

spectroscopy detects the presence of a stable helical conformation, while CD spectroscopy detects the presence of diastereomeric excess. The solvophobicity of the hydrocarbon backbone, which is presumably much larger than that of the polar side chains, could explain why the backbone adopts helical order well before bias is imparted to the helix twist sense. From the CD data, the diastereomeric excess originates at approximately the same chloroform composition regardless of chain length (Figure 3b). Based on this observation it is plausible that ordering of the solvated side chains, a process that lags behind helix formation, is the mechanism by which chirality is transferred to the backbone. The analogy might be made to the "molten globular state" of proteins, a state in which the peptide backbone possesses a native-like conformation while having disordered side chains.^[21, 22]

An alternative way to explain the observed transition behavior is to consider the dynamics and conformational uniqueness of the backbone. At high chloroform compositions (but when the oligomers are still helical, as judged by UV spectroscopy) there are possibly a large number of energetically similar, helical-like backbone conformations that interconvert rapidly. Here the analogy might be made to the "compact denatured state" of proteins, a collapsed form in which there is a broad ensemble of backbone and side-chain conformations even though there is extensive hydrophobic clustering.^[23] The UV spectrum simply fails to provide the needed resolution to distinguish between a well-ordered, conformationally unique backbone and a mixture of helical-like conformers. The dynamics and structural diversity available to the backbone in this conformational state may preclude cooperative interactions among the side chains that give rise to the twist sense bias. Upon increasing the amount of acetonitrile, a smaller set of backbone helical conformations becomes populated, allowing the side chains to order and transfer their chirality to the main chain. Regardless of which of these explanations is correct, the transfer of chirality appears to be a highly cooperative process that requires a progression of conformational order beyond the initially formed helical state. The sharpness of the CD transition points toward a high twist sense bias that obviously cannot be deduced from the magnitude of the Cotton effect.

In conclusion, we have demonstrated that it is possible to bias the twist sense of a solvophobicity driven helical conformation by the attachment of chiral side chains. These results show that the side chains can play more than just an ancillary role in these conformationally ordered oligomers. The diastereomeric bias only appears after the backbone acquires a conformationally ordered state. Solvent denaturation studies showed that a helical conformation is a necessary, but not a sufficient condition for inducing a diastereomeric bias. In particular, the onset of the twist sense bias was shown to lag significantly behind the appearance of helical conformations, possibly because a large ensemble of "collapsed" conformations is initially formed. To further elucidate the nature of the folding and chirality transfer, additional experiments in more polar media will be undertaken.

Received: April 14, 1999
Revised: August 4, 1999 [Z13281]

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Mixed-Valent Heptairon Complex with a Ground-State Spin Value of $S = 12/2$ Constructed from a Triiron Cluster Ligand**

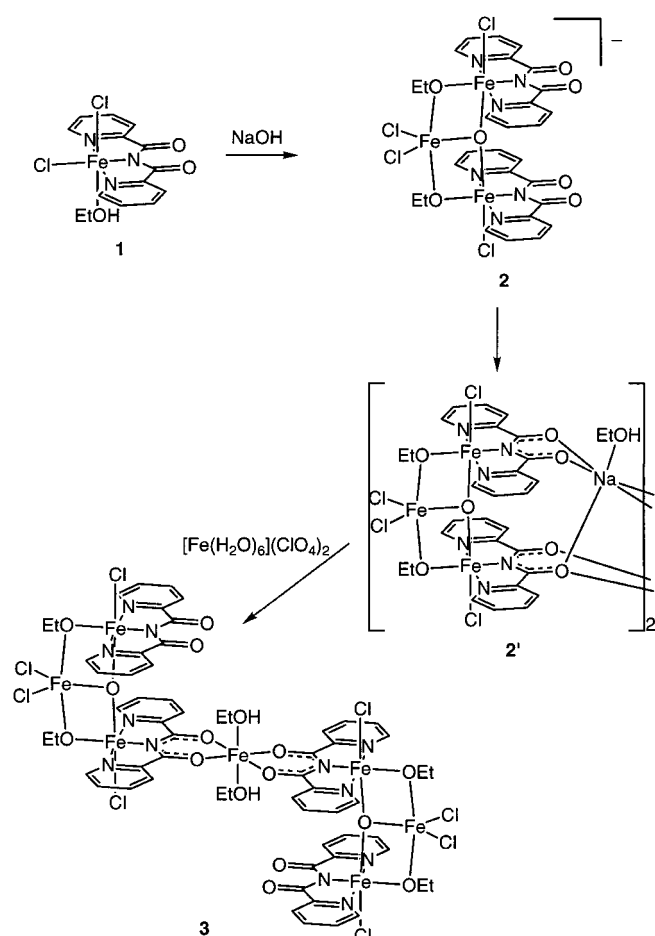
Takashi Kajiwaru and Tasuku Ito*

Complexes assembled from metal-containing subunits^[1–12] have attracted much attention in view of their very interesting structures, for example, ferric wheels,^[1] and properties, for example, molecular-based magnetism,^[2] and multistep, multi-electron redox reactions.^[3] Designing the spatial arrangement

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[**] This work was supported by a Grant-in-Aid for Scientific Research on Priority Area "Metal-Assembled Complexes" (No. 0149102) and the Encouragement of Young Scientists (No. 11740366) from the Ministry of Education, Science, Sports, and Culture, Japan.

of metal ions and tuning the metal–metal interactions are challenging tasks. One beneficial way of constructing metal assemblies is to use “complex ligands” such as metal–cyanide,^[4, 5] metal–oxalate,^[6] metal–thiolate,^[7] metal–oximate,^[8, 9] and metal–oxamide complexes.^[10] In most cases, the resulting multimetal compounds containing complex ligands of these types are either discrete molecules with low nuclearity or dimensional solids, and examples of discrete molecules with high nuclearity are rather rare.^[5, 9, 11] A “metal cluster complex ligand” would be effective in making such a high nuclear compound. We reported recently on novel trinuclear complexes constructed with the bis-bidentate bridging complex ligands $[M(\text{bpca})_2]$ ($M = \text{Fe}^{\text{II}}, \text{Mn}^{\text{II}}$; Hbpca = bis(2-pyridylcarbonyl)amine).^[12] Herein we report on a “cluster complex ligand” containing $[\text{Fe}(\text{bpca})]^{2+}$ moieties that act as ligating sites and leads to a heptairon complex (Scheme 1).



Scheme 1. Preparation of **3** from cluster ligand **2**.

An anionic triiron(III) cluster complex ion, $[\text{Fe}_3(\mu_3\text{-O})(\text{bpca})_2\text{Cl}_4(\text{EtO})_2]^-$ (**2**), was formed and isolated as the sodium salt $[\text{Na}_2(\text{2})_2(\text{EtOH})_2]$ (**2'**) when $[\text{Fe}(\text{bpca})\text{Cl}_2(\text{EtOH})]$ (**1**)^[13] was allowed to react with sodium hydroxide in EtOH. The reaction of **2'** with iron(II) perchlorate in the presence of [18]crown-6 in ethanol/nitromethane afforded the mixed-valent heptairon complex $[\text{Fe}(\text{2})_2(\text{EtOH})_2]$ (**3**), with the ground-state spin value of $S = 12/2$.

The structures of **2'**^[14] and **3**^[14] are shown in Figures 1 and 2, respectively. Both complexes crystallize in the same $P2_1/n$ space group and possess a crystallographic inversion center at

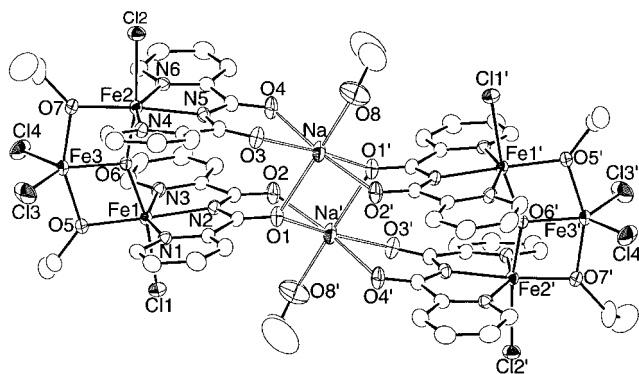


Figure 1. ORTEP drawing of **2'** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted. Selected distances [Å]: Fe1...Fe2 3.7305(8), Fe1...Fe3 3.0440(7), Fe2...Fe3 3.0320(8), Fe1...Na 6.0116(17), Na...Na' 3.506(4).

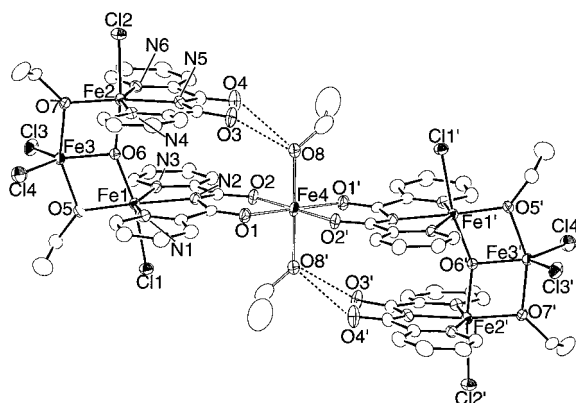


Figure 2. ORTEP drawing of **3** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted. Selected distances [Å]: Fe1...Fe2 3.7387(9), Fe1...Fe3 3.0439(9), Fe1...Fe4 5.5830(7), Fe2...Fe3 3.0150(9).

the midpoint between the two sodium atoms (**2'**) or on the Fe4 atom (**3**), thus making each half of each molecule crystallographically independent.

Complex **2'** consists of two anionic cluster ligands (depicted with filled bonds), two sodium ions, and coordinating ethanol molecules. The structure can be taken as the coordination of cluster ligand **2** to Na^+ ions. Three iron(III) centers in the cluster ligand form an approximate isosceles triangle with two equal sides of 3.0440(7) (Fe1–Fe3) and 3.0320(8) Å (Fe2–Fe3) and a base of 3.7305(8) Å (Fe1–Fe2). The μ_3 -oxo atom (O6) is bound to three iron atoms at almost the same distances (1.925(2), 1.919(2), and 1.934(2) Å). The Fe1–O6–Fe3 and Fe2–O6–Fe3 angles are 104.13(11) and 103.78(11)°, respectively, while the Fe1–O6–Fe2 angle of 152.07(13)° is much larger. The central iron ion (Fe3) is five coordinate, has two chloro ligands, and possesses a slightly distorted trigonal-bipyramidal geometry. A very similar $\text{Fe}_3^{\text{III}}(\mu_3\text{-O})$ core structure has been found in a hexanuclear ferric complex reported by Christmas et al.^[15] The distances between the iron and donor atoms in **2** are typical of high-spin Fe^{III} complexes. In this moiety four carbonyl groups on two bpca[−] ligands are

disposed toward the same direction and coordinate to sodium ions in a multidentate fashion.

In **3**, two cluster ligands coordinate to an iron(II) ion (Fe4) in a bidentate fashion, and coordination-free carbonyl oxygens (O3 and O4) form hydrogen bonds with a coordinated ethanol molecule ($O \cdots O$ 2.726(5) and 3.165(6) Å, respectively). The structure of the triiron(III) cores in **3** differs slightly from that found in **2'** (Fe1–Fe3 3.0439(9), Fe2–Fe3 3.0150(9) Å; Fe1–O6–Fe3 105.05(14), Fe2–O6–Fe3 101.77(13)°), probably as a result of the interaction with the central iron(II) ion. The divalent iron ion Fe4 is in an octahedral environment with an O_6 donor set at distances in the range of 2.090(3)–2.113(4) Å, which is similar to that found in $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_2(\text{acac})_2]$ ^[16] (acac^- = acetylacetonate), although the equatorial and axial coordination bonds are slightly elongated and shortened in **3**, respectively.

Figure 3 shows the magnetic behavior of **2'** and **3**. The $\chi_M T$ value for **2'** decreases continuously as the temperature is lowered. From the structural analysis **2'** can be considered to consist of two well-separated, trinuclear iron(III) cluster units with a closest approach of 12.129(1) Å (Fe1–Fe1'). The

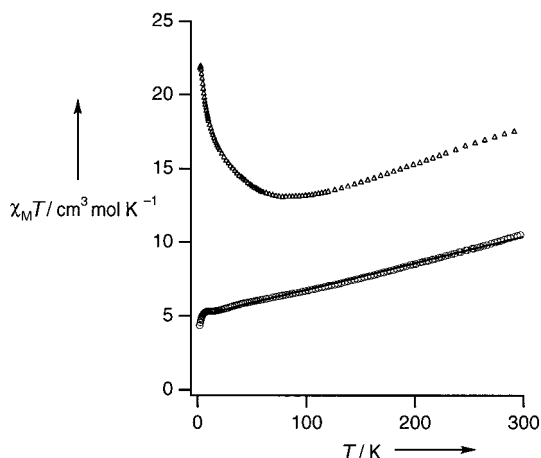


Figure 3. Plots of $\chi_M T$ versus T for **2'** (○, at 5000 G) and **3** (△, at 1000 G). The $\chi_M T$ values are calculated for discrete molecules containing six iron atoms for **2'** and seven iron atoms for **3**. The solid line represents the theoretical fit to the data.

temperature dependence of $\chi_M T$ for **2'** was analyzed by the isolated three-spin model ($H = -2J(\mathbf{S}_{\text{Fe1}} \cdot \mathbf{S}_{\text{Fe3}} + \mathbf{S}_{\text{Fe2}} \cdot \mathbf{S}_{\text{Fe3}}) - 2J'\mathbf{S}_{\text{Fe1}} \cdot \mathbf{S}_{\text{Fe2}}$) with the intertrimer interactions θ . The best fit parameters were calculated using the data in the range 20–300 K to avoid the influence of zero-field interactions, and were determined as $J = -15.2(1) \text{ cm}^{-1}$, $J' = -36.3(2) \text{ cm}^{-1}$, and $\theta = 4.2(1) \text{ K}$ ($2.9(1) \text{ cm}^{-1}$) with $g = 2$ (fixed). Several triiron(III) complexes containing a μ_3 -oxo bridge have been studied for their spin-frustration behavior, and it has been reported that the ground-state spin multiplicity depends on the ratio J/J' .^[15, 17] The ground-state spin value of each triiron(III) unit in our system was calculated to be $S = 3/2$.^[18]

The magnetic behavior of the mixed-valent heptairon complex **3** differs drastically from that of its precursor **2'**. The $\chi_M T$ value for **3** is larger than that of **2'** by roughly 7 emu K mol^{-1} in the range 300–80 K, reaches a minimum around 80 K, and then shows a sharp increase below this

temperature to reach the maximum of 22.0 emu K mol^{-1} at 2 K. This maximum value corresponds to a theoretical value of 21.0 emu K mol^{-1} for the $S = 12/2$ ground state with $g = 2$, which is larger than the value calculated for ferromagnetically coupled high-spin Fe^{II} ions with $S = 4/2$ and two Fe_3^{III} cores with an $S = 3/2$ ground state (see earlier discussion). The dependence of the magnetization on the field is also in accord with the ground state S being equal to or greater than 11/2 (Figure 4). There is not any significant contact among neighboring complexes, and this magnetic behavior arises from interactions within a molecule. The theoretical analysis for **3** has not been carried out because of the complexity of the spin states that arises from seven iron atoms.

It is clear, however, that the central iron(II) ion and two cluster ligands interact strongly to generate a relatively high ground spin state. The ground-state spin of each of cluster ligand unit might be changed in **3**.

We have shown that cluster ligand **2** is very useful in constructing metal assemblies. Ligand **2** can coordinate to a variety of metal ions in a bidentate, tridentate, and even tetradentate fashion. Related studies are now in progress in our laboratories.

Experimental Section

2': A solution of NaOH in EtOH (0.1M, 2.5 mL) was added to a hot solution of $[\text{Fe}(\text{bpca})\text{Cl}_2(\text{EtOH})]$ (100 mg, 0.25 mmol) in ethanol/nitromethane (1/1, 10 mL). The dark red solution was heated at reflux for 2 h, and the resulting deep orange solution allowed to stand for one day. Complex **2'** crystallized as red-orange prismatic crystals.

3: A suspension of **2'** (40 mg, 0.04 mmol) in ethanol/nitromethane (1/1, 6 mL) was heated gently under an atmosphere of nitrogen until a clear solution was obtained. A solution of [18]crown-6 in ethanol (0.1M, 0.4 mL) was then added. The diffusion of a solution of $[\text{Fe}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ in ethanol (0.05M, 0.4 mL) into the solution resulted in the color changing from orange to black, and after several hours, **3** crystallized as black prismatic crystals.

Received: August 5, 1999 [Z13834]

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- [14] Crystal structure determination of $2 \cdot 4\text{CH}_3\text{NO}_2$: An orange crystal (ca. $0.38 \times 0.32 \times 0.18$ mm) was analyzed with a Bruker SMART CCD-based diffractometer at 200 K with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å). Monoclinic, space group $P2_1/n$, $a = 14.9174(8)$, $b = 15.4925(8)$, $c = 19.8300(11)$ Å, $\beta = 105.4740(10)^\circ$, $V = 4416.7(4)$ Å³, $Z = 2$, $\rho_{\text{calc}} = 1.593$ g cm⁻³, $\mu(\text{MoK}\alpha) = 1.289$ mm⁻¹, $F(000) = 2156$. ω -scans, 27813 reflections measured ($2\theta_{\text{max}} = 55^\circ$), of which 9940 were independent and 7236 were observed [$I > 2\sigma(I)$], 545 refined parameters, $R = 0.0510$, $wR2 = 0.1347$, residual electron density max./min. $1.247/-0.569$ e Å⁻³, max./min. transmission 0.8014/0.7022. Crystal structure determination of $3 \cdot 3\text{CH}_3\text{NO}_2$: A black crystal (ca. $0.32 \times 0.28 \times 0.15$ mm) was analyzed with a Bruker SMART CCD-based diffractometer at 193 K with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å). Monoclinic, space group $P2_1/n$, $a = 14.6914(9)$, $b = 19.0764(11)$, $c = 15.2417(9)$ Å, $\beta = 91.1990(10)^\circ$, $V = 4270.7(4)$ Å³, $Z = 2$, $\rho_{\text{calc}} = 1.655$ g cm⁻³, $\mu(\text{MoK}\alpha) = 1.486$ mm⁻¹, $F(000) = 2164$. ω -scans, 26851 reflections measured ($2\theta_{\text{max}} = 55^\circ$), of which 9656 were independent and 5646 were observed [$I > 2\sigma(I)$], 538 refined parameters, $R = 0.0553$, $wR2 = 0.1274$, residual electron density max./min. $0.831/-0.509$ e Å⁻³, max./min. transmission 0.8621/0.6109. Data reduction for both compounds was performed with the SAINT software, which corrects for Lorentz and polarization factors as well as decay. Absorption corrections were applied with SADABS supplied by G. Sheldrick (Universität Göttingen). The structures were solved by direct methods with the SHELXS-97 program and refined by the least squares method on F^2 , (SHELXL-97, incorporated in SHELXTL-PC version 5.10). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated by geometrical methods and refined as a riding model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-132694 and CCDC-132695. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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- [18] This result is also supported by the dependence of the magnetization of **2** on the field.

Encoded Helical Self-Organization and Self-Assembly into Helical Fibers of an Oligoheterocyclic Pyridine–Pyridazine Molecular Strand**

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Jean-Claude Homo, and Marc Schmutz

Helices and superhelices are key structural features of proteins, nucleic acids, and oligosaccharides. It is therefore no surprise that helical structures and superstructures have received increasing attention in biomimetic and synthetic supramolecular systems.^[1] Helical organization in synthetic systems has been obtained through covalent conformational restrictions,^[2] metal complexation,^[3] solvophobic effects,^[4] intermolecular interactions,^[5] and nonbonding intramolecular interactions.^[6] Several approaches to the generation of helical entities have been pursued in our group^[7] starting from double-helical metal complexes (helicates),^[8] followed by triple helicates,^[9] circular helicates,^[10] and helically wound, supramolecular liquid crystalline polymers.^[11] More recently

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[**] L.A.C. thanks the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Centre National de la Recherche Scientifique (CNRS), France, for financial support. J.-C.H. and M.S. acknowledge the financial support of INSERM, CNRS, and l'Hôpital Universitaire de Strasbourg.