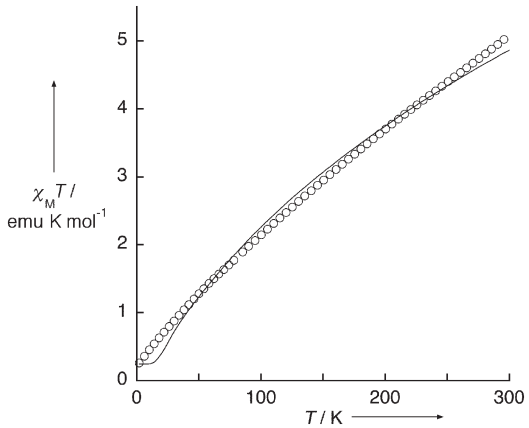

Figure 3. Temperature dependence of $\chi_M T$ for **1**; χ_M = magnetic susceptibility; experiment: circles, fit: line; see text for details.

in the low-spin state ($S=0$), each occupy distorted octahedral coordination environments composed of six nitrogen atoms, two from each of three L^- ligands. Together, the two $[Fe^{II}L_3]^-$ units function as a complex ligand to enclose the $[Fe^{II}{}_3O]^{4+}$ core, like a candy in a wrapper, by using the remaining coordination sites of the L^- ligands. The coordination environments of the Fe(1), Fe(2), and Fe(2*) ions of the core each consist of one O^{2-} ion and four nitrogen atoms from two L^- ligands, which form distorted N_4O trigonal bipyramids (with trigonality indices of $\tau=0.73$ (Fe(1)) and 0.87 (Fe(2)/Fe(2*)).[10] Therefore, it is plausible that the Fe(1) and Fe(2)/Fe(2*) ions are in the high-spin state ($S=2$), consistent with the Mössbauer spectrum. Although many oxo-centered trinuclear iron(III) complexes have been reported,[8,12] to our knowledge, the cation of **1** contains the first example of an oxo-centered trinuclear iron(II) unit. The cation has a pseudo three-fold axis passing through Fe(3) and Fe(3′). Unlike the long organic ligand strands that are generally used for the construction of helicates with high nuclearities, the planar L^- ligand is short and rigid. However, the π stacking of the L^- ligands of the two homochiral $[Fe^{II}L_3]^-$ units leads to bis(triple-helical) strands. The central $[Fe^{II}{}_3O]^{4+}$ core is bound by the remaining coordination sites of these $[Fe^{II}L_3]^-$ units.

The temperature dependence of the magnetic susceptibility (χ_M) of **1** is shown in Figure 3, in the form of a $\chi_M T$ versus T plot. The $\chi_M T$ value at 300 K is approximately 5 emu K mol^{-1} per formula unit, which is smaller than the spin-only value for three high-spin iron(II) ions (9.003 emu K mol^{-1}). Below 300 K, $\chi_M T$ decreases monotonically with decreasing temperature, indicating intramolecular antiferromagnetic coupling. Thus, we fit the essential features of the experimental curve by using the simple triangle model ($H=-2JS_AS_B$),[13] resulting in $J=-29.0$ cm^{-1} and $g=2.29$. Unfortunately, no similar systems with well-characterized Fe^{II}-O-Fe^{II} magnetic interactions are available for comparison with the properties of **1**. However, weak antiferromagnetic interactions have been reported for $[Mn^{III}{}_3(\mu\text{-}O)(O_2CMe)_6(py)_3](py)$ (py = pyridine; $J=-10.9$ cm^{-1}), and ferromagnetic interactions have been reported for $[Mn^{III}{}_3(\mu\text{-}O)(\mu\text{-bamen})_3](ClO_4)\cdot 2H_2O$ (H_2bamen = 1,2-bis(biacetylmonoximeimino)ethane) and $[Mn^{III}{}_3(\mu\text{-}O)(O_2CMe)_3(mpko)_3](ClO_4)\cdot 3CH_2Cl_2$ (Hmpko = methyl 2-pyridyl ketone oxime).[13,14] These findings can be rationalized by noting that the high-spin d^4 manganese(III) ion has an electronic configuration of $(t_{2g})^3(e_g)^1$ in an octahedral field, whereas the high-spin d^6 iron(II) ion has an electronic configuration of $(e'')^3(e')^2(a_1')^1$ in a trigonal bipyramidal field. Unpaired electrons in the e_g or e' orbitals contribute to antiferromagnetic exchange pathways, because the e_g or e' orbitals are involved in σ interactions.

In conclusion, we have shown that L^- and iron(II) ions undergo homochiral self-assembly into a bis(triple-helical) cluster in which an $[Fe^{II}{}_3O]^{4+}$ core is stabilized by bridging two mononuclear $[Fe^{II}L_3]^-$ units. We believe that this synthetic strategy could offer new possibilities for the construction of helicates with unique cluster cores and novel properties.

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[9] An aqueous solution (2 mL) of $FeCl_2 \cdot 4H_2O$ (3.7 mM) was transferred into a glass tube, and then a 1:1 methanol/water mixture (2 mL) of HL (4.5 mM), NaNCS (1.5 mM), and NaOH (4.5 mM) was added without mixing under an N_2 stream. Dark orange crystals began to form at ambient temperature after 2 days. Yield 80%. Elemental analysis (%) calcd for $C_{80}H_{74}N_{26}O_{11}S_2Fe_5$: C 50.05, H 3.94, N 18.97; found: C 49.04, H 3.70, N 19.14. MS (positive ESI; 1:3 CH_3OH/H_2O): *m*/*z*: 811 $[\{Fe^{II}(\mu\text{-}L)_3\}_2Fe^{II}_3(\mu\text{-}O)]^{2+}$.

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[11] Crystal structure analysis for **1**: The data collection was carried out on a Rigaku RAXIS-RAPID diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation. The structure was solved by direct methods (Rigaku CrystalStructure, Molecular Structure Corporation) and refined with full-matrix least-squares techniques (SHELXL97[15]). Crystal data: $C_{80}H_{74}N_{26}O_{11}S_2Fe_5$, $T = 93$ K, dark orange, tetragonal, space group $I\bar{4}$, $Z = 1$, $a = 16.897(2)$, $c = 29.980(5)$ Å, $V = 8559(2)$ Å^3, $\rho_{calcd} = 1.489$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 9.51$ cm^{-1}, 50290 reflections collected, $2\theta < 59.9°$, 12349 independent reflections ($R_{int} = 0.026$), 610 parameters, all non-hydrogen atoms anisotropic, all hydrogen atoms in calculated positions, $R_1 = 0.0396$ (for 11207 $F < 4\sigma(F)$), $wR_2 = 0.1243$, Flack parameter = 0.006(10), GOF = 1.062. CCDC-604887 (**1**) contains 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.

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