Mixed-Valence Heptanuclear Iron Complexes with Ferromagnetic Interaction

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ABSTRACT: Three new Prussian blue analogues, heptanuclear mixed-valence iron complexes of the type [FeII(CN)6]3−{FeIII(1−2H)}5−Cl−·nH2O, were synthesized and structurally and spectrally characterized, and their magnetic properties were investigated. (1−2H) corresponds to doubly deprotoned Schiff-base pentadentate ligands 1a, N,N′-bis(2-hydroxybenzylidene)-1,5-diamo-3-azapentane, 1b, N,N′-bis(3-ethoxy-2-hydroxybenzylidene)-1,7-diamo-4-azaheptane, or 1c, N,N′-bis(3-methoxy-2-hydroxybenzylidene)-1,6-diamo-3-azaheksane. These compounds were formed by assembling the [Fe(CN)6]3− building block with mononuclear complexes of the [Fe(1−2H)]Cl− type. X-ray structure analysis revealed that the complexes adopt a star-like architecture: the Fe(II) ion lies at the very center, and on its octahedral nodes the Fe(III) sites are coordinated in the FeII−C≡N−FeIII manner. The Schiff-base pentadentate ligand moiety 1−2H coordinates a single Fe(III) center in two complexes 3b and 3c. Ligands 1a−2H in the complex cation of 3a adopt an unusual coordination mode: three donor atoms of the same ligand (one O and two N) coordinate one Fe(III), whereas the remaining N′ and O′ donor atoms coordinate the neighboring Fe(III) center creating the {Fe(ON)2(N′O′)N} chromophore involving two 1a−2H ligand moieties. Moreover, three Fe(III) centers are interconnected with three 1a−2H ligands in such a manner that two {FeIII(1−2H)} units form two intramolecular rings. Magnetic investigation of the heptanuclear complexes revealed the high-spin state of all six Fe(III) coordination sites (s = 5/2), while the very central Fe(II) site is in the low-spin state (s = 0). At low temperature, the ferromagnetic exchange interactions stay evident for all three complexes. Mössbauer spectra of compounds 3a and 3b revealed a presence of two different doublets for both compounds: the major doublet is related to six Fe(III) high-spin coordination sites and the minor doublet refers to the low-spin very central Fe(II).

1. INTRODUCTION

Prussian blue analogues (PBAs) have adopted extraordinary importance in the research field of coordination chemistry. The hexadenticy of the [M(CN)6]3− central bridging anion brings about many opportunities in the syntheses of polynuclear compounds when the ambidentate CN− ligands allow coordination of peripheral M′ metal ions via the nitrogen donor atoms, M−C≡N−M′. Polynuclearity of such resulting substances is particularly important in the construction of perspective materials with tunable structural, optical, magnetic, and electric properties. Scientific exploration of PBAs began many years ago, and heretofore, thousands of new materials with interesting magnetic properties have already been prepared and characterized; they cover single-molecule magnets, spin cross-over systems, photoinduced and electrochemically tuned magnets, or materials with magnetic ordering like ferro- and ferrimagnets.

When polydentate ligands are used for coordination to peripheral metal ions M′, a subsequent complexation with the [M(CN)6]3− anion can lead to a supramolecular architecture where 3D, 2D, or 1D coordination networks are formed. As an example of this synthetic strategy, especially when aiming at the dimensionality of the resulting compounds, the use of the pentadentate N3O2 Schiff-base ligands can be mentioned. The remaining sixth coordination site can then be occupied by the chlorido ligands or solvent molecules X, and this labile M′−X bond is easily replaceable by the nitrogen atoms of the cyanido ligands. In such a manner, various 0D polynuclear coordination compounds have already been prepared possessing high-spin properties, behaving as...
Herein, we report on the synthesis and spectral, structural, and magnetic characterization of novel heptanuclear mixed-valence Fe(II)−Fe(III)6 complexes adopting a star-like architecture. Their preparation consists of three consecutive steps, i.e., synthesis of N3O2− donor Schiﬀ base ligands (1a−c), coordination with FeCl3 which results in formation of the [Fe(1−2H)Cl] mononuclear complexes 2a−c (where 1−2H is a double-deprotonated Schiﬀ-base N 3O2− donor ligand), and actual synthesis of the polynuclear Fe(II)−Fe(III)6 compounds by coordination of the [Fe(1−2H)Cl] species on the hexacyanoferrate anion. Structural investigation of the mononuclear complexes conﬁrmed the expected coordination of one pentadentate ligand with one Fe(III) central atom, where the sixth coordination site is occupied by the Cl− ligand. The same coordination manner of the Schiﬀ-base ligands was found in two Fe(II)−Fe(III)6 polynuclear systems (3b and 3c). However, the crystal structure of the third heptanuclear complex (3a) revealed unusual interconnection of one Fe(III) coordination center by two pentadentate ligands and formation of two intramolecular coordination circles. The magnetic properties (magnetic susceptibility and magnetization) of the prepared compounds have been studied in detail and revealed the high-spin state of the Fe(III) central atoms in mononuclear as well as polynuclear systems.

2. EXPERIMENTAL SECTION

2.1. General. All purchased chemicals were used as received. Methanol, acetonitrile, and diethyl ether were used as solvents without any further puriﬁcation. Elemental analysis of carbon, hydrogen, and nitrogen was carried out by an automated analyzer (Vario, Micro Cube). IR spectra were measured in KBr pellets in the 4000−400 cm−1 region (Magna FTIR 750, Nicolet). Electronic spectra were measured in a Nujol mull (Specord 200, Analytical Jena) in the range of 9000−50 000 cm−1. 1H and 13C NMR spectra were recorded with the solvent protons as an internal standard (DPX 300, Bruker). Mass spectrometric analytical data were acquired using a matrix-assisted laser desorption/ionization time of ﬂight workstation (MALDI-ToF, Voyager-DE, PRO Bio) and/or electrospray ionization time of ﬂight spectrometer (ESI-ToF, microOTOF-Q II, Bruker).

2.2. Synthesis. Synthesis of heptanuclear compounds 3a, 3b, and 3c consists of three steps (Figure 1): (i) preparation of ligands 1a, 1b, and 1c; (ii) preparation of mononuclear Fe(III) complexes 2a, 2b, and 2c of general formula [Fe(1−2H)Cl] (where 1−2H is a deprotonated form of 1a, 1b, and 1c ligands); and (iii) assembling of heptanuclear mixed-valence iron complexes. Mononuclear complex 2d was prepared in order to explain the crystal structure of heptanuclear compound 3a.

Ligand 1a. The pentadentate ligand N,N′-bis(2-hydroxybenzylidene)-1,5-diamino-3-azapentane (1a) was prepared by Schiff condensation between 2-hydroxybenzaldehyde (5 mmol) and 1,5-diamino-3-azapentane (2.5 mmol) in a methanol solution (30 cm3). Both reactants were mixed together at room temperature, and the mixture was stirred at 40 °C for 2 h. After solvent removal the yellow oily material was isolated in more than 95% yield. 1H NMR (300 MHz, CD3Cl2, 25 °C, δ/ppm): 13.32 (s, OH), 8.35 (s, 2H, HCC=NC).
2.3. Crystal Structure Determination. Single-crystal X-ray diffraction experiments were conducted using a Gemini R CCD
diffraactometer (Oxford Diffraction) or Oxford diffraactometer Xcalibur2 with the Sapphire CCD detector and fine-focused sealed tube (Mo Kα radiation, λ = 0.71073 Å) source and equipped with an Oxford Cryosystem nitrogen gas-flow apparatus. Data reduction and analytical absorption correction were performed by Crysalis RED.46–47 Structures were solved by direct methods using SHELXS-97 or SIR-97 and refined by full-matrix least-squares procedure with the SHELXL-97 program.38–40 The chloride anions and water molecules in the heptanuclear complexes are strongly disordered in the cavities between the [Fe(CN)6][Fe(L)]6 cations. Attempts in resolving the disorder adequately failed, and therefore, the program PLATON-SQUEEZE was used to remove diffuse electronic density.46–47 The crystal structure of 3a contains in the unit cell four voids of 1005 Å3 containing 45 electrons. This matches the presence of two chloride anions and one water molecule in the empirical formula [Fe(CN)6][Fe- (1a⋯3a)]6Cl2·H2O. The crystal structure of 3b contains in the unit cell two voids of 860 Å3 referring to 239 electrons. This fits to the presence of two chloride anions and 20.5 water molecules in the empirical formula [Fe(CN)6][Fe(1b⋯3b)]6Cl2·20.5H2O. The crystal structure of 3c possesses in the unit cell a single void of 2132 Å3 containing 299 electrons and three voids of 25 Å3 containing 14 electrons. This refers to the presence of 2 chloride anions and 10 water molecules in the empirical formula [Fe(CN)6][Fe(1c⋯3c)]6·Cl3·10H2O.

2.4. Magnetometry. Magnetic measurements were performed using a SQUID magnetometer (MPMS-XL5 and MPMS-XL7, Quantum Design) in the DC and/or RSO mode of detection. In all cases, the temperature dependence of magnetic moment was recorded at 0.1 K as an external magnetic field and the temperature sweeping rate was 1 K/min. The gelatin-made capsules as sample holders were used, and their small diamagnetic signal had a negligible contribution to the overall magnetization, which was dominated by the sample. The diamagnetic corrections to the molar magnetic susceptibilities were applied using Pascal constants.42

2.5. Mössbauer Spectroscopy. A conventional Mössbauer spectrometer in the transmission mode with the 57Co/Rh source was utilized. The spectrometer was calibrated at α-Fe at room temperature. All output data are in mm s−1.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Spectroscopic Characterization. The pentadentate N3O2-donor Schiff-base ligands 1a (N,N'-bis(2-hydroxybenzylidene)-1,5-diamo-no-3-azapentane), 1b (N,N'-bis(3-ethoxy-2-hydroxybenzylidine)-1,7-diamino-4-aza-heptane), and 1c (N,N'-bis(3-methoxy-2-hydroxybenzylidine)-1,6-diamo-no-3-azahexane) were prepared in almost quantitative yields by Schiff condensation between a derivative of 2-hydroxybenzaldehyde and an aliphatic triamine. In the consecutive complexation with Fe(III) salts, the mononuclear complexes 2a, 2b, and 2c of general formula [Fe(1⋯3H)]CI were synthesized (where 1⋯3H is a double-deprotonated form of the Schiff-base ligand 1a, 1b, or 1c). Single crystals of mononuclear complexes 2b and 2c were obtained from the acetone and methanol solution, respectively. Compounds 2b and 2c were characterized by single-crystal X-ray diffraction. In order to explain the unusual coordination observed in the case of heptanuclear 3a compound, the mononuclear complex of formula [Fe(1a⋯3a)NCS] (2d) was prepared and structurally characterized.

Reaction between the building blocks [Fe(1⋯3H)]CI and [Fe(CN)6]3- resulted in three heptanuclear mixed-valence iron compounds with general formula [Fe(CN)6][Fe(1⋯3H)]6Cl2·nH2O. Single crystals suitable for X-ray analysis were obtained by slow evaporation of the mother liquid in a refrigerator. Single-crystal X-ray analysis confirmed formation of heptanuclear dications with formula [Fe(CN)6][Fe(1⋯3H)]62+; crystal structures of all three compounds also contain the molecules of crystal water, and the compounds can be described by the following formulas: [Fe(CN)6][Fe(1a⋯3a)]6Cl2·H2O (3a), [Fe(CN)6][Fe(1b⋯3b)]6Cl2·20.5H2O (2b), and [Fe(CN)6][Fe(1c⋯3c)]6Cl3·10H2O (3c). The solid state electronic spectra of the herein reported iron complexes were recorded in the Nujol mull as a thin film in transmission mode (Figure 2). The color difference of the dark purple-violet mononuclear and dark blue heptanuclear complexes predestinates different absorption bands in the visible area of the spectra. The visible absorption bands of the mononuclear complexes refer to the phenolato → Fe(III) charge transfer.43 which is situated at 19 493 cm−1 (513 nm) for 2a, 18 547 cm−1 (539 nm) for 2b, and 19 157 cm−1 (522 nm) for 2c. On the contrary, the visible electronic absorption bands of the heptanuclear Prussian blue analogues are slightly shifted to the lower energies: 16 340 cm−1 (612 nm) for 3a, 17 336 cm−1 (577 nm) for 3b, and 17 638 cm−1 (567 nm) for 3c. It was previously shown that replacement of the chlorido ligand for cyanido nitrogen atoms does not affect the absorption of the Fe(III) coordination centers; therefore, the shift of the electronic absorptions can be attributed to the intervalence charge transfer Fe(II) → Fe(III). The second absorption band of the heptanuclear complexes occurs around 29 000 cm−1 (345 nm), and it is analogous to the absorptions of other reported iron Prussian blue analogues of the same structural type.24,27,35

Infrared spectroscopy investigation revealed that the heptanuclear Prussian blue analogues 3a–c show many common vibration bands with the corresponding mononuclear complexes 2a–c (see Supporting Information S1), especially in...
The dihedral angle region. The major difference lies in the presence of the strong vibration below 2100 cm⁻¹, which is related to the C≡N stretching. In comparison to the uncoordinated [Fe(CN)₆]⁴⁻ anion, which shows a multiple band centered at 2024 cm⁻¹, the cyanido vibration frequencies are slightly shifted to higher energies. The cyanido bridging ligand vibrations of 3a and 3c are unsplit and positioned at 2055 and 2084 cm⁻¹, respectively. However, compound 3b shows the cyanido vibration split to a 2083 and 2059 cm⁻¹ doublet.

3.2. Crystal Structures. Crystal Structures of Mononuclear Complexes. Crystal data for the mononuclear Fe(III) complexes 2b–d are listed in Table 1. Single crystals of complex 2b were obtained by recrystallization from acetone. The diffraction experiment revealed that the complex consisted of one Fe(III) central atom coordinated with the deprotonated 1b ligand and one chlorido ligand (Figure 3).

![Figure 3. Molecular structure of mononuclear complex 2b (50% probability level of thermal ellipsoids). Hydrogen atoms are omitted for clarity.](image-url)

The crystal structure of 2b contains one nonbonded acetone molecule per formula unit, and four [Fe(1b-3H₂).Cl]·CH₃COCH₃ entities are contained in the unit cell. The solvent molecule is connected with the [Fe(1b-3H₂)Cl] moiety by a weak hydrogen bond existing between the O1S oxygen of the acetone molecule and the C14 carbon atom of the imino bond (3.372(6) Å). The Fe–N(imino) bond lengths are 2.104(4) and 2.097(4) Å, the Fe–N(amine) bond length is 2.234(4) Å, and the longest one is found for the Fe–Cl bond, 2.340(1) Å which brings the possibility for replacement by the cyanido ligand. Two of three trans chromophore bond angles O1–Fe1–O2 and C11–Fe1–N2 are very close to linearity (176.93(9)° and 175.7(1)°, respectively); the third angle O–Fe–N is distorted significantly (163.7(1)°). Contrary to the other herein reported iron complexes with a similar type of pentadentate Schiff base ligands, the oxygen donor atoms are situated in the trans position. The chlorine atom is involved in a weak hydrogen bond with the amino nitrogen atoms of the neighboring complex molecule (N2···Cl1, 3.433(3) Å), thus creating a 1D quasichain (see Supporting Information, Figure S5).

Single-crystal X-ray diffraction study of 2c revealed a mononuclear Fe(III) complex with the deprotonated 1c ligand (Figure 4), and four [Fe(1c-3H₂)Cl] molecules are involved in the unit cell. The chromophore [FeO₃N₂Cl] refers to a distorted octahedron. The Fe–N bond distances involving the imino bonds (2.091(2) and 2.103(2) Å) are shorter than that involving the amino nitrogen atom (2.199(2) Å). The Fe–O bond lengths are equal to 1.919(2) and 1.967(2) Å, and the Fe–Cl bond is much longer, 2.405(1) Å. Angles N–Fe–N and N2–Fe1–O1 significantly differ from linearity (161.23(9)° and 166.66(8)°). Due to the flexibility of the chlorido ligand, the deviation of the O2–Fe1–Cl1 angle is very small and the value

| Table 1. Crystallographic Data for the Mononuclear Complexes |
|-----------------|-----------------|-----------------|
|                | 2b              | 2c              | 2d              |
| formula        | C₂₇H₃₇ClFeN₃O₅ | C₂₁H₂₅ClFeN₃O₄ | C₂₀H₂₃FeN₄O₃S  |
| fw/g mol⁻¹     | 574.90          | 474.74          | 455.34          |
| cryst color    | dark violet     | dark violet     | dark violet     |
| temperature/K  | 100(2)          | 100(2)          | 100(2)          |
| wavelength/Å   | 0.71073         | 0.71073         | 0.71073         |
| cryst syst     | monoclinic      | monoclinic      | monoclinic      |
| space group    | P2₁/c           | P2₁/c           | P2₁/n           |
| a/Å            | 7.5009(2)       | 9.0997(7)       | 13.6178(11)     |
| b/Å            | 13.0058(4)      | 20.5346(12)     | 10.1175(8)      |
| c/Å            | 28.1789(9)      | 10.9418(8)      | 14.9168(13)     |
| α/deg          | 90              | 90              | 90              |
| β/deg          | 93.124(3)       | 109.064(8)      | 101.184(8)      |
| γ/deg          | 90              | 90              | 90              |
| V/Å³           | 2744.91(14)     | 2104.5(2)       | 2016.2(3)       |
| Z              | 4, 1.391        | 4, 1.498        | 4, 1.500        |
| μ/mm⁻¹         | 0.688           | 0.877           | 0.881           |
| μ(000)         | 1212            | 988             | 948             |
| cryst size/mm  | 0.40 × 0.40 × 0.32 | 0.35 × 0.28 × 0.22 | 0.32 × 0.30 × 0.06 |
| final R indices [I > 2σ(I)] | R₁ = 0.0599 | R₁ = 0.0386 | R₁ = 0.0654 |
|                | wR₁ = 0.1344    | wR₁ = 0.0680    | wR₁ = 0.1096    |
| R indices (all data) | R₁ = 0.0687 | R₁ = 0.0816 | R₁ = 0.1089 |
|                | wR₁ = 0.1369    | wR₁ = 0.0741    | wR₁ = 0.1177    |
| GoF on F²      | 1.258           | 0.898           | 0.967           |
| CCDC ref. no.  | 838229          | 838230          | 838231          |
Figure 4. Crystal structure of mononuclear complex 2c (50% probability level of thermal ellipsoids). Hydrogen atoms are omitted for clarity.

Figure 5. Molecular structure of mononuclear complex 2d (50% probability level of thermal ellipsoids). Hydrogen atoms are omitted for clarity.

is very close to the flat angle (178.68(6)°). The oxygen donor atoms are in the cis arrangement and form an angle of 90.75(8)°. The chlorine atom creates intermolecular weak hydrogen bonds with the hydrogen atoms of the amino nitrogen atoms (N2−Cl1, 3.250(3) Å), thus creating a 1D quasichain (see Supporting Information, Figure S6).44

The asymmetric unit of 2d consists of one complex molecule of formula [Fe(1a−2H)NC] and one molecule of methanol (Figure 5). Four [Fe(1a−2H)NC]-CH3OH entities are included in the unit cell. The bond lengths Fe−O (1.924(2) and 1.951(3) Å), Fe−N(thiocyanato) (2.061(3) Å), and two Fe−N(imino) show similar distances (2.151(4) and 2.236(3) Å), while the Fe−N(amino) is the longest one (2.236(3) Å). The angles between the central atom and the opposite donor atoms are significantly different from 180° (O1−Fe1−N2 = 159.4(1)°, N1−Fe1−O2 = 173.8(1)°, and O2−Fe1−N4 = 158.0(1)°), and they confirm that the {FeN2N′O2} chromophore forms a distorted octahedron. The oxygen donor atoms are positioned in the cis arrangement with the angle O−Fe−O = 89.5(1)°. The thiocyanato ligand is almost linear, and it is slightly bent with respect to the central atom (S1−N4−Fe1 = 173.06(5)°). A detailed inspection of the crystal structure reveals the existence of the supramolecular dimeric [Fe(1a−2H)NC]2 structure created by hydrogen bonds between the phenolato oxygen and the amino nitrogen atoms (O2−N2, 2.882(3) Å, see Supporting Information, Figure S7) of the neighboring [Fe(1a−2H)NC]2 molecules and a weak hydrogen bond is present between thiocyanido sulfur and the oxygen atom from methanol (S1−O1, 3.272(4) Å; see Supporting Information, Figure S7).44

Crystal Structures of Heptanuclear Compounds 3a, 3b, and 3c. Crystallographic data for the heptanuclear complexes are listed in Table 2. Single-crystal X-ray diffraction study of all three heptanuclear compounds confirmed the presence of the heptanuclear [Fe(CN)6{Fe(1a−2H)}2]2+ dications, two disordered chloride counteranions, and a few molecules of crystal water.

Heptanuclear Compound 3a [Fe(CN)6{Fe(1a−2H)}2Cl2H2O]. This compound contains one water molecule per complex unit, and four [Fe(CN)6{Fe(1a−2H)}2]2+Cl2H2O entities are included in the unit cell. Diffraction data were collected at two temperatures (100 and 293 K) using the same crystal. For both measurements, the experiment revealed cubic Pn−3 symmetry. Thermal variation caused only negligible differences between the low- and the room-temperature structures. The inversion center of the heptanuclear dication is at the low-spin Fe(II) central atom, and the {Fe5C6} chromophore refers to the regular octahedron with Fe1−Cl bond distances 1.915(47) Å at 100 K and 1.937(7) Å at room temperature.

Structural investigation of the complex cation [{III(1a−2H)}NC]2Fe22+ (Figure 6) revealed a unique coordination of the 1a−2H ligand moiety. Contrary to the so far published24,26,34 or herein reported heptanuclear compounds, one ligand connects two Fe(III) centers. Such an exceptional coordination can be explained in two ways. It could be connected to an oligo- or a polymeric structure of 2a mononuclear complex, where one 1a−2H ligand coordinates two Fe(III) central atoms in the same manner as in the structure of 3a. Unfortunately, attempts to grow suitable single crystals of 2a failed, but the high-resolution ESI ToF mass spectroscopy investigation of complex 2a (see Supporting Information, Figure S4) revealed the presence of oligo/polymeric fragments (Supporting Information, Figure S4) and thus supports this idea. On the other hand, single-crystal X-ray analysis of 2d with the same 1a−2H ligand moiety shows a standard coordination of one Schiff-base ligand to a single Fe(III) center. Therefore, the second possible explanation of the unusual structure of 3a can be based on the kinetic lability of 2a. Replacement of the chlorido for a cyanido group might cause a structural rearrangement of the donor atoms of the 1a−2H ligand moiety.

The centrosymmetry of the [Fe(CN)6{Fe(1a−2H)}2]2+ cation is the reason for the structural equivalence of all six peripheral Fe(III) environments. The shape of the {FeN2N′O2} chromophore can be attributed to a distorted tetragonal bipyramid where the Fe−N bond lengths indicate the high-spin state at both temperatures of the experiment (Table 3). At 100 K, the bond lengths Fe−O are equal to 1.882(4) and 1.894(3) Å, respectively. The distances Fe−N(imino) are
2.077(4) and 2.088(4) Å, and they are shorter than the Fe–N(amine) bond length which is 2.231(3) Å. The distance between the FeIII–N(cyanido) is 2.079(4) Å, and it is close to that found in Prussian blue.46

Significant deviations from linearity are obvious for all three angles between the Fe(III) central atom and the transpositioned donor atoms (N1–Fe2–N1 = 164.5(1)°, N1–Fe2–N2 = 176.5(2)°, N1–Fe2–N3 = 165.0(1)°). The oxygen donor atoms adopt the cis configuration, and they form the angle O–Fe–O = 97.0(1)°, which is a higher value than that found in the mononuclear complex 2d. The FeII–C–N linkage is almost linear (177.9(4)°); however, the angle FeIII–N–C exhibits a significant deviation from linearity (162.3(3)°).

The diffraction study of the compound 3b was carried out at T = 100 K (Table 2). The compound crystallizes with 20.5 molecules of crystal water, and two [Fe(CN)6{Fe{1a−2H}}6]Cl2 entities can be found within the unit cell. The center of symmetry is represented by the diamagnetic Fe(II)
central atom, coordinated by six cyanido ligands via the carbon atoms; the bond distances Fe−C vary in the range of 1.873−1.927 Å. Six peripheral Fe(III) centers are connected to the [Fe(CN)_6]^{4−} building block through the nitrogen donor atoms of the cyanido bridge (Figure 7). Every {Fe^{III}(1b−2H)} unit is structurally equivalent with that in the trans position, and the bond lengths of the {Fe^{III}(1c−2H)} coordination polyhedra indicate the high-spin state of Fe(III) at 100 K (Table 3). The shortest bonds are found for Fe−O (1.922(2)−1.957(2) Å); Fe^{III}−N(cyanido) bond lengths are comparable to those found in 3a, 3b, and Prussian blue; the longest bonds are detected for Fe−N(amine) = 2.191(2) Å. The three trans angles are considerably declined from linearity: O1−Fe2−N1 = 174.6(2), O2−Fe2−N20 = 167.5(1), O2−Fe2−N1 = 174.6(2). The angle between the central atom and cis-positioned oxygen donor atoms is O1−Fe−O2 = 91.0(1). Also in this complex, the Fe^{III}−C=N angle is very close to the flat angle (178.1°), but the C−N−Fe^{III} angle is considerably bent and reaches 168.9°.

### Table 3. Selected Bond Lengths in the Heptanuclear Compounds

<table>
<thead>
<tr>
<th></th>
<th>3a</th>
<th>3b center Fe2</th>
<th>3b center Fe3</th>
<th>3b center Fe4</th>
<th>3c</th>
</tr>
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<tr>
<td>Fe^{III}−O_{(a)}</td>
<td>1.882(4) [1.924(2)]</td>
<td>1.901(4)</td>
<td>1.941(5) [1.957(3)]</td>
<td>1.933(4)</td>
<td>1.922(2) [1.919(2)]</td>
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<tr>
<td>Fe^{III}−O_{(a)}</td>
<td>1.894(3) [1.951(3)]</td>
<td>1.922(4)</td>
<td>1.994(4) [1.946(3)]</td>
<td>1.966(4)</td>
<td>1.976(5) [1.967(2)]</td>
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<tr>
<td>Fe^{III}−N(===C)</td>
<td>2.077(4) [2.151(5)]</td>
<td>2.117(4)</td>
<td>2.105(5) [2.104(4)]</td>
<td>2.119(6)</td>
<td>2.089(7) 2.085(2) [2.091(2)]</td>
</tr>
<tr>
<td>Fe^{III}−N(===C)</td>
<td>2.088(4) [2.090(5)]</td>
<td>2.108(4)</td>
<td>2.127(5) [2.097(4)]</td>
<td>2.119(6) 2.118(7) 2.103(2) [2.103(2)]</td>
<td></td>
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<tr>
<td>Fe^{III}−N(H)</td>
<td>2.231(3) [2.236(3)]</td>
<td>2.266(3)</td>
<td>2.228(6) [2.233(4)]</td>
<td>2.224(5) 2.242(5) 2.191(2) [2.199(2)]</td>
<td></td>
</tr>
<tr>
<td>Fe^{III}−N(===C)</td>
<td>2.079(4)</td>
<td>2.110(4)</td>
<td>2.042(6) 2.058(6) 2.026(7) 2.053(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe^{III}−C(===N)</td>
<td>1.918(6)</td>
<td>1.937(7)</td>
<td>1.922(8) 1.873(8) 1.927(9) 1.901(3)</td>
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</table>

*For comparison, bond lengths in related mononuclear complexes 2d, 2b, and 2c are given in brackets. Bond distances at 293 K.*

The C−N−Fe^{III} angles show a slight deviation from the flat angle (173.4° on average). Single-crystal X-ray diffraction study of 3c revealed that the compound contains the heptanuclear dication [Fe(CN)_6]^{4−}[Fe^{III}(1c−2H)]_{3}^{2+}, 2 disordered Cl^− counteranions, and 10 molecules of crystal water (Table 2, Figure 8). The very central Fe(II) atom represents an inversion center of the heptanuclear dication complex, and the chromophore [Fe_{6}C] refers to a perfect octahedron with bond lengths of 1.901(3) Å. The centrosymmetric complex dication contains six peripheral structurally equivalent Fe(III) sites, and the bond lengths of the {Fe^{III}(1c−2H)} coordination polyhedra indicate the high-spin state of Fe(III) at 100 K (Table 3). The shortest bonds are found for Fe−O (1.922(2)−1.957(2) Å); Fe^{III}−N(cyanido) bond lengths are comparable to those found in 3a, 3b, and Prussian blue; the longest bonds are detected for Fe−N(amine) = 2.191(2) Å. The three trans angles are considerably declined from linearity: O1−Fe2−N1 = 174.6(2), O2−Fe2−N20 = 167.5(1), O2−Fe2−N1 = 174.6(2). The angle between the central atom and cis-positioned oxygen donor atoms is O1−Fe−O2 = 91.0(1). Also in this complex, the Fe^{III}−C=N angle is very close to the flat angle (178.1°), but the C−N−Fe^{III} angle is considerably bent and reaches 168.9°.

### 3.3. Magnetic Properties of Mononuclear Complexes.

The temperature variable magnetic investigation revealed a...
Isothermal magnetizations were measured at Below 50 K the $S = 5/2$ spin state affects intermolecular interactions. Indeed, in the case of compounds $\text{Fe}^{III}$ complexes, and in the temperature range of 300 K, the Curie law is obeyed (Figure 9). The effective magnetic moment $\mu_{\text{eff}}$ is constant in the temperature range of 50–300 K, and the room-temperature values of 5.85 for 2a, 5.80 for 2b, 6.04 for 2c, and 6.02 for 2d (in units of $\mu_B$) are close to the spin-only value expected for the $S = 5/2$ system ($5.92 \mu_B$). Below 50 K the $\mu_{\text{eff}}$ vs $T$ curve adopts a decreasing character which is a fingerprint of the zero-field splitting and intermolecular interactions: $\mu_{\text{eff}}$ at 2 K falls to 3.79 for 2a, 2.64 for 2b, 3.85 for 2c, and 3.13 for 2d (in units of $\mu_B$). Isothermal magnetizations were measured at $T = 2$ and 5 K up to $B = 4.5$ or 7 T, and experimental data corresponds to the $S = 5/2$ spin state affected by ZFS and/or weak antiferromagnetic interactions. Indeed, in the case of compounds 2b and 2d, the magnetic susceptibility passes through a rounded maximum $\gamma / 0.347$ when only the isotropic exchange applies.42

First, the magnetic properties of 2d are discussed. It results from X-ray analysis that a quasidimer is formed through the N···H–O hydrogen bonds (Supporting Information), and therefore, the following spin Hamiltonian was used in the magnetic data analysis

$$\hat{H}_u = -J(\hat{S}_1 \cdot \hat{S}_2) + \sum_{A=1}^{2} D(\hat{S}_{A,z}^2 - \hat{S}_{A}^2/3) + \sum_{A} \mu_B B_{0A} \hat{S}_{A,z}$$

(1)

where $= x$ and z. The first term stands for the isotropic exchange, the second term represents the zero-field splitting ($D$ = an axial ZFS parameter), and the last contribution is the Zeeman term. As a result, 36 magnetic levels $e_i = f(J, D, g, B_z)$ are used to calculate the partition function $Z_u$ and subsequently the components of the molar magnetization

$$M_{\text{mol,}u} = N_u k T \left( \frac{\partial \ln Z_u}{\partial B_z} \right)_T$$

(2)

Then the magnetization of the powder sample is computed as an average over three Cartesian components: $M_u = (2M_\alpha + M_\beta)/3$. The fitting procedure confirmed weak antiferromagnetic exchange ($< 0$) together with positive $D$ parameter; the final magnetic parameters are listed in Table 4.

### Table 4. Magnetic Parameters for Mononuclear Complexes

<table>
<thead>
<tr>
<th></th>
<th>2a</th>
<th>2a</th>
<th>2b</th>
<th>2c</th>
<th>2d</th>
</tr>
</thead>
<tbody>
<tr>
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<td>dimer</td>
<td>1D chain</td>
<td>1D chain</td>
<td>1D chain</td>
<td>dimer</td>
</tr>
<tr>
<td>$g$</td>
<td>1.98</td>
<td>1.98</td>
<td>2.00</td>
<td>2.04</td>
<td>2.01</td>
</tr>
<tr>
<td>$(D/\mu c)^{-1}$</td>
<td>+0.78</td>
<td>+0.68</td>
<td>+1.18</td>
<td>+0.61</td>
<td>+1.35</td>
</tr>
<tr>
<td>$(j/\mu c)^{-1}$</td>
<td>−0.30</td>
<td>−0.18</td>
<td>−0.40</td>
<td>−0.20</td>
<td>−0.38</td>
</tr>
</tbody>
</table>

X-ray structures of 2b and 2c point to formation of quasi 1D chains, in both cases through the N–H···Cl hydrogen bonds (Supporting Information). Thus far, there are no analytical equations for 1D uniform chains with $s = 5/2$ including zero-field splitting. Therefore, we used the finite-size closed chain (ring) model with five centers

$$\hat{H}_a = -J\left(\hat{S}_1 \cdot \hat{S}_5\right) + \sum_{A=1}^{K} D(\hat{S}_{A,z}^2 - \hat{S}_A^2/3) + \sum_{A=1}^{K} \mu_B B_{0A} \hat{S}_{A,z}$$

(3)

The number of magnetic centers ($K = S$) is supposed to be sufficient taking into account a very weak exchange as found in...
2d. Now, the number of magnetic energy levels is \((2s + 1)^3 = 7776\), and with the aim to speed up the computation, the symmetry-adapted basis set was generated using the spin permutational symmetry of the spin Hamiltonian\(^{47}\) and \(D_3\) point group of symmetry. Consequently, the whole interaction matrix is divided according to the irreducible representations to block \(A_1\) (\(N = 888\)), \(A_2\) (\(N = 672\)), \(E_1\) (\(N = 3108\)), and \(E_2\) (\(N = 3108\)). An analogous method has been recently applied to 1D zoom of low-temperature data. (Right) Isothermal magnetization data for 

The temperature variation of the effective magnetic moment for 3a–c is shown in Figure 10. It can be seen that the overall dependence is mutually similar; room-temperature data is close to the spin-only value expected for six uncoupled \(s = 5/2\) centers: \(\mu_\text{eff}/\mu_\text{B} = g(6s(s + 1))^{1/2} = 14.5\). On cooling, sample 3b exhibits a gradual increase of the effective magnetic moment that becomes rapid below 20 K. This behavior is a fingerprint of the overall ferromagnetic exchange. The inverse susceptibility is nearly linear, and it extrapolates to a zero value at slightly positive temperature (\(\Theta > 0\)).

Herein, we studied the magnetic properties of 3b in more detail. First, the purely isotropic model was used taking into account that the paramagnetic iron(III) centers are interconnected through diamagnetic hexacyanidoferrate(II). Therefore, the following spin Hamiltonian including the isotropic exchange and the Zeeman term was postulated to interpret magnetic properties (\(N = 6\))

\[
\hat{H} = -\sum_{A=1}^{N} \sum_{B<C}^{N} J(\hat{S}_A \cdot \hat{S}_B) + \sum_{A=1}^{N} \mu_B g \hat{S}_{Az}
\]

(4)

The advantage of this Hamiltonian is that an analytical expression for energy levels is available in the coupled basis set

\[
\epsilon(S, M_S) = -JS(S + 1)/2 + \mu_B g M_S
\]

(5)

where \(S\) is the final spin state and \(M_S\) its projection. The individual spin states \(S = 0, 1, \ldots, 15\) occur \(d_S = 111, 315, 475, 575, 609, 581, 505, 405, 300, 204, 126, 70, 35, 15, 5, 1\) and 1 times. Now, all 46,656 magnetic energy levels are used to calculate the molar magnetization

\[
M_{\text{mol}} = \frac{N_S \mu_B g \sum_{S_0} \sum_{M_{S_0} = -S}^{S_0} d_S M_S \exp[-\epsilon(S, M_S)/kT]}{\sum_{S_0} \sum_{M_{S_0} = -S}^{S_0} d_S \exp[-\epsilon(S, M_S)/kT]}
\]

(6)

The fitting procedure resulted in \((J/\hbar c) = +0.057\) cm\(^{-1}\) and \(g = 2.01\), thus confirming the weak ferromagnetic exchange present in 3b. The reconstructed data are displayed in Figure 11 (gray lines). The experimental reduced magnetization data \(M_{\text{mol}} = f(B/T)\) for two temperatures do not coincide; thus, we can suppose that also the magnetic anisotropy plays an important role in this compound, as demonstrated for 2a and 2b.

Therefore, the spin Hamiltonian was enriched by the single-ion zero-field splitting term as follows

\[
\hat{H} = -\sum_{A=1}^{N} \sum_{B<C}^{N} J(\hat{S}_A \cdot \hat{S}_B) + \sum_{A=1}^{N} D(\hat{S}_{Az}^2 - \hat{S}_{Az}^2/3) + \sum_{A=1}^{N} \mu_B g \hat{S}_{Az}
\]

(7)

Unfortunately, there is no analytical formula for energy levels, and all 46,656 magnetic levels must be treated numerically. In order to make this calculation feasible, the symmetry-adapted local basis set was generated using spin permutational symmetry of the spin Hamiltonian\(^{57}\) and \(D_3\) point group of symmetry. Consequently, the whole interaction matrix is divided according to the irreducible representations to blocks \(A_1\) (\(N = 4291\)), \(A_2\) (\(N = 3535\)), \(B_1\) (\(N = 4145\)), \(B_2\) (\(N = 3605\)), \(E_1\) (\(N = 15470\)), and \(E_2\) (\(N = 15610\)). Subsequently, magnetization was calculated using eq \(2\), and the fitting procedure resulted in \((J/\hbar c) = +0.052\) cm\(^{-1}\), \((D/\hbar c) = +0.49\) cm\(^{-1}\).
and g = 2.01 (Figure 11, black lines). The D parameter has a similar value to the herein reported mononuclear precursors 2a and 2b, and very good agreement was found between experimental and calculated isothermal magnetizations.

Samples 3a and 3c show slightly different behavior in comparison with 3b. First, there is a small decrease of the effective magnetic moment on cooling from room temperature, and then below 50 K a rapid increase occurs. This suggests that dominant ferromagnetic interactions are prevailing; however, also other phenomena must be present as the saturation value of $M_{\text{sat}}/N_\gamma \mu_B$ at 2 K is significantly reduced in contrast with the theoretical value of $M_{\text{sat}}/N_\gamma \mu_B = 30$ for $S_{\text{max}} = 30/2$. We found that this behavior was observed for several independently prepared batches of 3a and 3c, so it seems to us that it is an intrinsic property of these two compounds. To rationalize this behavior, several hypotheses were tested.

First, the phase purity of investigated samples was tested before magnetic investigation, so the presence of various polymorphic forms with a different number of lattice solvent molecules can be ruled out (Figure S9, Supporting Information). The second hypothesis is that subtle changes in the structure of 3a and 3c (the $\{\text{Fe}^{\text{II}}\text{CN}\}$ chromophore in complexes 3a and 3c is octahedral; in 3b is rhombohedral) may result in competition of ferromagnetic and antiferromagnetic interaction among Fe(III) centers through diamagnetic ferrocyanide (Figure S10, Supporting Information). However, this model is not capable to explain the temperature dependence of $\mu_{\text{eff}}/\mu_B$ and reduced saturation limit of the isothermal magnetization.

Another presumption is that a minor amount of iron(III) central atoms undergo a gradual spin cross-over phenomenon analogously, e.g., to $[\text{Cr}((\text{CN})\text{Fe}(\text{5L}))_3(\text{CN})_3](\text{5LH}_2 = N_N^N$-bis(1-hydroxy-2-benzylidene)-1,7-diamino-4-azaheptane).\(^{33}\) This would explain the decrease of $\mu_{\text{eff}}/\mu_B$ on cooling with subsequent increase of the effective magnetic moment due to ferromagnetic interaction in heptanuclear complexes and also reduction of the saturation limit of magnetization. For instance, a combination of $S = 1/2 \times \text{Fe} \ (\text{HS}, S = S/2, g = 2.0)$ and $1 \times \text{Fe} \ (\text{LS}, S = 1/2, g = 2.2)$ would result in a decrease of $\mu_{\text{eff}}/\mu_B$ from 14.5 to 13.4, and $M_{\text{sat}}/N_\gamma \mu_B$ would saturate to 26.1.

The last assumption is that a spin admixing is taking place. Spin-admixed states were observed in tetra-, penta-, and also hexacoordinated\(^{51}\) iron(III) complexes. In reported complexes, the peripheral Fe(III) centers are far from the octahedral environment owing to the different nature and lengths of Fe–O and Fe–N bonds, respectively. As the local excited state $^3A_2$ for a distorted hexacoordinate Fe(III) system is close to the ground state $^3A_2$, it is legitimate to deal with the spin-admixed states $^3(A_2, A_2')$.\(^{42,52,53}\) Such interaction would lead to mixing of $S = S/2$ and 3/2 states resulting in lowering the effective magnetic moment and also the saturation limit of the isothermal magnetization ($M_{\text{sat}}/N_\gamma \mu_B = 28$ and 25 for 3a and 3c, respectively). Accepting these data as the saturation values, the percentage of the intermediate $s$ is readily calculated as $P = 7$ and 15% (g = 2 is assumed). Despite the fact that a simplified model for spin-admixed states, the so-called Maltempo model,\(^{54,55}\) exists, it is beyond the scope of this work to extend such model to six interacting Fe(III) centers (the model space is spanned by $N = 10^6$ spin–orbital functions). As a result, we leave these last two hypotheses as a possible explanation of peculiar magnetic behavior of compounds 3a and 3c.

### 3.5. Mössbauer Spectroscopy

The transmission $^{57}$Fe Mössbauer spectra for compounds 2a, 3a, and 3b were collected at room temperature, and in the case of 2a and 3b also the low-temperature spectra were acquired. Analysis of the experiments for mononuclear complex 2a revealed single-component spectra with parameters typical for the high-spin Fe(III) coordination center at both temperatures, Table 5. The isomer shift decreases on increasing temperature, which can be attributed to the second-order Doppler effect,\(^{56}\) and also the reduction of quadrupole splitting upon heating is observed. In the case of the heptanuclear mixed-valence complex 3a, the room-temperature spectrum consists of two doublets: the dominant one is assigned to the high-spin Fe(III) centers and the minor one corresponds to the low-spin Fe(II) center. The former one has similar properties ($\delta$ and $\Delta E_Q$) as in the mononuclear complex 2a. Similar features were observed for the spectra of 3b taken at 300 K (Figure 12). Upon cooling the sample to 25 K, the increase of the isomer shift and quadrupole splitting is detected, which is in accordance with the temperature dependence of the Mössbauer spectra of 2a (Table S). The area ratio between two components of 3b at 25 K is 85:15, which is in excellent agreement with the expected value of 86:14 for the 6:1 ratio of the Fe(III)/Fe(II) ions in the heptanuclear complex. However, the area ratio is changed at 300 K to 77:23 for 3b and 79:21 for 3a, which might be caused by the different temperature dependence of Debye–Waller factors for the high-spin Fe(III) and low-spin Fe(II) centers.\(^{57–59}\)

<table>
<thead>
<tr>
<th>compound</th>
<th>T/K</th>
<th>$\delta$/mm s$^{-1}$</th>
<th>$\Delta E_Q$/mm s$^{-1}$</th>
<th>$A$/%</th>
<th>site assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>25</td>
<td>+0.37</td>
<td>0.63</td>
<td>100</td>
<td>Fe$^{\text{III}}$ HS</td>
</tr>
<tr>
<td>3a</td>
<td>300</td>
<td>+0.26</td>
<td>0.59</td>
<td>100</td>
<td>Fe$^{\text{III}}$ HS</td>
</tr>
<tr>
<td>3b</td>
<td>300</td>
<td>+0.28</td>
<td>0.64</td>
<td>79</td>
<td>Fe$^{\text{III}}$ HS</td>
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<tr>
<td></td>
<td></td>
<td>−0.26</td>
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</tr>
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</tr>
<tr>
<td></td>
<td></td>
<td>−0.04</td>
<td>0.20</td>
<td>15</td>
<td>Fe$^{\text{II}}$ LS</td>
</tr>
</tbody>
</table>

Four parameters refer to each deconvolution line: quadrupole splitting $Q$, isomer shift $\delta$, height, and width of the Lorenzian line; the parameter set is enlarged by a baseline. The area $A_i$ for individual quadrupole doublets has been evaluated by a numerical integration

### 4. CONCLUSIONS

Three new Prussian blue analogues—the heptanuclear mixed-valence iron complexes 3a, 3b, and 3c of the $[\text{Fe}^{\text{II}}(\text{CN})_6][\text{Fe}^{\text{III}}(1-2\text{b})\text{Cl}_3]_n\text{H}_2\text{O}$ general formula (3a with $n = 1$, 3b with $n = 20.5$, and 3c with $n = 10$)—were synthesized and structurally and spectrally characterized, and their magnetic properties were investigated in detail. Preparation of the heptanuclear complexes consists of three steps. In the first, the free pentadentate ligands 1a, 1b, and 1c were prepared by Schiff condensation between the derivatives of salicylaldehydes and various aliphatic triamines. In the next step, the “in situ” prepared ligands were reacted with the Fe(III) central ions and three mononuclear complexes 2a, 2b, and 2c of general formula $[\text{Fe}(1-2b)\text{Cl}]_n$ were formed (1–2a are doubly deprotonated forms of the Schiff base ligand 1). In the final part, the mononuclear $[\text{Fe}(1-2b)\text{Cl}]_n$ precursors are clustered on the $[\text{Fe}(\text{CN})_6]^{3-}$
bridging anion, which rises into formation of the heptanuclear mixed-valence complexes. Also, a mononuclear complex 2d of formula \([\text{Fe}(1_{-2d})\text{NCS}]\) was prepared for a comparative study with 2a and 3a.

Structural study of the mononuclear complexes showed coordination of one pentadentate \(\text{N}_2\text{O}_2\) Schiff-base ligand to a single \(\text{Fe(III)}\) central atom, and the sixth coordination site is occupied by the chlorido and/or thiocyanato ligand. Two oxygen donor atoms of the ligand moiety can coordinate the \(\text{Fe(III)}\) atom either in the cis or in the trans configuration. A detailed look into the crystal structures revealed the presence of intermolecular connectivity via hydrogen bonds. Magnetometry confirms that all mononuclear \(\text{Fe(III)}\) complexes exist in the high-spin state. Short Fe···Fe contacts were identified in the crystal structure of 2b, 2c, and 2d; these rationalize the presence of weak magnetic exchange interactions. The magnetic data (temperature and field dependence of the magnetization) were fitted to a dimeric model for 2d and a 1D chain model for 2b and 2c. For 2a both models were investigated (the monomeric model gave unsatisfactory results). The exchange interaction is weak-negative, whereas the axial zero-field splitting is weak-positive.

The crystal structures of 3a, 3b, and 3c contain a heptanuclear complex dication which consists of the ferrocyanide core whose octahedral nodes are coordinated by six peripheral \(\{\text{Fe(1}_{-2d})\}\) units. Compound 3a shows an unusual type of coordination, where one pentadentate ligand moiety interconnects two neighboring \(\text{Fe(III)}\) centers and forms intramolecular rings. Complexes 3b and 3c exhibit usual coordination modes with one pentadentate ligand capping one \(\text{Fe(III)}\) central atom. Magnetic investigation of heptanuclear complexes also revealed the high-spin state of all six \(\text{Fe(III)}\) coordination sites \((s = 5/2)\), whereas the very central \(\text{Fe(II)}\) site is in the low-spin state \((s = 0)\). At low temperature, the ferromagnetic exchange interactions stay evident owing to which the ground state is \(S = 15\) (30 unpaired electrons) for all three cases. Furthermore, the advanced theoretical treatment, including single-ion axial zero-field splitting parameter \(D_\text{Fe}\) for all six \(\text{Fe(III)}\) ions, was found necessary for proper description of the experimental magnetic data. Direct comparison of \(D\) in mononuclear precursor 2b \((D_\text{Fe} = +1.18\ \text{cm}^{-1})\) and final heptanuclear compound 3b \((D_\text{Fe} = +0.49\ \text{cm}^{-1})\) reveals information about the change of the magnetic anisotropy upon coordination of building blocks into more complex structures, information which is important for the class of single-molecule magnets and the height of their energy barrier for spin reversal. The magnetic behavior of 3a and 3c is very similar and slightly differs from 3b. We assume that besides the dominant ferromagnetic interaction, the unusual minimum in the \(\mu_\text{eff} vs T\) curve indicates the presence of either gradual and incomplete spin transition or spin-admixing effect. Mössbauer spectroscopy of the mononuclear complex 2a confirmed the high-spin state of the \(\text{Fe(III)}\) central atom which is in agreement with the magnetic data. For heptanuclear complexes 3a and 3b it revealed the presence of two different doublets for both compounds. The first major doublet is related to six \(\text{Fe(III)}\) high-spin coordination sides and the second minor doublet refers to the low-spin very central \(\text{Fe(II)}\).

Only two reports of X-ray structural data have been reported for a compound analogous to 3a, 3b, and 3c so far,24,26,35 so that the present study enriches the structural and magnetic data for this class of star-like high-spin molecular compounds.

**ASSOCIATED CONTENT**

Supporting Information

Details of the infrared and ESI ToF spectra and structural and magnetic information. The cif files for the reported structure can be retrieved from the Cambridge Crystallographic Data center. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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