The template effect of a SiF$_6^{2-}$ guest drives the formation of a heteroleptic Fe(II) coordination helicate
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Nuria Capó, Leoni A. Barrios, Joan Cardona, Jordi Ribas-Arriño, Simon J. Teat, Olivier Roubeau and Guillem Aromí*

The anion SiF$_6^{2-}$ exerts a strong template effect, driving the assembly of two different bispiridyl/pyrazolyl ligands into a triple stranded Fe(II) dinuclear heteroleptic helicate, engendering a new class within the large family of coordination helicates.

Supramolecular metallo-helicates of the type [M,$L_m$]$_n$ ($m = 0$ or $+n$) are an important class of coordination assemblies. They arise from the confluence of the geometric requirements of their two essential components, metal ions and multi-topic ligands, through a self-recognition process. The latter can be perceived as the realization of an interactional algorithm following the processing of molecular information. The most common are triple- and double-stranded dinuclear helicates, [M,$L_2$]$^n$ and [M,$L_2$]$^{2n}$, usually arising from tetra- and six-coordinate metals, respectively, together with bis-bidentate ligands. Quadruple stranded helicates, [M,$L_4$]$^{2n}$, are less common and necessitate metals with high coordination numbers.

Very often, the internal cavity within dinuclear helicates is occupied by a guest. The cavity-guest volume relationship is crucial, but other conditions for a good fit are the symmetry or electronic properties of both, the guest and the capsule. In the host, these are mainly controlled by the strands of the helicate. On the other hand, one can find cationic, neutral or anionic guests. This multipartite nature allows introducing molecular functions of different components. Thus, i) the metals may introduce single-molecule magnet (SMM) behavior, spin crossover (SCO) or luminescent properties; ii) the strands may bring properties such as fluorescence or photo-isomerization ability; and iii) the guest may be exploited to introduce optical properties or differential guest-exchange properties. This provides an entry into multifunctional systems, ideally producing synergic effects.

We have discovered here the selective formation of heteroleptic [Fe$_2$($L_1$)($L_1'$)]$^{4+}$ and [Fe$_2$($L_2$)($L_2'$)]$^{4+}$ helicates, driven by the template effect of an SiF$_6^{2-}$ guest, that perfectly accommodates inside the cavity of this specific ligand combination. On the contrary, the guest ClO$_4^-$ does not have the symmetry to facilitate this assembly, thus favoring the exclusive formation of the new homoleptic helicates (ClO$_4^-$@[Fe($L_3'$)]$^{4+}$) helicates, reported here.

Mixing in MeOH $L_1$ and $L_2$ together with Fe(BF$_4$)$_2$ and excess Bu$_4$NPF$_6$ furnishes a homogeneous crystalline phase, following the diffusion of Et$_2$O into the resulting red solution. Single crystal X-ray diffraction (SCXRD) data unveiled the composition of this phase as SiF$_6$@[Fe($L_1$)($L_2$)]($PF_6$)$_2$ (1), see details in the SI). The inclusion of SiF$_6^{2-}$ was unexpected, since silicon was not part of any reagent. It originates from the transfer of BF$_4^-$ fluoride ions to the silica (SiO$_2$) glass of the tubes. In situ F$^{-}$ formation from decomposition of BF$_4^-$ has been previously observed to generate SiF$_6^{2-}$ from glass. Here, bulk generation of SiF$_6^{2-}$ from glass and BF$_4^-$ may be driven by the strong template effect leading to 1. The presence of side products arising from aerial oxidation of Fe(II) to Fe(III) was avoided by performing the reaction in an inert atmosphere. The derivative SiF$_6$@[Fe($L_1$)($L_2$)]($BF_4$)$_2$ (1a) was then prepared under stoichiometric conditions, using the precursors Fe(BF$_4$)$_2$ and (Bu$_4$N)SiF$_6$ according to the reaction depicted in eq. 1, in a polypropylene container. In this case, the inert atmosphere is not necessary presumably, because the ready availability of the guest accelerates the main reaction.

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\text{(Bu}_4\text{N)}\text{SiF}_6 + 2\text{Fe(BF}_4\text{)}_2 + \text{L}_2 & \rightarrow \\
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diketone that was then converted to the corresponding bis-
pyrazolylpyridine with hydrazine (See SI). The procedures to
obtain 1 were carried out using L3 (both, glass or
(Bu₄N)₂SiF₆ as source of silicon), yielding crystals of
SiF₆@[Fe(L1)(L3)](BF₄)₂ (2) and SiF₆@[Fe(L1)(L3)](ClO₄)₂ (2a),
respectively, suitable for SCXRD.
The asymmetric unit of 1 contains one (SiF₆@[Fe(L1)(L3)])⁺²
supramolecular assembly (Fig. 2, S1 and S2) and two PF₆⁻
cations that ensure electroneutrality, in addition of
crystallization solvents. The main component is a triple
stranded helicate made of one L3 and two L2 ligands that
chelate and keep two pseudo-octahedral Fe(II) centers
10.170 Å apart. The ligands’ conformations generate a cavity
perfectly suited to accommodate a SiF₆⁻² guest, fixed by six
strong [F···H–N] hydrogen bonds (Table S3). The combination
of ligands keeps the guest’s center of gravity separated from
the Fe···Fe axis (Fig. S2), as gauged by a Fe–Si–Fe angle of
152.84°. Both enantiomers of the helicate are present in the
racemic unit cell. At 100 K, the average Fe–N bond distances are
2.18 and 2.14 Å for Fe1 and Fe2, respectively, indicating that,
that the first ion lies in the high-spin (HS) state, while a
portion of the Fe2 centres exhibits low spin (LS). The structure
of 1a (Fig. S3) is very similar to that of 1, with BF₄⁻ counter-ions
instead of PF₆⁻ (see all structural details in the SI). This causes
both ions to exhibit distinctly different spin states, with
average Fe–N distances of 2.19 Å (HS) and 2.03 Å (LS), for Fe1
and Fe2, respectively.
In turn, the lattice of 2 contains one (SiF₆@[Fe(L1)(L3)])⁺² unit
(Fig. S4) and two PF₆⁻ anions crystallographically independent
(plus solvents). The supramolecular assembly in 2 is analogous
to that of 1, with a core almost identical; the Fe(II) atoms
separated 10.172 Å and a Fe–Si–Fe angle of 153.04°. The effects of the methyl substituents of L3 lead here to a marked
difference between the magnetic states of both Fe centers.
Thus, at 100K, the Fe–N bond distances average 2.17 and 2.04
Å for Fe1 and Fe2, respectively, demonstrating that they are
fully in the HS and LS state. The structure of 2a (Fig. S5) is very
similar to that of 2, with BF₄⁻ counter-ions instead of PF₆⁻ (see all structural details in the SI). In contrast to the other three
dervatives, both Fe centers of 2a are found clearly to be fully
in the HS state at 100K (average Fe–N distances of 2.20 and
2.18 Å for Fe1 and Fe2, respectively). This difference is also
mirrored by the bulk magnetic properties (see below).

Heteroleptic [M,L,L']ⁿ⁺ metallohelicates have virtually no
precedent. A related example is a double heterostranded system of two [Re(CO)₅]³⁻ centres connected by one bis-
monodentate and one bis-chelating ligand, capitalizing on the
favourable combination of donors to saturate the vacant
coordination sites of Re(I). The system reported here is thus the
first one where the template effect of a guest drives the
assembly of a heteroletic helicate.
The template effect by SiF₆⁻² is corroborated by the fact that no
helicate with this guest can be isolated with neither of both
types of ligands. This exclusive formation of the mixed-ligand
construct is in contrast to that of the homoleptic counterparts,
X@[Fe(L1)(L')](ClO₄)²⁻ (X= Cl, Br)²⁻ and (ClO₄)₂@[Fe,(L')₂]⁺² (L’ = L2; 3;
L3, 4, see below) accommodating a small and a large guest,
respectively. While ClO₄⁻ is not bigger than SiF₆⁻², it does not
have the symmetry to template the formation of the mixed
ligand system. The persistence of the (SiF₆@[Fe(L1)(L')])⁺²
architectures in solution was assessed by ²⁹F NMR on
compound 2a. The spectrum in MeCN (S6) furnishes signals for
BF₄⁻ and SiF₆⁻² that approximately integrate for the expected
2:1 concentration ratio (4:3 ratio in F) and are attributed to the
free ions and guest species, respectively. Indeed, the latter
signal shows a much larger broadening than the other, caused
by the proximity of the paramagnetic Fe(II) centers. A small
signal with intensity one order of magnitude smaller is
attributed to an impurity of free SiF₆⁻². This was corroborated
by the subsequent addition of SiF₆⁻² (in form of its Bu₄N⁺ salt)
to the tube, increasing the intensity of this signal without
modifying the intensity ratio of the other two peaks (Fig. S6).
An intriguing observation is the drive for SiF₆⁻² encapsulation
in contrast to PF₆⁻, which was never found in the cavity. This
differential selectivity was quantified through DFT calculations.
The calculated energy associated to the process in eq. 2, after
group optimization and including the influence of the solvent
(MeOH and MeCN) was −38 kcalmol⁻¹ for both, L’ = L2 and L3 (see SI for details).

\[
\text{PF}_6^{-2} + \text{SiF}_6^{-2} \rightarrow \text{SiF}_6^{-2} + \text{PF}_6^{-2}
\]

(2) The remarkable energy advantage of encapsulated SiF₆⁻² wrt PF₆⁻ is attributed to much more efficient [E···F···H–N] hydrogen bonds for E=Si than for E=P and/or to the much higher affinity
for a guest with two negative charges rather than only one, by
a host with charge +4.
The reactions of Fe(ClO₄)₂ with L2 or L3 in MeOH produce,
respectively, the complex salts ClO₄@[Fe(L2)](ClO₄)₁ (3) and
ClO₄@[Fe(L3)](ClO₄)₁ (ClO₄)₄, made by homoleptic helicates.
The asymmetric unit of 3, obtained from recrystallization in
MeCN, includes the host-guest assembly (ClO₄@[Fe(L2)]⁺²)²⁻,
three ClO₄⁻ anions, four defined solvent molecules and
additional diffuse solvent (details in the SI). The unit
(ClO₄@[Fe(L2)]⁺² (Fig. 3 and S7) is a homoleptic helicate
made of three bis-pyrazolylpyridine L2 ligands that chelate two
Fe(II) centers (separated by 11.018 Å) encapsulating a ClO₄⁻
guest. The geometrical mismatch between the guest and the
host breaks the idealized binary symmetry of the assembly (eg.
the Fe···Cl separations are 6.075 and 4.983 Å) yielding an array

Figure 2. Representation of the supramolecular assembly SiF₆@[Fe(L1)(L2)]⁺² of 1.
Large yellow balls are Fe(II), small yellow balls are H from N–H groups (rest of hydrogen
not shown), red balls are atoms from L1, green balls are atoms from L2, central moiety in
stick style is SiF₆⁻², hydrogen bonds are shown as black, dashed lines.
of [Cl−O···H−N] hydrogen bonds of diverse strengths (Fig. 3 and S7, caption, Table S3).

Figure 3. Representation of the supramolecular assembly ClO_4@[Fe_2(L3)]_2+ of 3. Large red balls are Fe(II), small yellow balls are H from N−H groups (rest of hydrogen not shown), grey balls are C, central moiety in stick style is ClO_4−, hydrogen bonds are shown as black dashed lines.

The average Fe−N bond distances of the pseudo-octahedral Fe(II) centers are 1.970 and 1.972 Å for Fe1 and Fe2, respectively, showing that both centers lie in the LS state (at 100 K, temperature of the data collection), in sharp contrast with the heteroleptic counterparts.

Compound 4 is the analogue of 3 with ligand L3. The lattice contains one (ClO_4@[Fe_2(L3)])_2+ unit (Fig. S8), three ClO_4− anions, and solvent molecules. The main structural parameters of 3 are reproduced in 4 (see SI) with Fe−Fe and Fe−Cl separations of 11.531, 6.698 (Fe1) and 4.839 (Fe2) Å, respectively, and average Fe−N distances of x.xxx (Fe1) and x.xxx (Fe2), thus, also showing LS centers.

The diversity in solid-state magnetic properties of compounds 1 to 4 inferred by their structural parameters was corroborated through variable temperature magnetic susceptibility measurements, carried out under a constant magnetic field of 0.5 T. The χT vs T plots (Fig. 4) show that the Fe(II) centers in all cases are spin active.

Figure 4. Plots of χ_T vs T for compounds 1, 1a, 2, 2a, 3 and 4 (see legend). The measurements were collected on freshly prepared crystals that never reached temperatures above 300 K.

Compounds 1, 1a, 2 and 2a exhibit a sharp increase of χT with T at very low temperature, caused by HS Fe(II) centers not following the Curie Law in this range. This sharp increase attenuates rapidly in the 10 to 20 K range to values of 3 to 3.5 cm^3 K mol^−1 for 1, 1a and 2, and around 6 cm^3 K mol^−1 for 2a. This shows that the first group of compounds exhibit one Fe in the HS and the other in LS, whereas the Fe ions of 2a are all HS (as suggested by the SCXRD data at 100 K, see above). The mixed-spin compounds exhibit a pseudo plateau suggesting the persistence of approximately 50% of Fe centers in either the HS or the LS state up to around 70 K. Further warming causes a gradual increase of the χT vs T curve indicating a broad conversion to the HS state of the ca. one half of the metal centers that were in the LS state. Compound 2a shows upon warming only a slight and broad increase of χT up to 7.6 cm^3 K mol^−1 at 300K, suggesting that a very small fraction of Fe(II) being in the LS state at low temperatures experience a very gradual transition to the HS state. Compounds 3 and 4 are almost diamagnetic over most of the temperature range examined, therefore they contain only LS Fe(II) centers. In both cases, the gradual raise of χT vs T occurring especially beyond 250 K, denotes a slow conversion to the HS state of these centers that is far from completion at 300 K (approximately 40 to 50%). All these data correspond to samples never been warmed beyond 300 K. Below this temperature, the magnetic response remains fully reversible with temperature. Beyond room temperature the data were not analyzed since they exhibit irreversible changes that are caused most likely by the desorption of lattice solvent molecules, leading expectedly to changes to the SCO behavior.33

In summary, this report demonstrates that within the cavity of coordination metallohelicates, the presence of H-bonding groups can be exploited to drive the quantitative formation of heteroleptic assemblies via a template effect. This can be exploited to introduce combinations of functions or properties within the assembly thanks to the ability of incorporating different ligands into the architecture. To generalize this methodology, the preparation of analogues of different divalent metals is now under investigation.

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Conflicts of interest
There are no conflicts to declare.

Notes and references
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