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Anion-Dependent Spin Crossover and Coordination Assembly Based on [Fe(tpa)]²⁺ [tpa = tris(2-pyridylmethyl)amine] and [N(CN)₂]⁻: Square, Zigzag, Dimeric, and [4+1]-Cocrystallized Complexes

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Rong-Jia Wei,^[a] Jun Tao,^{*[a]} Rong-Bin Huang,^[a] and Lan-Sun Zheng^[a]

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A series of Fe^{II} complexes based on $[Fe(tpa)]^{2+}$ building units and $[N(CN)_2]^-$ bridging ligands with different anions for charge balance has been prepared and characterized. They have a general formula $[Fe(tpa)\{N(CN)_2\}]_x$ ·Y·Z, where x = 4 (1^{4+}) , $Y = 4ClO_4^-$, and $Z = 2H_2O$ for $1 \cdot (ClO_4)_4(H_2O)_2$; x = n (2^{n+}) , Z = 0, and $Y = nClO_4^-$, nPF_6^- , $nAsF_6^-$, and $nBPh_4^-$ for $2 \cdot (ClO_4)_n$, $2 \cdot (PF_6)_n$, $2 \cdot (AsF_6)_n$, and $2 \cdot (BPh_4)_n$, respectively; x = 2 (3^{2+}) , Z = 0, and $Y = 2BPh_4^-$ for $3 \cdot (BPh_4)_2$; x = 4 (4^{4+}) , $Y = 3SbF_6^- + [N(CN)_2]^-$, and $Z = [Fe(tpa)\{N(CN)_2\}_2]$ $(5) + 4H_2O$ for (4+5). Single-crystal X-ray diffraction studies reveal that these complexes show various structures that are affected by different counteranions, i.e., square $1 \cdot (ClO_4)_4(H_2O)_2$, zigzag polymers $[2 \cdot (ClO_4)_n, 2 \cdot (PF_6)_n, 2 \cdot (AsF_6)_n, and 2 \cdot (BPh_4)_n]$, dimeric $3 \cdot (BPh_4)_2$, and [4+1]-cocrystallized (4+5). Magnetic

Introduction

Spin-crossover (SCO) complexes are one of the most spectacular examples of switchable materials.^[1] By tuning ligand-field strength, the electronic configurations of metal ions in SCO complexes are interconvertible between the high-spin (HS) and low-spin (LS) states in response to heat, pressure fluctuation, and/or light irradiation.^[2] The dramatic changes in physical properties such as color and magnetic moment in association with spin crossover suggest that SCO materials are potential candidates for futuristic applications in memory and electronic display devices.^[3]

Whereas mononuclear Fe^{II} complexes were focused on for a long time in early SCO systems,^[4] the design and synthesis of polynuclear and polymeric SCO Fe^{II} complexes have been the subject of much recent research.^[5] The fundamental reason for this change is based on the expectation that, in polynuclear and polymeric SCO Fe^{II} complexes, bridging the metal ions could significantly enhance the studies show that the square complex $1 \cdot (\text{ClO}_4)_4(\text{H}_2\text{O})_2$ undergoes a two-step complete spin crossover, whereas the dimer $3 \cdot (\text{BPh}_4)_2$ is high-spin in the whole temperature range, and all zigzag polymer $2 \cdot \text{anions}$ show spin-crossover (SCO) behavior, the transition temperature ($T_{1/2}$) of which increases with increasing anion size. Interestingly, complex (4+5) displays a gradual two-step spin crossover, which is different from that of $1 \cdot (\text{ClO}_4)_4(\text{H}_2\text{O})_2$ and originates from the cocrystallized spin-crossover tetranuclear and monomeric species. Detailed studies on the crystal structures and magnetic properties have unveiled a remarkable anion-dependent formation of different structures and SCO behavior of these complexes.

communication between SCO centers in the crystal lattice, which plays an important role in achieving bistable properties.^[6] For example, some dinuclear,^[7] trinuclear,^[8] and tetranuclear^[9] as well as a number of 1D, 2D, and 3D polymeric^[10] SCO Fe^{II} complexes have been synthesized.

On the other hand, it is well known that secondary coordination sphere species such as solvent molecules^[11] and noncoordinated counterions^[12] in the crystal lattice can also significantly influence SCO behavior by communicating with SCO entities through hydrogen bonds and/or altering the lattice phonon distribution that affects crystal packing modes and intermolecular interactions.^[3b]

As part of our continuous interest in SCO systems,^[13] we have recently investigated a very interesting complex, [Fe(tpa)(NCS)₂], which shows successive polymorphic transformations from polymorph II to IV that are accompanied with distinct changes in SCO behavior;^[13d] this complex also shows a solvent-vapor-induced single-crystal to single-crystal (SCSC) transformation from polymorph I to its solvated product,^[13c] and more interestingly, this complex can recrystallize in various solvents and forms two solvated product types, yellow [Fe(tpa)(NCS)₂]·X (Fe/X = 1:1, X = *n*PrOH, *i*PrOH, CH₂Cl₂, CHCl₃, and MeCN) and red [Fe(tpa)(NCS)₂]₂·Y (Fe/Y = 2:1; Y = MeOH and EtOH), and between them solvent-vapor-induced reversible and irreversible guest molecule exchanges take place in the solid state followed by dramatic transformations in color, struc-



[[]a] State Key Laboratory of Physical Chemistry of Solid Surfaces and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, P. R. China Fax: +86-592-2188138 E-mail: taojun@xmu.edu.cn

Homepage: http://chem.xmu.edu.cn/english/faculty/professor/ chemistry/tao_j.html

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ture and SCO behavior.^[13e] Inspired by these results, we thought that the $[Fe(tpa)]^{2+}$ unit with two accessible coordination sites would be a good SCO precursor as it can be linked by a linear bridging ligand, e.g. dicyanamide group,^[14] to generate square^[9] or 1D-zigzag-chain^[15] SCO complexes. A new square SCO Fe^{II}₄ complex, [Fe(tpa)-{N(CN)₂}]₄·(BF₄)₄(H₂O)₂ [1·(BF₄)₄(H₂O)₂], has thus been reported, which is constructed with [Fe(tpa)]²⁺ and dicyanamide.^[13f] This complex shows both thermally and light-induced two-step SCO and undergoes a reversible SCSC transformation between 1·(BF₄)₄(H₂O)₂ and its solvent-free form, 1·(BF₄)₄, induced by water desorption and resorption.

As we already knew that guest molecules remarkably affect the SCO properties of the [Fe(tpa)(NCS)₂] system^[13e] and we have successfully synthesized a square SCO $[Fe(tpa){N(CN)_2}]_4 \cdot (BF_4)_4 (H_2O)_2$ complex,^[13f] we anticipated that complexes constructed from [Fe(tpa)]²⁺ and dicyanamide with counteranions other than BF₄⁻ could also be obtained and their SCO behavior could be affected by various counteranions. It has been revealed that variation of counteranions can shift reaction equilibria and result in products with different structures and physicochemical properties,^[16] thus it is possible to attain specific products by changing counteranions. In principle, the assembly representing the lowest free-energy state is preferred for a given set of conditions.^[17] In the past few years, counteranions have been successfully employed to control the formation of specific molecules and assemblies.^[18] For example, Dunbar and co-workers^[19] recently reported an anion-directed assembly of Ni^{II} and Zn^{II} metallacyclophanes with 3,6bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) as a bridging ligand; tetrahedral BF_4^- and ClO_4^- ions direct the formation of molecular squares, $[{M_4(bptz)_4(CH_3CN)_8}X][X]_7$ (M = Zn^{II} , Ni^{II}; X = BF₄, ClO₄), whereas octahedral SbF₆ induces the formation of pentagonal [{Ni₅(bptz)₅- $(CH_3CN)_{10}$ SbF₆ [SbF₆]₉.

In order to further understand the influences of counteranions on the assembly and SCO properties of the [Fe(tpa)]²⁺/dicyanamide system, we have recently synthesized a series of complexes based on the building units $[Fe(tpa)]^{2+}$ and $[N(CN)_2]^-$ with the general formula $[Fe(tpa){N(CN)_2}]_x \cdot Y \cdot Z$, where x = 4 (1⁴⁺), $Y = 4ClO_4^{-}$, and Z = 2H₂O for 1·(ClO₄)₄(H₂O)₂; x = n (2^{*n*+}), Z = 0, and $Y = nClO_4^-$, nPF_6^- , $nAsF_6^-$, and $nBPh_4^-$ for $2 \cdot (ClO_4)_n$, $2 \cdot (PF_6)_n$, $2 \cdot (AsF_6)_n$, and $2 \cdot (BPh_4)_n$, respectively; $x = 2 (3^{2+})$, Z = 0, and $Y = 2BPh_4^-$ for $3 \cdot (BPh_4)_2$; $x = 4 \ (4^{4+})$, Y = $3SbF_6^- + \{N(CN)_2\}^-$, and $Z = [Fe(tpa)\{N(CN)_2\}_2]$ (5) + $4H_2O$ for (4+5). These complexes display various structural geometries (Figure 1) and different SCO behaviors, i.e., square complex $1 \cdot (ClO_4)_4 (H_2O)_2$ shows a well-defined twostep SCO, 1D zigzag complexes $2 \cdot (ClO_4)_n$, $2 \cdot (PF_6)_n$, and $2 \cdot (AsF_6)_n$ display a one-step incomplete SCO, and $2 \cdot (BPh_4)_n$ undergoes almost complete SCO, dimeric complex 3. (BPh₄)₂ remains in high-spin state in the whole temperature range, and the [4+1]-cocrystallized complex (4+5)shows a gradual two-step SCO originating from the tetranuclear and mononuclear species.



Figure 1. Schematic representation of the anion-dependent assembly based on $[Fe(tpa)]^{2+}$ and $[N(CN)_2]^-$ building units.

Results and Discussion

Synthesis

All complexes based on $[Fe(tpa)]^{2+}$ and $[N(CN)_2]^-$ building units were prepared by the reaction of FeSO₄, NaN(CN)₂, tpa, and the sodium or potassium salt of the corresponding anion in equimolar ratio. The 1D zigzag chainlike complexes $2 \cdot Y_n$ (Y = ClO₄⁻, PF₆⁻, or AsF₆⁻) were easily obtained as yellow crystals in a water/ethanol (5:1) solution, whereas red crystals of $2 \cdot (BPh_4)_n$ and yellow crystals of dimeric complex 3-(BPh₄)₂ grew simultaneously in a test tube and were separated manually under a microscope. The square complex $1 \cdot (ClO_4)_4(H_2O)_2$ was synthesized in the same way as that of chainlike complex $2 \cdot (ClO_4)_n$; except a single-crystal of 1·(BF₄)₄(H₂O)₂^[13f] was used as a seed, around which red crystals of $1 \cdot (ClO_4)_4(H_2O)_2$ crystallized in several hours, and the crystal seed of $1 \cdot (BF_4)_4 (H_2O)_2$ was then removed manually. Crystals of $1 \cdot (ClO_4)_4(H_2O)_2$ and $2 \cdot (ClO_4)_n$ could also be obtained simultaneously at a higher concentration [0.5 mmol of each component in 6 mL water/ ethanol (5:1) solution] without the addition of a seed of $1 \cdot (BF_4)_4 (H_2O)_2$. Under an optical microscope, the two complexes with different color could be easily separated by hand. The complex (4+5) was obtained through a transformation from the kinetically favored product to the thermodynamically stable one through an in situ recrystallization process. An aqueous solution of FeSO₄, NaN(CN)₂, and KSbF₆ mixed with an ethanol solution of tpa without stirring gave rise to a turbid red solution with a large amount of brown precipitate, which generally dissolved and red crystals of (4+5) simultaneously crystallized. Elemental analysis showed that the brown precipitate had similar C, N, and H percentages to those of crystalline (4+5), and magnetic measurements revealed that it underwent an incomplete SCO; powder XRD (PXRD) indicated that it was an amorphous solid (Supporting Information). Attempts to synthesize complexes under different conditions, such as replacing ethanol with methanol and changing the ratios of Fe/tpa/dicyanamide/anion, were performed. Little influence was observed on the formation of chains vs. dimers vs. squares.

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Crystal Structures

Single-crystal X-ray diffraction studies were carried out at various temperatures in order to correlate the structures with the different SCO phases identified by magnetic measurements.

Complex $1 \cdot (ClO_4)_4(H_2O)_2$ is isostructural to complex $1 \cdot (BF_4)_4(H_2O)_2^{[13f]}$ and crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit is composed of half a cationic 1^{4+} square (two crystallographically distinct Fe1 and Fe2 ions), one water molecule, and two ClO_4^- counteranions. The $[Fe(tpa)]^{2+}$ units are bridged by $\mu_{1,5^-}$ N(CN)₂⁻ groups in a square-shaped arrangement and adopt a *trans*-[Fe1–Fe2–Fe1–Fe2] geometric configuration, as is shown in Figure 2.



Figure 2. ORTEP drawing of the structure of 1^{4+} in $1 \cdot (ClO_4)_{4-}$ (H₂O)₂ with 30% thermal ellipsoid probability. Counteranions, water molecules, and hydrogen atoms are omitted for clarity. Symmetry operation: -x + 1, -y + 2, -z.

The crystal data of 1·(ClO₄)₄(H₂O)₂ were collected at 150, 250, and 350 K. Selected bond lengths and parameters showing salient features of the structure are summarized in Table 1. At 150 K, the Fe-N bond lengths range from 1.938 to 1.987 Å with average values of 1.971 and 1.967 Å for Fe1 and Fe2, respectively, which indicate that all Fe^{II} ions in the cationic 1^{4+} square are in an LS state at 150 K. Upon warming to 250 K, the average Fe1-N bond length shows a sizeable increase to 2.116 Å, whereas that of the Fe2-N bonds varies slightly from 1.967 to 1.992 Å, implying that the crystal is in an intermediate configuration, $[Fe1_{HS}]$ $Fe2_{LS}$ - $Fe1_{HS}$ - $Fe2_{LS}$], at this temperature. When further heated to 350 K, the crystal of $1 \cdot (ClO_4)_4 (H_2O)_2$ becomes the dehydrated form, $1 \cdot (ClO_4)_4$, by an SCSC transformation process. The average Fe-N bond lengths are 2.151 and 2.140 Å for Fe1 and Fe2, respectively, indicating that all Fe^{II} ions in the cationic 1^{4+} square at this temperature are in an HS configuration. A two-step $(Fe^{II}_{LS})_4 \leftrightarrow [Fe1_{HS}]_{+}$ $Fe2_{LS}-Fe1_{HS}-Fe2_{LS}] \leftrightarrow (Fe^{II}_{HS})_4$ spin crossover is thus suggested in this temperature range.

Table 1. Selected bond lengths and parameters of $1 \cdot (ClO_4)_4(H_2O)_2$ and $1 \cdot (ClO_4)_4$.

	1·(ClO ₄) ₄ (H ₂	$1 \cdot (ClO_4)_4$	
T [K]	150	250	350
$< d_{\rm Fe1-N} > [a] [Å] / \Sigma^{[b]} [°]$	1.971/59.53	2.116/88.1	2.151/95.8
$< d_{\rm Fe2-N} >^{[a]} [Å] / \Sigma^{[b]} [°]$	1.967/55.40	1.992/55.9	2.14/91.7
$C-H\cdots\pi$ interactions ^[c] [Å]	3.687(2)	3.640(2)	3.951(4)
	3.544(2)	3.599(2)	3.826(3)
C–H···O interactions ^[d] [Å]	3.311(2)	3.385(3)	3.398(4)
	3.152(4)	3.324(3)	3.321(6)
O–H····O interactions ^[e] [Å]	2.862(3)	2.560(1)	_
	3.084(3)	3.139(2)	_

[a] $\langle d_{\text{Fe-N}} \rangle$ is the average Fe–N bond length. [b] The distortion parameter Σ is defined as the sum of the absolute values of the deviations of the 12 *cis* N–Fe–N angles from 90°.^[20] [c] Distance between tpa carbon atom to the centroid of the pyridyl group of adjacent tpa. [d] Distance between ClO₄⁻ ion and pyridyl carbon atom. [e] Distance between ClO₄⁻ ion and water molecule.

The 3D supramolecular structure of complex $1 \cdot (ClO_4)_4$ - $(H_2O)_2$ can be viewed as 2D layers containing cationic 1^{4+} squares, ClO_4^- ions, and water molecules that stack along the *b* axis (Figure 3). Moderate C–H··· π interactions are also found between the pyridine rings of adjacent 1^{4+} squares (Table 1). The ClO_4^- ions (denoted as Cl1 and Cl2) and water molecules occupy the voids formed between the cationic 1^{4+} squares. The ClO₄⁻ ions contact with the 1^{4+} squares through C-H···O hydrogen bonds with C···O separations of 3.311(2) and 3.152(4) Å at 150 K and 3.385(3) and 3.324(3) Å at 250 K, for Cl1 and Cl2, respectively; the closest O···O distances of the O-H···O hydrogen bonds between the ClO₄⁻ ions and water molecules vary from 2.862(3) to 2.560(1) Å and 3.084(3) to 3.139(2) Å upon temperature increases from 150 to 250 K, for Cl1 and Cl2, respectively. At 350 K, the crystal packing of dehydrated complex $1 \cdot (BF_4)_4$ is similar to that of $1 \cdot (BF_4)_4 (H_2O)_2$.



Figure 3. Packing diagram of $1 \cdot (ClO_4)_4(H_2O)_2$ viewed along the *b* axis. ClO_4^- counteranions are shown as tetrahedra, and water molecules are shown as spheres. Hydrogen atoms are omitted for clarity.

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Complex (4+5) crystallizes in the monoclinic space group C2/m, and the asymmetric unit contains half a cationic 4^{4+} square (crystallographically distinct Fe1 and Fe2 ions), half a neutral complex 5 (denoted as Fe3 site), three half SbF_6 anions and half an [N(CN)₂]⁻ free anion. In addition, there are four water molecules per formula unit, as indicated in the difference density map and elemental analysis (Experimental Section); however, these are severely disordered and are therefore removed when the structure is refined by using the SQUEEZE^[21] function. The molecular structures of the cationic 4^{4+} square and neutral complex 5 are shown in Figure 4. The $[Fe(tpa)]^{2+}$ units of 4^{4+} are interlinked by $\mu_{1,5}$ -N(CN)₂⁻ groups to form a square structure that is similar to that of 14+ but adopts a cis-[Fe1-Fe1-Fe2-Fe2] geometric configuration (Figure 4a). In the neutral mononuclear complex 5, the $[Fe(tpa)]^{2+}$ unit is coordinated by two η^1 -N(CN)₂⁻ anions (Figure 4b).

Based on the average Fe-N distances determined from variable-temperature X-ray diffraction studies (Table 2), we can conclude that the Fe1 and Fe2 ions in the cationic 4^{4+} square have already undergone SCO at 270 K, whereas the Fe3 ion in the mononuclear molecule 5 remains in the HS state until 230 K and, therefore, complex (4+5) is in the $\{[IP]_4 + HS\}$ (IP = intermediate phase between HS and LS states, which indicates a continuous change of the bond length and an averaged population of HS and LS states in each SCO metal ion) state in this temperature range. Upon cooling to 130 K, each Fe^{II} ion in the cationic 4^{4+} square has converted to an LS configuration, whereas the Fe3 ion in the mononuclear molecule 5 is in the IP state (Table 2), thus the mononuclear complex 5 undergoes an incomplete SCO below 230 K. At higher temperatures, e.g. > 300 K, complex (4+5) would properly reach the {[HS]₄+HS} state and would show an $\{[HS]_4 + HS\} \leftrightarrow \{[IP]_4 + HS\} \leftrightarrow \{[LS]_4\}$ + IP} two-step SCO, which originates from the SCO-active nonequivalent units in the cocrystallized structure.

It should be mentioned that, from the structural point of view, the cationic 4^{4+} square in complex (4+5) displays an

Table 2. Selected bond lengths and parameters of complex (4+5).

T [K]	270	230	130
$< d_{\text{Fel}-N} > [Å] / \Sigma [°]$	2.077/69.2	2.032/59.5	1.974/45
$\langle d_{\rm Fe2-N} \rangle$ [Å]/ Σ [°]	2.083/73.8	2.037/61.3	1.969/46.5
$\langle d_{\rm Fe3-N} \rangle [\rm Å] / \Sigma [^{\circ}]$	2.161/85.8	2.157/80.7	2.026/57.2
Anion π interaction ^[a] [Å]	3.273(1)	3.208(2)	3.105(1)
C–H··· π interaction ^[b] [Å]	3.444(3)	3.375(2)	3.299(4)
C–H··· π interactions ^[c] [Å]	3.525(2)	3.558(4)	3.495(1)
	3.757(2)	3.754(5)	3.701(2)
C–H····π interactions ^[d] [Å]	3.571(1)	3.525(1)	3.460(1)
	3.985(1)	3.929(1)	3.837(1)

[a] Distance between the central N atom of $[N(CN)_2]^-$ of 4^{4+} and the centroid of the pyridyl group of **5**. [b] Distance between the pyridyl carbon atom of **5** and the pyridyl group centroid of 4^{4+} . [c] Distance between the pyridyl carbon atom and the pyridyl centroid of adjacent 4^{4+} squares in the *ab* plane. [d] Distance between the pyridyl carbon atom and the pyridyl carbon atom and the pyridyl carbon the pyridyl centroid of adjacent 4^{4+} squares in the *ab* plane. [d] Distance between the pyridyl carbon atom and the pyridyl centroid of adjacent 4^{4+} squares in the *ac* plane.

[HS]₄-to-[LS]₄ one-step SCO that lacks an intermediate [HS]₂[LS]₂ state, which is a typical characteristic of its congeners $1 \cdot (BF_4)_4(H_2O)_2^{[13f]}$ and $1 \cdot (ClO_4)_4(H_2O)_2$. Because the two Fe^{II} ions (Fe1 and Fe2) in the cationic 4^{4+} square undergo SCO almost synchronously, as revealed by changes in the Fe–N bond lengths of Fe1 and Fe2, the desired multiple SCO steps of the cationic 4^{4+} square are not resolved crystallographically. Instead, in the cationic 1^{4+} square the two different Fe^{II} ions show crystallographically different changes in the Fe–N bond lengths, thus showing two successive SCO processes.

As shown in Figure 5, the cationic 4^{4+} square and the neutral molecule 5 interact with each other through a strong anion… π interaction^[22] [3.105(1) Å at 130 K, Table 2] between the central N atom of the [N(CN)₂]⁻ group of 4^{4+} and one of the pyridyl groups of molecule 5, and through strong C–H… π interactions [3.299(4) Å at 130 K] between the pyridyl group of molecule 5 and the pyridyl group of the cationic 4^{4+} square. Meanwhile, the cationic 4^{4+} squares form intersquare π … π interactions [3.495(1)]



Figure 4. ORTEP drawings (30% thermal ellipsoid probability) of the structure of 4^{4+} (a) and the neutral molecule 5 (b) in complex (4+5). Counteranions, water molecules, and hydrogen atoms are omitted for clarity. Symmetry operation: x, -y, z.

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and 3.701(1) Å at 130 K] to give chainlike stacks along the *c* axis. The resulting { $4^{4+} + 5$ } units are parallel stacked to form 2D layers in the *bc* plane (Figure 5a) that are further antiparallel stacked along the *a* axis (ABAB mode) to form a 3D structure (Figure 5b), both through $\pi \cdots \pi$ and C–H $\cdots \pi$ interactions between the cationic 4^{4+} squares; the voids in the 3D supramolecular structure are occupied by SbF₆⁻ ions, free [N(CN)₂]⁻ ligands, and disordered water molecules.



Figure 5. Perspective view of the anion··· π and C–H··· π interactions between 4⁴⁺ and 5 and C–H··· π interactions between 4⁴⁺ squares in the *bc* plane (a) and the packing diagram of cocrystallized complex (4+5) (b). SbF₆⁻ counteranions are shown as octahedra, hydrogen atoms are omitted for clarity.

Complexes $2 \cdot (ClO_4)_n$, $2 \cdot (PF_6)_n$, and $2 \cdot (AsF_6)_n$ crystallize in the monoclinic space group $P2_1/c$ with asymmetric units at 270 K containing one $[Fe(tpa)]^{2+}$ unit, one $[N(CN)_2]^$ group, and one associated counteranion. All Fe^{II} ions are in an HS state at 270 K with average Fe–N bond lengths (Tables 3 and 4) of 2.162, 2.165, and 2.161 Å for $2 \cdot (ClO_4)_n$, $2 \cdot (PF_6)_n$, and $2 \cdot (AsF_6)_n$, respectively. The adjacent Fe^{II} ions are bridged by $\mu_{1,5}$ -N(CN)₂⁻ groups to form 1D zigzag chains along the *b* axis, as shown in Figure 6a–c. The zigzag chains interact with each other through strong anion… π interactions [3.306(3), 3.596(4), and 3.871(5) Å at 270 K for $2 \cdot (ClO_4)_n$, $2 \cdot (PF_6)_n$, and $2 \cdot (AsF_6)_n$, respectively, Tables 3 and 4] between the [N(CN)₂]⁻ groups and the pyridyl groups of adjacent zigzag chains, and through strong C– H···π interactions [3.621(4), 3.678(5), and 3.613(9) Å for $2 \cdot (\text{ClO}_4)_n$, $2 \cdot (\text{PF}_6)_n$, and $2 \cdot (\text{AsF}_6)_n$ at 270 K, respectively] between the pyridyl groups of adjacent chains.

Table 3. Selected bond lengths and parameters of complexes $2 \cdot (ClO_4)_n$ and $2 \cdot (PF_6)_n$.

	2 ·(ClO ₄),	7	$2 \cdot (\mathrm{PF}_6)_n$		
T [K]	270	110	270	110	
$\langle d_{\text{Fel}-N} \rangle$ [Å]	2.162	2.067	2.165	2.066	
Σ [°]	92.81	67.7	93.68	73.51	
Anion••• π interactions ^[a] [Å]	3.306(3)	3.306(6)	3.596(4)	3.624(2)	
C–H··· π interactions ^[b] [Å]	3.621(4)	3.586(9)	3.678(5)	3.612(3)	

[a] Distance between the central N atom of $[N(CN)_2]^-$ and the pyridyl centroid of adjacent chain. [b] Distance between two pyridyl groups of adjacent chains.

Table 4. Selected bond lengths and parameters of $2 \cdot (AsF_6)_n$ and $2 \cdot (AsF_6)_n^{LT}$.

	$2 \cdot (AsF_6)_n$	$2 \cdot (AsF_6)_n^{LT}$	$2 \cdot (AsF_6)_n^{LT}$		
	270	173	110		
$\langle d_{\text{Fel-N}} \rangle [\text{A}] / \Sigma [^{\circ}]$ $\langle d_{\text{Fel-N}} \rangle [\text{Å}] / \Sigma [^{\circ}]$	2.161/94.3	2.166/98.7 2.138/78	2.1/0/101.96 1.982/48.06		
Anion••• π interactions ^[a] [Å]	3.871(5)	3.973(7) 3.724(2)	3.967(6) 3.717(1)		
C–H··· π interactions ^[b] [Å]	3.613(9)	3.689(7) 3.665(9)	3.739(6) 3.575(6)		

[[]a] Distance between the N atom of $[N(CN)_2]^-$ and the pyridyl centroid. [b] Distance between the pyridyl C atom and the pyridyl centroid in the adjacent chain.

For $2 \cdot (ClO_4)_n$ and $2 \cdot (PF_6)_n$, the unit-cell volumes slightly shrink, and the space groups remain unchanged upon temperature decrease to 110 K, and at this temperature the average Fe-N bond lengths are 2.067 and 2.066 Å for $2 \cdot (ClO_4)_n$ and $2 \cdot (PF_6)_n$, respectively, indicating that the two complexes may undergo incomplete SCO. For $2 \cdot (AsF_6)_n$, the space group also remains unchanged but with an elongation of the *a* axis (25%) and *c* axis (50%) and doubling of the cell volume upon temperature decrease; the asymmetric unit of $2(AsF_6)_n$ at 173 K [denoted as $2 \cdot (AsF_6)_n^{LT}$] contains two crystallographically different Fe^{II} centers (Fe1 and Fe2 sites) that are alternatively linked by $[N(CN)_2]^-$ spacers to form 1D zigzag chains running along the b axis (Figure 6d). Based on the Fe-N distances (Table 4) determined at variable temperature, we can conclude that the Fe2 center in the zigzag chain has already undergone SCO at 173 K and reaches the LS state at 110 K, whereas the Fe1 center remains in the HS state at 110 K. The crystal packing of **2**·(AsF₆)_n^{LT} is similar to that of **2**·(AsF₆)_n at 270 K, except for some changes in intermolecular interactions upon SCO.

The crystal structure of complex $2 \cdot (BPh_4)_n$ was determined at 295 and 150 K. Selected bond lengths and parameters showing the salient features of structure are summarized in Table 5. Compound $2 \cdot (BPh_4)_n$ crystallizes in the space group $P2_1/c$ in all of the temperature range and shows no phase transition as expected for gradual SCO behavior (see Magnetic Properties). The structure contains two crystallographically different chains, denoted as the $\{Fe1\}_n$ and $\{Fe2\}_n$ chains, which both run along the *b* axis and stack alternately along the *a* axis (Figure 6e). The chains interact



Figure 6. Packing diagrams of $2 \cdot (ClO_4)_n$ (a), $2 \cdot (PF_6)_n$ (b), $2 \cdot (AsF_6)_n$ (c), $2 \cdot (AsF_6)_n$ ^{LT} (d), $2 \cdot (BPh_4)_n$ (e), and $3 \cdot (BPh_4)_2$ (f). Counteranions are shown as polyhedra. For (d) and (e), Fel atoms are shown as black spheres, and Fe2 atoms are shown as gray spheres. Hydrogen atoms are omitted for clarity.

with each other only through C-H··· π interactions (Table 5). At 150 K, the average Fe-N bond lengths are 1.965 and 1.975 Å for Fe1 and Fe2, respectively, indicating that the two Fe^{II} centers are in the LS state. At 298 K, the corresponding values for the Fe1 and Fe2 centers increase to 2.055 and 2.102 Å, respectively, which shows that the Fe^{II} ions in the two independent zigzag chains have partly undergone SCO (incomplete SCO below room temperature). Actually, $2(BPh_4)_n$ would propably reach the [Fe1_{HS} + $Fe2_{HS}$ state at higher temperature (> 380 K, see Magnetic Properties).

Table 5. Selected bond lengths and parameters for $2 \cdot (BPh_4)_n$ and **3**·(BPh₄)₂.

	$2 \cdot (BPh_4)_n$		$3 \cdot (BPh_4)_2$
T [K]	295	150	200
$\langle d_{\text{Fel}-N} \rangle [\text{Å}] / \Sigma [^{\circ}]$	2.055/63.68	1.965/37.43	2.166/111.92
$\langle d_{\text{Fe2-N}} \rangle [\text{Å}] \Sigma [^{\circ}]$	2.102/71.61	1.975/42.18	_
C–H···π interactions ^[a] [Å]	3.742(7)	3.675(4)	_
	3.540(8)	3.493(5)	_
	3.967(7)	3.902(2)	_
C-H···anion interaction ^[b] [Å]	-	-	3.312(7)

[a] Distance between pyridyl C atom and the pyridyl group centroid of adjacent chain. [b] Distance between the pyridyl group C atom and the N atom of $[N(CN)_2]^-$ of adjacent dimer.

Complex $3 \cdot (BPh_4)_2$ crystallizes in the monocline space group $P2_1/c$, and the asymmetric unit contains half of the dimer and one BPh4- anion, and the molecular dimer, $[Fe(tpa){N(CN)_2}]_2^{2+}$ (3²⁺), is located on a crystallographic inversion center. In the solid state, the packing of $3 \cdot (BPh_4)_2$ can be described as layers with alternate 3^{2+} and BPh_4^- chains parallel to the *ab* plane. Between the chains of 3^{2+} , the complex units are connected though weak C-

H---anion hydrogen bonds involving the N atom of an [N(CN)₂]⁻ group and a C atom of an adjacent tpa ligand (Table 5). No obvious $\pi \cdots \pi$ or C–H $\cdots \pi$ interaction is found between the 3^{2+} units. The average Fe–N bond length is 2.166 Å at 200 K, which is in the range expected for an HS Fe^{II}–N bond. Specifically, the [FeN₆] coordination octahedron is highly distorted with an octahedral distortion parameter (Σ) of 111.92° at 200 K. The octahedral distortion parameter is calculated as the sum of the deviation of each of the 12 cis angles from 90°.^[20] A larger Σ value should be associated with a weaker ligand field, and, therefore, a decrease in the transition temperature and stabilization of the HS state of the metal ion. $^{\left[23\right] }$ In the present case, the Σ value of $3 \cdot (BPh_4)_2$ is much larger than those of the other Fe^{II} complexes, indicating a weaker ligand field on the Fe^{II} center in 3·(BPh₄)₂, and as a result 3·(BPh₄)₂ retains the HS state at all temperatures.

Magnetic Properties

The magnetic susceptibilities of the seven complexes were measured at a sweep rate of 1 K min⁻¹ under a 0.5 T applied field. The $\chi_M T$ vs. T plots for $1 \cdot (ClO_4)_4(H_2O)_2$ (per Fe₄ unit), the 1D chain series $[2 \cdot (ClO_4)_n, 2 \cdot (PF_6)_n, 2 \cdot (AsF_6)_n]$ and $2 \cdot (BPh_4)_n$, per Fe unit], $3 \cdot (BPh_4)_2$ (per Fe₂ unit) and (4+5)·S (per [Fe₄+Fe₁] unit), are shown in Figure 7a–d.

The magnetic measurement of $1 \cdot (ClO_4)_4 (H_2O)_2$ was carried out in a 300-100-380 K temperature cycle (Figure 7a). In the first cooling mode, the $\chi_M T$ value is $12.02 \text{ cm}^3 \text{mol}^{-1} \text{K}$ at 300 K, which decreases continuously and reaches a declining plateau between 250 and 230 K that

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Figure 7. $\chi_M T$ vs. T plots of $1 \cdot (ClO_4)_4(H_2O)_2$ (per Fe4 unit) (a), the 1D chain series $[2 \cdot (ClO_4)_n, 2 \cdot (PF_6)_n, 2 \cdot (AsF_6)_n$ and $2 \cdot (BPh_4)_n]$ (per Fe atom) (b), $3 \cdot (BPh_4)_2$ (per Fe₂ unit) (c), and (4+5) (per [Fe_4+Fe_1] unit) (d).

corresponds to an [HS_{Fe1}-LS_{Fe2}-HS_{Fe1}-LS_{Fe2}] state (see Crystal Structures). The $\chi_{\rm M}T$ value then decreases smoothly and attains a constant value of 0.05 cm³mol⁻¹K between 160 and 100 K. In the warming process, the $\chi_{\rm M}T$ vs. T curve is similar to that of the first cooling process and reaches a value of 14.14 cm³ mol⁻¹ K at 380 K, indicating that 1·(ClO₄)₄(H₂O)₂ undergoes complete SCO and is in the $(Fe^{II}_{HS})_4$ state above 350 K. However, the complex at this temperature is in fact the hydrated form $1 \cdot (ClO_4)_4$, as revealed by structural determination, and thermogravimetric analysis (Figure S1 in Supporting Information) also shows that dehydration is completed at the conclusion of this warming process, so in the second cooling process magnetic measurements were performed by using the in situ obtained solvent-free sample. Upon cooling, the $\chi_M T$ value remains constant until 340 K, then decreases continuously and completely overlays that of the first cooling process below 300 K. Above 300 K, the SCO shows hysteretic behavior (width 6 K, Figure 7a inset) that is most probably due to the dehydration process. This small apparent hysteresis can be reproduced by using a fresh sample of $1 \cdot (ClO_4)_4 (H_2O)_2$. This overall profile indicates that complex $1 \cdot (ClO_4)_4(H_2O)_2$ displays a two-step complete SCO with critical temperatures of $T_1 = 209$ K and $T_2 = 290(\downarrow)/296(\uparrow)$ K, respectively. The dehydration of complex $1 \cdot (ClO_4)_4(H_2O)_2$ does not significantly change the magnetic behavior. The BF₄⁻ analogue shows a more obvious dehydration effect on SCO with $T_{1/2}$ values of 302 (T_1) and 194 (T_2) K and 294 (T_1) and 211 (T_2) K for $1 \cdot (BF_4)_4(H_2O)_2$ and $1 \cdot (BF_4)_4$, respectively. The different dehydration effect between the two isostructural complexes obviously originates from the different hydrogen-bond interactions induced by different counteranions.

Complex 2·(ClO₄)_n displays an abrupt, incomplete SCO with $T_{1/2} = 126$ K (Figure 7b). The $\chi_M T$ value per Fe^{II} unit is 3.07 cm³mol⁻¹K at 300 K, which begins to decrease rapidly from 150 K and reaches a plateau of 1.57 cm³mol⁻¹K between 108 and 30 K that is followed by a further decrease of the $\chi_M T$ value, because of the zero-field effect of residual HS Fe^{II} ions. Complex 2·(PF₆)_n displays a continuous, incomplete SCO with $T_{1/2} = 168$ K. At 300 K, the $\chi_M T$ value is 3.07 cm³mol⁻¹K, which is in good agreement with the value expected for HS Fe^{II} ions. On cooling, the $\chi_M T$ value decreases sharply between 200 and 130 K and then reaches a plateau of 1.62 cm³mol⁻¹K, indicating a near "half" SCO.

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Complex 2·(AsF₆)_n shows an incomplete SCO with slightly complicated behavior (Figure 7b). The room-temperature $\chi_{\rm M}T$ value is 3.08 cm³mol⁻¹K, which is similar to the expected value for an HS Fe^{II} ion. Upon temperature decrease, the $\chi_{\rm M}T$ value firstly remains constant until 240 K and then decreases smoothly to reach a narrow plateau of $2.67 \text{ cm}^3 \text{mol}^{-1} \text{K}$ between 190 and 186 K. As has been revealed by crystallographic studies, the asymmetric unit of $2 \cdot (AsF_6)_n$ undergoes a phase transition and contains two crystallographically different Fe^{II} centers, one remains in an HS state (Fe1) and the other one (Fe2) keeps on undergoing SCO below 173 K. So, the appearance of a narrow plateau (width 4 K) is most probably due to the phase transition. This strange step is reproducible. The $\chi_M T$ value below this plateau further decreases and reaches a wide plateau between 130 and 30 K (1.65 $\text{cm}^3 \text{mol}^{-1}$ K), followed by a sudden drop due to the zero-field effect of the HS Fe^{II} ion (Fe1).

Complex 2·(BPh₄)_n displays gradual SCO behavior over a wide temperature range between 380 and 150 K with $T_{1/2}$ = 276 K (Figure 7b). The $\chi_{\rm M}T$ value per Fe^{II} unit at 380 K (2.98 cm³ mol⁻¹ K) is in agreement with the expected value for an HS Fe^{II} ion and decreases gradually upon temperature lowering and reaches the minimum value of 0.20 cm³ mol⁻¹ K at 150 K, corresponding to an LS Fe^{II} ion.

In complete contrast to the other six complexes, $3 \cdot (BPh_{4})_2$ is paramagnetic in the whole temperature range (Figure 7c). From the structural point of view, the $[Fe(tpa)]^{2+}$ units in $3 \cdot (BPh_4)_2$ are doubly bridged by $[N(CN)_2]^-$ groups, forming highly distorted coordination geometries (Table 5) and consequently resulting in the weakest ligand field among these complexes.

Magnetic studies on complex (4+5) were performed in the 2-390 K temperature range (Figure 7d). Upon temperature increase from 2 to 10 K, the $\chi_{\rm M}T$ value increases slightly from 0.77 to 0.87 cm³ mol⁻¹ K and remains constant until 130 K, consistent with the $\{[LS]_4 + IP\}$ state revealed by crystallographic studies; after this temperature, the $\chi_{\rm M}T$ value increases in a multiple step manner separated at 245 and 298 K (Figure 7d inset) and finally attains a value of $16.19 \text{ cm}^3 \text{mol}^{-1} \text{ K}$ at 390 K that corresponds to the {[HS]₄ + HS} state. The $\chi_M T$ value at 245 K is 9.14 cm³ mol⁻¹ K, which may originate from the $\{[IP]_4 + HS\}$ intermediate state revealed by structural analysis (Table 2, 230 K). Thermogravimetric analysis (Figure S2 in Supporting Information) indicates that the $\chi_M T$ increase at 298 K is accompanied by desorption of guest water molecules, which starts at room temperature and is complete at ca. 360 K. Because the desorption is completed at the conclusion of the heating process (390 K), magnetic studies in the cooling process were performed by using the in situ obtained dehydrated sample. Upon cooling, the $\chi_M T$ value remains constant until 370 K, then decreases continuously and overlays completely that of heating process below 290 K.

Anion Effect on SCO

It is obvious that the SCO properties of the seven complexes are profoundly influenced by various counteranions. Counteranions with different shapes and electronegativities are expected to modify the structures and intermolecular interactions of the assembled system, thus resulting in different degrees of "chemical pressure" on the SCO-active centers and subsequently influences their SCO behavior. Moreover, for the 1D zigzag chain family, there is an approximately linear relationship between anion size and the SCO critical temperature. All 1D complexes show similar packing structures, in which different counteranions do not observably change interchain interactions but significantly influence the SCO properties. The transition temperatures, $T_{1/2}$, of the zigzag chain complexes are 126, 168, 158, and 276 K for $2(ClO_4)_n$, $2(PF_6)_n$, $2(AsF_6)_n$, and $2(BPh_4)_n$, respectively, which correlates approximately with the sizes of counteranions in the order $ClO_4^- < PF_6^- < AsF_6^- <$ BPh₄⁻. However, the detailed mechanism of the relationship between the size of the counteranion and SCO $T_{1/2}$ is still unclear.^[20] Tuchagues reported a series of SCO complexes with formula $[Fe(trim)_2]X_2^{[24]}$ [trim = 4-(4-imidazolylmethyl)-2-(2-imidazolylmethyl)imidazole, $X = I^{-}, Br^{-}, Cl^{-}$, of which the transition temperature follows the order $X^- = I^ (T_{1/2} = 380 \text{ K}) > \text{Br}^- (340 \text{ K}) > \text{Cl}^- (180 \text{ K})$. In these complexes, the halide counteranions interact with the complex cation through hydrogen bonds and reduce the basicity of neighboring ligand donor groups. As a result, strong cation ... anion hydrogen bonds are expected to stabilize the high-spin state and decrease the transition temperature. However, some complexes exhibit the exact opposite behavior.[12b-12d,25] Meanwhile, counteranions may prevent SCOactive species from achieving cooperative lattice interactions, thus leading to gradual SCO (gradual and nonhysteretic).^[26] In the present case, all complexes show nonhysteretic SCO behavior, which indicates that the presence of counteranions remarkably eliminates interchain or intersquare cooperative interactions.

Conclusions

A series of Fe^{II} complexes based on $[Fe(tpa)]^{2+}$ and $[N(CN)_2]^-$ building units with various counteranions has been synthesized. Magnetic studies have revealed that the SCO properties of these complexes are profoundly influenced by the counteranions. Complex $1 \cdot (ClO_4)_4(H_2O)_2$ undergoes a two-step complete SCO, $3 \cdot (BPh_4)_2$ is in HS state in the whole temperature range. Complex (4+5) displays a gradual two-step SCO originated from the different SCO-active tetranuclear and mononuclear species cocrystallized in the lattice. The 1D chainlike complexes are inclined to undergo an SCO with a higher transition temperature and more gradual transition behavior with larger counteranions. The present study may contribute a feasible route toward exploring anion-direct synthesis and assembly of SCO complexes.

Experimental Section

Materials and Physical Measurements: All starting materials were obtained commercially and were used without further purification.

Anion-Dependent Spin Crossover and Coordination Assembly



Elemental analyses for C, H, and N were performed with a Vario EL III analyzer. Thermogravimetric measurements were taken with a TG 209F1 thermogravimetric analyser. The IR spectra (KBr pellets) were recorded in the range 400–4000 cm⁻¹ with an AVA-TAR330 FTIR spectrophotometer. PXRD studies were performed with a Panalytical X-Pert PRO diffractometer with Cu- K_{α} radiation ($\lambda = 0.15418$ Å, 40.0 kV, 30.0 mA). Magnetic susceptibility measurements were performed with a Quantum Design MPMS XL7 magnetometer at a sweeping rate of 1 K min⁻¹ under a magnetic field of 5000 Oe. Magnetic data were calibrated with the sample holder, and diamagnetic corrections were estimated from Pascal's constants.

Crystallographic Data Collection and Structure Refinement: Diffraction data were collected with Oxford Gemini S Ultra and Bruker Apex 2000 diffractometers by using graphite-monochromated Mo- K_a ($\lambda = 0.71073$ Å) and Cu- K_a ($\lambda = 0.15418$ Å) radiation. Crystal structures were solved and refined by using the SHELXTL program suite.^[27] Direct methods yielded all non-hydrogen atoms, which were refined anisotropically, and hydrogen atoms were positioned in the riding model. The highly disordered free [N(CN)₂]⁻

group in (4+5) at 230 and 270 K was removed when the data were refined by using SQUEEZE, and in the lattice of this complex crystal there are four guest water molecules per formula unit, which are severely disordered and were also removed when the data were refined. Crystallographic data and structural refinement details for the seven complexes are presented in Tables 6 and 7. CCDC-860037 [for (4+5) at 270 K], -860038 [for (4+5) at 230 K], -860039 [for (4+5) at 130 K], -882699 [for 1·(ClO₄)₄(H₂O)₂ at 150 K], -882700 [for 1·(ClO₄)₄(H₂O)₂ at 250 K], -882701 [for 1·(ClO₄)₄ at 350 K], -882702 [for $2 \cdot (ClO_4)_n$ at 270 K], -882703 [for $2 \cdot (ClO_4)_n$ at 110 K], -882704 [for $2 \cdot (PF_6)_n$ at 270 K], -882705 [for $2 \cdot (PF_6)_n$ at 110 K], -882706 [for 2·(BPh₄)_n at 295 K], -882707 [for 2·(BPh₄)_n at 150 K], -882708 [for 2·(AsF₆)_n at 270 K], -882709 [for 2·(AsF₆)_n at 173 K], -882710 [for $2 \cdot (AsF_6)_n^{LT}$ at 110 K], -882711 [for $2 \cdot (BPh_4)_2$ at 200 K] contain 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.

 $1\cdot (ClO_4)_4 (H_2O)_2$: An aqueous solution (5 mL) of FeSO_4·7H_2O (0.1 mmol), sodium dicyanamide (0.1 mmol) and NaClO_4·xH_2O

Table 6. Crystal data and refinements for $1 \cdot (ClO_4)_4(H_2O)_2$, $2 \cdot (BPh_4)_n$, and (4+5).

	$1 \cdot (ClO_4)_4(H)$	$(I_2O)_2$	$1 \cdot (ClO_4)_4$	$2 \cdot (BPh_4)_n$		(4+5)		
Empirical formula Formula mass	C ₈₀ H ₇₆ Cl ₄ F 2082.89	e ₄ N ₂₈ O ₁₈	$\begin{array}{c} C_{80}H_{72}Cl_4Fe_4N_{28}O_{16}C_{88}H_{76}B_2Fe_2N_{14}\\ 2046.86 \\ 1462.95 \end{array}$		$\frac{C_{104}H_{98}F_{18}Fe_5N_{41}O_4Sb_3}{2972.73}$			
Crystal system	monoclinic		monoclinic	monoclinic		monoclinic		
Space group	$P2_1/c$		$P2_1/c$	$P2_1/c$		C2/m		
T[K]	150	250	350	295	150	270	230	130
a [Å]	17.7486(9)	18.0614(12)	18.5178(18)	25.958(3)	25.5990(9)	39.947(2)	39.777(3)	39.4291(10)
b Å	14.6375(8)	14.7280(10)	15.0730(14)	10.9101(13)	10.7891(4)	18.0746(12)	17.9767(9)	17.8352(4)
c [Å]	17.3299(9)	17.4153(12)	17.330(2)	27.037(3)	26.9584(9)	17.4747(9)	17.4208(10)	17.2743(4)
β [°]	108.858(6)	107.134(7)	107.957(12)	102.141(3)	102.229(3)	106.042(6)	105.828(7)	106.161(3)
V [Å ³]	4260.6(4)	4427.0(5)	4601.5(8)	7485.8(16)	7276.7(4)	12125.8(12)	11984.4(12)	11667.7(5)
Z	2	2	2	4	4	4	4	4
$D_{\rm calcd.} [\rm g cm^{-3}]$	1.624	1.563	1.477	1.298	1.335	1.628	1.648	1.692
$\mu \text{ [mm^{-1}]}$	0.881	0.848	0.813	0.445	0.458	10.694	10.820	11.114
Reflections collected	21467	22400	22879	40551	34199	32561	32992	30907
$R_1 [I > 2\sigma(I)]^{[a]}$	0.0644	0.0792	0.0910	0.1065	0.0762	0.0935	0.0804	0.0868
wR_2 (all data)	0.1612	0.1784	0.2965	0.2552	0.1569	0.2748	0.2600	0.2638

[a] $R_1 = ||F_o| - |F_c||/|F_o|$; $wR_2 = \{\overline{[w(F_o^2 - F_c^2)^2]}/[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma_2(F_o^2) + (ap)^2 + bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2]/3$; and $Rw = [w(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$.

Table 7. Crystal data and refinements for $2 \cdot (ClO_4)_n$, $2 \cdot (PF_6)_n$, $2 \cdot (AsF_6)_n$, $3 \cdot (BPh_4)_2$.

	$2 \cdot (ClO_4)_n$		$2 \cdot (PF_6)_n$		$2 \cdot (AsF_6)_n$	$2 \cdot (AsF_6)_n^{LT}$		$3 \cdot (BPh_4)_2$
Empirical formula Formula mass	C ₂₀ H ₁₈ ClFel 511.71	N ₇ O ₄	C ₂₀ H ₁₈ F ₆ Fe 557.23	N ₇ P	C ₂₀ H ₁₈ AsF ₆ FeN 601.18	¹ ₇ C ₄₀ H ₃₆ As ₂ F 1202.37	$_{12}Fe_2N_{14}$	C ₈₈ H ₇₆ B ₂ Fe ₂ N ₁₄ 1462.95
Crystal system	monoclinic		monoclinic		monoclinic	monoclinic		monoclinic
Space group	$P2_1/c$		$P2_{1}/c$		$P2_1/c$	$P2_1/c$		$P2_{1}/c$
<i>T</i> [K]	270	110	270	110	270	173	110	200
a [Å]	11.8968(7)	11.6605(9)	12.5418(9)	12.2910(7)	12.9495(12)	15.7697(8)	15.6729(6)	10.7102(11)
<i>b</i> [Å]	12.2573(7)	12.1480(10)	11.9957(7)	11.8209(6)	11.5443(8)	11.5582(5)	11.4801(4)	17.4267(18)
c [Å]	15.6197(10)	15.5343(12)	16.4189(13)	16.2532(9)	16.6774(15)	26.7570(18)	26.5369(13)	19.836(3)
β [°]	107.408(6)	106.593(8)	108.513(9)	108.233(6)	107.827(9)	108.157(5)	108.798(4)	92.696(10)
V [Å ³]	2173.4(2)	2108.8(3)	2342.4(3)	2242.9(2)	2373.4(3)	4634.1(4)	4520.0(3)	3698.1(7)
Z	4	4	4	4	4	4	4	2
$D_{\rm calcd.} [\rm g cm^{-3}]$	1.564	1.612	1.580	1.650	1.682	1.723	1.767	1.314
$\mu \text{ [mm^{-1}]}$	0.861	0.887	0.783	0.818	2.089	2.140	2.194	0.450
Reflections collected	10400	10520	8886	8258	11016	20802	19933	18039
$R_1 [I > 2\sigma(I)]^{[a]}$	0.0516	0.1350	0.0552	0.0417	0.0754	0.0937	0.0616	0.0780
wR_2 (all data)	0.1053	0.2871	0.1319	0.0742	0.2096	0.3100	0.1887	0.1455

[a] $R1 = ||F_0| - |F_c||/|F_0|$; $wR2 = \{[w(F_0^2 - F_c^2)^2]/[w(F_0^2)^2]\}^{1/2}$; $w = 1/[\sigma_2(F_0^2) + (ap)^2 + bp]$, where $p = [max(F_0^2, 0) + 2F_c^2]/3$; and $Rw = [w(|F_0| - |F_c|)^2/w|F_0|^2]^{1/2}$, where $w = 1/\sigma_2(|F_0|)$.

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(0.1 mmol) was poured without stirring into an ethanolic solution (1 mL) of 0.1 mmol tpa. A single-crystal seed of $1 \cdot (BF_4)_4(H_2O)_2$ was added to the resulting yellow solution, which was then kept under N₂; red $1 \cdot (CIO_4)_4(H_2O)_2$ crystallized in a few days. The crystal seed was removed manually, and red crystals of $1 \cdot (CIO_4)_4(H_2O)_2$ were collected by filtration. Yield: ca. 30 mg (60%). C₈₀H₇₆Cl₄Fe₄N₂₈O₁₈ (2082.86): calcd. C 46.13, H 3.68, N 18.83; found C 45.91, H 3.62, N 18.70. IR (KBr): $\tilde{v} = 3430$ (m), 2924 (w), 2315 (w), 2251 (s), 2162 (s), 1603 (m), 1480 (w), 1441 (m), 1383 (w), 1090 (s), 766 (m), 626 (m), 505 (w) cm⁻¹.

 $2 \cdot (ClO_4)_n$, $2 \cdot (PF_6)_n$, and $2 \cdot (AsF_6)_n$: An aqueous solution of FeSO₄·7H₂O (5 mL), sodium dicyanamide (0.1 mmol) and NaClO₄·xH₂O (0.1 mmol) was poured without stirring into an ethanolic solution (1 mL) of tpa (0.1 mmol). The mixture was put aside under N₂, and yellow crystals of $2 \cdot (ClO_4)_n$ were collected by filtration several days later. Crystals of $2 \cdot (PF_6)_n$ and $2 \cdot (AsF_6)_n$ were prepared similarly with KPF₆ and AsF₆, respectively. Yield of **2**·(ClO₄)_n: ca. 25 mg (50%). $C_{20}H_{18}ClFeN_7O_4$ [**2**·(ClO₄)_n] (511.71): calcd. C 46.94, H 3.55, N 19.16; found C 47.01, H 3.68, N 19.45. IR (KBr): $\tilde{v} = 3438$ (w), 2339 (w), 2247 (m), 2204 (s), 2175 (s), 1604 (m), 1447 (m), 1408 (m), 1098 (s), 1017 (m), 763 (m), 621 (m), 513 (w) cm⁻¹. Yield of $2 \cdot (PF_6)_n$: ca. 28 mg (50%). $C_{20}H_{18}F_6FeN_7P$ $[2 \cdot (PF_6)_n]$ (557.23): calcd. C 43.11, H 3.26, N 17.60; found C 43.33, H 3.04, N 17.70. IR (KBr): $\tilde{v} = 3412$ (w), 2344 (w), 2253 (m), 2207 (s), 2175 (s), 1700 (w), 1605 (m), 1447 (w), 1019 (w), 838 (s), 763 (m), 557 (m) cm⁻¹. Yield of $2 \cdot (AsF_6)_n$: 30 mg (50%). C₂₀H₁₈AsF₆FeN₇ [2·(AsF₆)_n] (601.18): calcd. C 39.96, H 3.02, N 16.31; found C 39.80, H 3.006, N 16.71. IR (KBr): $\tilde{v} = 3431$ (m), 2341 (m), 2254 (m), 2207 (s), 2174 (s), 1605 (m), 1445 (w), 1396 (w), 1019 (w), 765 (m), 701 (s) cm⁻¹.

 $2 \cdot (BPh_4)_n$ and $3 \cdot (BPh_4)_2$: A methanolic solution (5 mL) of FeSO₄·7H₂O (0.1 mmol), sodium dicyanamide (0.1 mmol), and NaBPh₄ (0.1 mmol) was stirred for 15 min and then filtered. The filtrate was placed in the bottom of a test tube. Above this solution, a methanolic solution (5 mL) of tpa (0.1 mmol) was layered. Red crystals of $2 \cdot (BPh_4)_n$ and yellow crystals of $3 \cdot (BPh_4)_2$ crystallized simultaneously in 3 d and were collected by filtration and separated manually under a microscope. Yield of $2 \cdot (BPh_4)_n$: ca. 28 mg (40%). C₈₈H₇₆B₂Fe₂N₁₄ (1462.95): calcd. C 72.25, H 5.24, N 13.40; found C 72.33, H 5.09, N 13.12. IR (KBr): $\tilde{v} = 3417$ (w), 3052 (m), 2294 (w), 2247 (w), 2167 (s), 1604 (m), 1575 (m), 1479 (m), 1442 (m), 1337 (w), 1156 (w), 1098 (w), 1052 (w), 1020 (w), 764 (m), 733 (s), 704 (s), 612 (m) cm⁻¹. Yield of 3·(BPh₄)₂: ca. 20 mg (30%). C88H76B2Fe2N14 (1462.95): calcd. C 72.25, H 5.24, N 13.40; found C 72.53, H 5.04, N 13.70. IR (KBr): $\tilde{v} = 3446$ (w), 3049 (w), 2312 (w), 2234 (w), 2187 (s), 1604 (w), 1572 (m), 1480 (w), 1439 (w), 1373 (w), 1152 (w), 1101 (w), 1052 (w), 1019 (w), 763 (w), 741 (w), 730 (w), 703 (m), 606 (m) cm⁻¹.

(4+5): An aqueous solution (5 mL) of FeSO₄·7H₂O (0.5 mmol), sodium dicyanamide (0.5 mmol), and KSbF₆ (0.5 mmol) was poured without stirring into an ethanolic solution (1 mL) of tpa (0.5 mmol); the resulting turbid red solution with a large amount of precipitate was sealed in a bottle under N₂. The precipitate generally transformed into red crystals of (4+5) in 2 weeks. Red crystals suitable for X-ray single-crystal diffraction were collected by filtration. Yield: ca. 18 mg (30%). C₁₀₄H₉₈F₁₈Fe₅N₄₁O₄Sb₃ (2972.64): calcd. C 42.02, H 3.32, N 19.32; found C 42.32, H 3.37, N 19.62 for crystals of (4+5); C 41.61, H 3.27, N 18.92 for the precipitate. IR (KBr): $\tilde{v} = 3448$ (m), 2924 (w), 2276 (w), 2191 (s), 2165 (s), 1604 (m), 1440 (m), 1394 (w), 1099 (w), 1052 (w), 1020 (w), 764 (w), 683 (w), 633 (m), 514 (w) cm⁻¹.

Supporting Information (see footnote on the first page of this article): TGA data of $1 \cdot (ClO_4)_4 (H_2O)_2$ and (4+5), PXRD data of (4+5)

and the precipitate before conversion to (4+5), magnetic properties of the precipitate before conversion to (4+5), and IR spectra of all complexes.

Acknowledgments

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Spin Crossover

R.-J. Wei, J. Tao,* R.-B. Huang, L.-S. Zheng 1–12

Anion-Dependent Spin Crossover and Coordination Assembly Based on $[Fe(tpa)]^{2+}$ [tpa = tris(2-pyridylmethyl)amine] and $[N(CN)_2]^-$: Square, Zigzag, Dimeric, and [4+1]-Cocrystallized Complexes

Keywords: Spin crossover / Coordination assembly / Anion dependence / Structure elucidation / Magnetic properties



A series of Fe^{II} complexes based on $[Fe(tpa)]^{2+}$ and $[N(CN)_2]^-$ [tpa = tris(2-pyr-idylmethyl)amine] building units in the presence of various counteranions has been

prepared. The complexes show various structures and diverse spin-crossover behaviors that are affected by the counteranions.