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Spectroscopic and Magnetic Properties of a Series of μ-Cyano Bridged Bimetallic Compounds of the Type M II–NC–Fe III (M = Mn, Co, and Zn) Using the Building Block [Fe III(CN) 3imidazole] 2–

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In this contribution, we describe the preparation and single-crystal X-ray diffraction of a new building block for bimetallic solid state materials. X-ray diffraction data of these complexes indicate that (PPh 3) 2[Fe(CN) 3imidazole] · 2H 2O crystallizes in the triclinic space group Pt with a = 9.8108(15) Å, b = 11.1655(17) Å, c = 23.8484(8) Å, α = 87.219(2)°, β = 85.573(2)°, γ = 70.729(2)°, and Z = 2, while its precursor Na 3[Fe(CN) 3(en)] · 5H 2O crystallizes in the monoclinic space group P2 1/n with a = 8.3607(7) Å, b = 11.1624(9) Å, c = 17.4233(14) Å, β = 90.1293(9)°, and Z = 4.

Spectroscopic and magnetic properties of a series of bimetallic materials obtained are reaction of the complex [Fe(CN) 3imidazole] 2– with hydrated transition metal ions [M(H 2O) 6] 2+ (M = Mn, Co, Zn; n = 4 or 6). The new bimetallic materials obtained are [Co(H 2O) 6][Fe(CN) 3imidazole] · 2H 2O (1), [Mn(CH 3OH) 2][Fe(CN) 3imidazole] (2), Zn[Fe(CN) 3imidazole] · 2H 2O (3), and [Mn(bpy)][Fe(CN) 3imidazole] · H 2O (4). All of the complexes crystallize in the orthorhombic system. X-ray single-crystal analysis of the compounds identified the Imma space group with a = 7.3558(10) Å, b = 14.852(2) Å, c = 13.767(9) Å, and Z = 4 for 1; the Pnma space group with a = 7.385(5) Å, b = 13.767(9) Å, c = 14.895(10) Å, and Z = 4 for 2; the Pnma space group with a = 13.783(2) Å, b = 7.167(11) Å, c = 12.599(2) Å, and Z = 4 for 3; and the Pnma space group with a = 13.196(3) Å, b = 7.2248(16) Å, c = 22.294(5) Å, and Z = 4 for 4. The structures of 1, 2, and 4 consist of two-dimensional network layers containing, as the repeating unit, a cyclic tetramer [M 2Fe 2(CN) 6] (M = Mn, Co). H bonding between the layers in the structure of 1 results in a quasi-three-dimensional network. The structure of 3 was found to be three-dimensional, where all of the cyano ligands are involved in bridging between the metal centers. The bridging character of the cyano is confirmed spectroscopically. The magnetic properties have been investigated for all of the bimetallic systems. Compound 1 shows ferromagnetic behavior with an ordering temperature at 25 K, which is higher than the corresponding Prussian Blue analogue Co 3 [Fe(CN) 6] · 2H 2O. Compound 2 shows weak ferromagnetic behavior and an interlayer antiferromagnetic character, while 3, as expected, shows paramagnetic character due to the diamagnetic character of Zn 2+. Compound 4 shows antiferromagnetic behavior.

Introduction

Strong σ-donor properties and the ability to coordinate via the C or N atom or both have placed the CN− ligand centrally in the preparation of ligand-bridged multimetallic complexes. This is especially the case for Prussian Blue analogues where the mixing of a hydrated transition metal ion, e.g., [M(H 2O) 6] 2+, with hexacyanoferrate ions [Fe(CN) 6] 3− has provided bimetallic compounds of the type M 2[Fe(CN) 6] · zH 2O (where M is a transition metal), the so-called Prussian Blue analogues. 4 Importantly, the short intranuclear separation provided for by the CN− ligand allows for such bimetallic systems to exhibit magnetic and optical properties not observed in the individual components. Bimetallic complexes in particular are of special interest for their electro- and optomagnetic properties because of their potential application in information storage and quantum computing. However, the study of such systems has been hampered by the insolubility of such compounds and the difficulty encountered in obtaining single-crystalline materials suitable for X-ray structure determination.
The physical behavior of the Prussian Blue analogs was shown to be influenced by the degree of defects in their structure. These defects can be controlled by the proportion and/or type of alkali cation employed during preparation. The [Fe(CN)₆]³⁻ paradigm can also be extended through the use of a substituted cyanoferrate complex as a building block. In addition to tuning the molecular properties, this also results in changes to the structural properties of the bimetallic material formed. The dimensionality of these bimetallic systems can be tuned further by adding a multidentate ligand to the system. To date, the substituted pentacyano ferrate complex of the type [Fe(CN)₅L]⁻ has been seen most widespread use is sodium nitroprusside ([Fe(CN)₅NO]²⁻), not least because the photoirradiation of this anion has been shown to enhance the magnetization of the nickel nitroprusside complex of the type [Fe(CN)₅L]²⁻.

The complex Li₂[Fe(CN)₅imidazole], in which the Fe(III) ion is coordinated by five cyano ligands and one of the nitrogen atoms of the imidazole ligand, is potentially an alternative to nitroprusside. In this report, the [Fe(CN)₅imidazole]⁻ ion (Figure 1) is employed as a building block in the preparation of a new series of bimetallic compounds in which the cyano ligands form bridges between the metal centers. The presence of the imidazole ligand in the structure can influence the bimetallic compounds formed in terms of their general properties compared to the corresponding Prussian Blue analogs.

The new cyanide-bridged bimetallic materials of the type M[Fe(CN)₅]₃[Fe(CN)₅imidazole]:xH₂O (M = Mn, Co, and Zn) formed are characterized by single-crystal X-ray diffraction, vibrational and electronic spectroscopy, and magnetic

**Experimental Section**

Material. Chemicals were used as received unless stated otherwise. Li₃[Fe(CN)₅imidazole]-5H₂O was prepared by metathesis of (PPh₄)₂[Fe(CN)₅imidazole]-2H₂O with LiClO₄ in acetonitrile.

**Caution!** Perchlorate salts are potentially explosive. Only small quantities should be prepared and must be handled with suitable protective safeguards.

**Caution!** Sources of HCN should be treated with care and used in small quantities. Contact with acids should be avoided.

Na₃[Fe(CN)₅,(en)]·5H₂O. Na₃[Fe(CN)₅(en)]·5H₂O was prepared by modification of the method of Olabe and Ayamino: Na₃[Fe(CN)₅(NO)₂]·3H₂O (6 mmol, 2 g) and sodium acetate (12 mmol, 1 g) were dissolved in a mixture of water (20 mL) and ethanol (15 mL). After 30 min, an excess of ethylenediamine (10 mL) was added to the solution, and the solution was heated between 40 and 60 °C with stirring. After 30 min, an excess of ethanol (15 mL) was added to the solution. The solution was filtered hot and allowed to cool to room temperature. Yellow crystals of Na₃[Fe(CN)₅(en)]·5H₂O were obtained following slow evaporation at room temperature and were collected by filtration. Yield: 86% (2.35 g). Anal. Caled for Fe₃C₃N₇Na₃H₁₈O₅Na₃[Fe(CN)₅(en)]·5H₂O: C, 20.76; H, 4.48; N, 24.20. Found: C, 20.97; H, 4.56; N, 23.79%.

PPh₄[Fe(CN)₅(imidazole)]·2H₂O. Air was bubbled for 30 min through an aqueous solution (20 mL) of Na₃[Fe(CN)₅]C₂H₅N₃[5H₂O (1.2 mmol, 1 g). Over 2 h, a color change from yellow to orange was observed. The solution was added slowly to a stirred solution (50 mL 3:2 water/ethanol) of tetraphenylphosphonium chloride (2.4 mmol). Red brownish crystals of (PPh₄)₂[Fe(CN)₅-imidazole]·2H₂O formed upon standing (56%, 1.35 g). Anal. Caled for FeC₇N₅P₄H₉O₅: C, 69.43; H, 4.99; N, 10.12. Found: C, 69.52; H, 4.88; N, 10.08%.

**Preparation of Bimetallic Materials.** Co(H₂O)₆[Fe(CN)₅imidazole]·2H₂O (1). Compound 1 was obtained by slow diffusion between two test tubes (a small test tube placed within a larger test tube) of an aqueous solution of the Li₃[Fe(CN)₅imidazole] (100 mg) in the inner test tube and an aqueous solution of CoCl₂·6H₂O (100 mg) in the larger test tube. The solution was heated at 42 °C and allowed to stand in the dark. Dark red block crystals of 1 were collected after two weeks (yield 30 mg). Anal. Caled for C₆H₁₄O₃Fe₃N₇O₂·2H₂O (1): C, 49.86; H, 3.14; N, 25.47. Found: C, 49.96; H, 3.20; N, 25.54%.

Mn(CH₃OH)₆[Fe(CN)₅imidazole] (2). The preparation of complex 2 was carried out using a procedure similar to that used for 1. A total of 2 mL of an aqueous solution of Mn(NO₃)₂·4H₂O (100 mg) and 2 mL of an aqueous solution of Li₃[Fe(CN)₅imidazole] (100 mg) were each gently layered on opposite sides of an H tube initially filled with 12 mL of methanol. The solution was maintained at 42 °C. Dark red crystals of 2 were collected after two weeks (yield 97 mg). Anal. Caled for C₆H₁₄O₃MnFe₃N₇O₂·2H₂O (2): C, 32.20; H, 3.34; N, 26.28. Found: C, 31.95; H, 2.88; N, 26.42.

Zn[Fe(CN)₅imidazole]·H₂O (3). The preparation of 3 was carried out as described for 1 except that ZnCl₂·6H₂O (100 mg) was used in place of CoCl₂·6H₂O. Dark red (3) crystals were collected after one week (yield: 110 mg). Anal. Caled for


Table 1. Crystal Data and Numerical Details of the Structure Determination of (PPh₄)₂[Fe(CN)₅C₃H₄N₂]·2H₂O and Na₃[Fe(CN)₅(en)]·5H₂O

<table>
<thead>
<tr>
<th>Property</th>
<th>(PPh₄)₂[Fe(CN)₅C₃H₄N₂]·2H₂O</th>
<th>Na₃[Fe(CN)₅(en)]·5H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>2[C₄H₈N₄Fe]·(C₄H₄N₅Fe)·2(H₂O)</td>
<td>3Na+(C₄H₈N₄Fe)·5(H₂O)</td>
</tr>
</tbody>
</table>

| fw (g mol⁻¹)                  | 968.34                      | 405.08                |
| crystal syst.                 | triclinic                   | monoclinic            |
| space group                   | P flattened                 | P₂₁/n                 |
| a, b, c/Å                     | 9.8108(15), 11.1655(17), 23.848(4) | 8.3607(7), 11.1624(9), 17.4233(14) |
| α, β, γ/deg                   | 87.219(2), 85.573(2), 70.729(2) | 90.1293(9)            |
| vol (Å³)                      | 2457.9(7)                   | 1626.0(2)             |
| Θ range unit cell: min–max (deg); refins | 2.49–28.94; 5165 | 2.70–29.46; 7779 |
| Z                             | 2                           | 4                     |
| D₀ (g cm⁻³)                   | 1.309                       | 1.655                 |
| F(000)                        | 1010                        | 832                   |
| μ(Mo Kα) (cm⁻¹)               | 4.22                        | 10.4                  |
| color, habit                  | red-brown, parallelepiped   | yellow, black         |
| approx. cryst. dimension, mm  | 0.53 × 0.38 × 0.32          | 0.49 × 0.34 × 0.23    |
| temp (K)                      | 100(1)                      | 100(1)                |
| Rf where F₀ ≥ 4σ(F₀)           | 0.0514                      | 0.0287                |
| wR₂                           | 0.1739                      | 0.0745                |
|                              |                             |                       |

C₃H₄ZnFe(C₅N₅)·0.54(H₂O)·3. Na₃[Fe(CN)₅(en)]·5H₂O. Mn(bpy)[Fe(CN)₅imidazole]·H₂O (4). A total of 3 mL of an aqueous solution containing MnCl₂·4H₂O (30 mg) and 2,2'-bipyridine (24 mg) was layered gently at the bottom of a test tube. A total of 2 mL of water was added as a second layer, and a third layer of 4 mL of an ethanolic solution of (Ph₄P)₂[Fe(CN)₅imidazole]·2H₂O was carefully layered over the second layer. The solution was allowed to stand, and red brown platelet crystals of 4 were collected after 2 weeks (yield 90 mg). Anal. Calcd for C₃H₄ZnFe(C₅N₅)·0.54(H₂O)·3. Na₃[Fe(CN)₅(en)]·5H₂O: C, 28.81; H, 1.54; N, 29.05. The solution was allowed to stand, and red brown platelet crystals of 4 were collected after 2 weeks (yield 90 mg). Anal. Calcd for C₃H₄ZnFe(C₅N₅)·0.54(H₂O)·3. Na₃[Fe(CN)₅(en)]·5H₂O: C, 28.81; H, 1.54; N, 29.05.

SMART APEX CCD diffractometer. The unit cell was identified as triclinic, space group P flattened for (PPh₄)₂[Fe(CN)₅C₃H₄N₂]·2H₂O. The E-statistics were indicative of a centrosymmetric space group. Reduced cell calculations did not indicate higher metric lattice symmetry. Examination of the final atomic coordinates of the structure did not yield extra crystallographic or metric symmetry elements. The hydrogen atoms of the phenyl groups for (PPh₄)₂[Fe(CN)₅C₃H₄N₂]·2H₂O were generated by geometrical considerations, constrained to idealized geometries, and allowed to ride on the carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. The unit cell was identified as monoclinic for Na₃[Fe(CN)₅(en)]·5H₂O. The space group P₂₁/n was derived from the systematic extinctions. A difference Fourier synthesis resulted in the location of all of the hydrogen atoms, and isotropic displacement parameters were refined for Na₃[Fe(CN)₅(en)]·5H₂O. Crystallographic data and numerical details on the structure determination of (PPh₄)₂[Fe(CN)₅C₃H₄N₂]·2H₂O and Na₃[Fe(CN)₅(en)]·5H₂O are given in Tables 1 and 2, respectively. Tables of atom positions, displacement parameters, distances, and angles and tables of F₀, Fc and σ(F₀) are available in the Supporting Information.

The overall data collection time was 7.8 h for 1, 3, and 4 and 17.9 h for compound 2. The crystal used in the experiment for compound 2 diffraction weakly; hence, a 30 s exposure time for each image was employed. The structures were solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF-08. Final refinement on F² was carried out by full-matrix least-squares techniques. The positional and (an)isotropic displacement parameters for the non-hydrogen atoms were refined on F² with full-matrix least-squares procedures minimizing the function Q = Σ[w(Fo² - k(Fc²))²], where w = 1/[σ²(Fo²) + (aP)² + bP], P = [max(Fo², 0) + 2Fc²]/3, and F₀ and Fc are the observed and calculated structure factor amplitudes, respectively. Apart from the hydrogen of solvate water molecules in 3, which were not detected, the hydrogen atoms were generated.

References:
Selected Interatomic Distances (Å) and Bond Angles (deg) of (PPh₄)₂[Fe(CN)₅(im)]·2H₂O

<table>
<thead>
<tr>
<th>Bond/Distance</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–N₆</td>
<td>1.999(2)</td>
</tr>
<tr>
<td>N₆–C₆</td>
<td>1.335(4)</td>
</tr>
<tr>
<td>Fe–C1</td>
<td>1.964(3)</td>
</tr>
<tr>
<td>N₆–C₈</td>
<td>1.382(4)</td>
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<tr>
<td>Fe–C₂</td>
<td>1.934(3)</td>
</tr>
<tr>
<td>N₇–C₆</td>
<td>1.339(4)</td>
</tr>
<tr>
<td>Fe–C₃</td>
<td>1.936(3)</td>
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<tr>
<td>N₇–C₇</td>
<td>1.365(4)</td>
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<tr>
<td>Fe–C₄</td>
<td>1.961(3)</td>
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<tr>
<td>C₇–C₈</td>
<td>1.360(4)</td>
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<tr>
<td>Fe–C₅</td>
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<td>N₁–C₁</td>
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<td>109.3(3)</td>
</tr>
<tr>
<td>Fe–C₁–N₁</td>
<td>178.7(3)</td>
</tr>
</tbody>
</table>

Results and Discussion

Structural Characterization of (PPh₄)₂[Fe(CN)₅(im)]·2H₂O. (PPh₄)₂[Fe(CN)₅(im)]·2H₂O was isolated by slow evaporation of a solution of Na₃[Fe(CN)₅(en)]·5H₂O and tetraphenylphosphonium chloride in water as large red brown crystals. These crystals have a triclinic unit cell with two molecules per unit cell. The asymmetric unit contains one formula unit, consisting of five moieties: an anionic Fe complex, two tetraphenylphosphonium cations, and two water molecules. These moieties are linked by hydrogen bonds, forming an infinite two-dimensional network along the base vectors [0 0 1] and [0 0 0]. The solid state structure of complex (PPh₄)₂[Fe(CN)₅(im)]·2H₂O is shown in Figure 2. It consists of five cyano (CN⁻) ligands and one imidazole (C₅H₄N₂) ligand coordinated to the iron center (FeIII). Four of the CN⁻ ligands are in the equatorial plane, while the fifth CN⁻ ligand is collinearly axial with the imidazole group. Two [Fe(CN)₅(im)]⁻ moieties are bonded together through a H bond in N7–H7⋯N3, forming asymmetric chains along the c axis and separated by two PPh₄ cations.

The Fe–C bond lengths are between 1.934(3) and 1.964(3) Å, as expected for a low-spin FeIII mononuclear complex (e.g., [Fe(CN)₅NO]²⁻ (1.927–1.971 Å)).

(20) A study of the mechanism for the formation of the imidazole ring from ethylene diamine will be reported elsewhere.

The unit cell (Figure 4). The structure of Clays, K.; Brunschwig, B. S.; Harris, J. A.; Garin, J.; Orduna, J. J. Am. Chem. Soc. 2006, 128, 12192–12204.

(0.03 Å; where MeQ⁺ is N-methyl-4,4’-bipyridinium), which is less, possibly due to the stronger π-acceptor capability of the MeQ⁺ ligand compared to ethylene diamine or ammonia.

Description of the Structures 1–4. Single crystals of materials 1–4 were obtained in general by the slow diffusion of solvents. For each complex, several approaches to crystallization were attempted until crystals suitable for X-ray diffraction analysis were obtained.

Structure of Co(H₂O)₂[Fe(CN)₅imidazole]·2H₂O (1). Co(H₂O)₂[Fe(CN)₅imidazole]·2H₂O (1) crystallizes in the orthorhombic space group Imma with four formula units in the unit cell (Figure 4). The structure of 1 is made up of neutral dinuclear entities of the formula [Co⁺(H₂O)₂(Fe⁺(CN)₅)imid]. The unit [Fe⁺(CN)₅]⁻ acts as a monodentate ligand to four trans-diaquacobalt(II) units through its four cyanide groups in equatorial positions; the axial cyanide ligand does not act as a bridging ligand. This leads to a two-dimensional network with all five cyanide ligands acting as π-back-bonding, which crystallizes in a face-centered space group forming a three-dimensional network with all five cyanide ligands acting as π-back-bonding, and with the cobalt coordinated to one water molecule.

The average of N–Co and O–Co distances in 1 are 2.107(2) and 2.119(9) Å, respectively, forming a bipyramidal shape with the N–Co bond constituting the planar base. The Fe ion is coordinated to cyanide ligands and one N atom from the imidazole ligand. The Fe–N bond (1.958(5) Å) is affected by π-back-bonding, which is less, possibly due to the stronger π-acceptor capability of the MeQ⁺ ligand compared to ethylene diamine or ammonia.

Table 4. Crystallographic Data for Co(H₂O)₂[Fe(CN)₅imidazole]·2H₂O (1), Mn(CH₃OH)₂[Fe(CN)₅imidazole] (2), Zn[Fe(CN)₅imidazole]·H₂O (3), and Mn(bpy)[Fe(CN)₅imidazole]·H₂O (4)
results in shortening by 0.032 Å of the Fe–Ctrans bond (from the CN situated trans to the imidazole) compared to the other Fe–Ceq bonds (1.951(3) Å). This leads to the distortion of the octahedral arrangement around the Fe ions, with the iron center located above the plane of the equatorial cyano ligands toward the imidazole (N–Fe–Ceq > 90°, Ceq–Fe–Ctrans < 90°). The presence of two different types of octahedra around the Fe and Co cations results in a serpentine arrangement of the crystal lattice (Figure 5). The serpentine appearance of the structure is also due to the deviation in planarity, which is associated with the divergence of the Co–N–C angle from 180° (178.8(2)°) compared to that of the N–Ceq–Fe angle (177.7(3)°).

The interlayer is occupied by overlapping imidazole ligands from each plane along the a axis and by water molecules. The interplanar imidazole–imidazole distance is 3.683 Å. The intramolecular Fe–Co distance through the cyano bridges is 5.201(1) Å, whereas the shortest interlayer metal–metal distances are 7.725(2) Å for Fe···Fe, 8.312(2) Å for Co···Co, and 7.957 Å and 8.312(2) Å for Fe···Co. Adjacent layers are connected through hydrogen bonds, yielding a quasi-3D network, i.e., hydrogen bonding between interlayer water molecules and the nonbridging trans-cyanide of the Fe ion of one layer and nitrogen of the imidazole ligand, as shown in Figure 6. The H-bond distances are 2.806(3) Å for OCo···OH2O, 3.032(9) Å for OCo···Nim, and 2.999(4) Å for OH2O···NCNtrans

### Structure of Mn(CH3OH)2[Fe(CN)5imidazole] (2).

The complex Mn(CH3OH)2[Fe(CN)5imidazole] crystallizes in the orthorhombic space group P212121 with four formula units in the unit cell (Figure 7). An extended two-dimensional neutral network is formed by cyclic tetrameric [–Mn–NC–Fe–]2 units with Fe and Mn atoms at the corners of a deformed square grid along the ab plan (Figure 8). This is in contrast to Mn[Fe(CN)5NO]·xH2O, which, although it has been reported to crystallize in either the monoclinic29 or orthorhombic30 space group, shows a three-dimensional network structure with all five cyanides bridging the manganese and iron ions. In 2, the [Fe(CN)5imidazole]2– ions are connected to four Mn(CH3OH)23+ cations through the four equatorial CN– ligands, while Mn(CH3OH)22+ cations are coordinated to four [Fe(CN)5imidazole]2– anions through the nitrogen atom of the equatorial CN– ligands.

The [Fe(CN)5imidazole]2– ions exhibit a distorted octahedral configuration of ligands around the iron with the

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four symmetrically equivalent equatorial bridging CN⁻ ligands slightly bent toward the axial cyanide (opposite the imidazole group). The average Fe–C and Fe–N bond lengths are 1.937(17) and 1.958(8) Å, respectively.

The MnII ion is in an octahedral environment coordinated to four equatorial cyanides via the nitrogen and to two axial oxygen atoms from methanol with average Mn–N and Mn–O bond distances of 2.20(13) and 2.20(4) Å, respectively. Due to the nonplanarity (Figure 8) of the structure, the metal–metal (Mn⋯Fe) bond intralayer distances are irregular and vary between 5.006(4) and 5.288(15) Å and distances of 7.532(6) Å (Fe⋯Fe) and 8.818(7) Å (Mn⋯Mn) between two adjacent layers.

Structure of Zn[Fe(CN)₅imidazole]·H₂O (3). Zn[Fe(CN)₅imidazole]·H₂O crystallizes in the orthorhombic space group Pnma with four formula units in the unit cell (Figure 9). X-ray crystallographic analysis reveals that 3 is composed of a 3D coordination network (Figure 10). The view along the b axis shows formation of an irregular basic square with a Zn₂Fe₃(CN)₄ structural motif. The N–Zn–N (86.20(8)° and 88.56(8)°) and C–Fe–C (92°) angles form a distorted square. The [Fe(CN)₅imidazole]⁻ unit is a distorted octahedral complex with an Fe–N bond distance of 1.966(3) Å and a Fe–Cₜₐₜₜ bond equal to 1.919(4) Å, which is shorter than the other Fe–Cₜₐₜₜ bond distances (1.942(2) Å). The [Fe(CN)₅imidazole]⁻ moiety acts as a penta-monodentate ligand toward the zinc atoms through its five cyanide ligands. The zinc atom is penta-coordinated by five cyano nitrogens. The irregular value of Zn–N–C angles (155.7(3), 174.4(2), and 175.7(2)°) results in a distorted ZnN₅ square pyramidal structure around the Zn atom. The values of the metal–metal Fe⋯Zn bond distances are 4.97(1) Å through the axial CN, 5.135(1) Å, and 5.836(1) Å through the equatorial CN, which are comparable with that reported for Zn[Fe(phenanthroline)₃(CN)₅]·4H₂O (5.132 and 5.187 Å).31 Two nitrogens in

Figure 7. Structure of 2. Thermal ellipsoids are drawn at 50% probability level.

Figure 8. Perspective view of 2 along the a axis. The metal centers are represented in blue (Mn) and olive (Fe).

Figure 9. Structure of Zn[Fe(CN)₅imidazole]·H₂O (3). Thermal ellipsoids are drawn at the 50% probability level.

the longest edges of the tetracuclear unit form hydrogen bonds with water molecules.

**Structure of Mn(bpy)[Fe(CN)₅imidazole].H₂O (4).** Mn-(bpy)[Fe(CN)₅imidazole]·H₂O crystallizes in the orthorhombic space group Pnma with four formula units in the unit cell. The structure of 4 is comprised of one central Mn(CN)₅imidazole⁻ anion linked to four Mn(bpy)²⁺ cations through its four equatorial CN⁻ ligands, forming an extended two-dimensional network along the a and b axes (Figure 11). The network system is formed by cyclic [-Mn–CN–Fe–]₂ units of deformed square grids with metal atoms at the corners. The Fe site exhibits a distorted octahedral environment around the Mn ion is distorted octahedral, with the four N’s of the CN resulting in a sinusoidal shape to the layers with Mn–N2–C2, 157.6(2)°, and Mn–N3–C3, 163.2(3)° (Figure 12). The Fe–Mn distance is 5.1930(14) Å.

The deformed planes are antiparallel to each other, and the neighboring sheets overlap along the b axis via the bipyridine ligands, which are separated by 3.66 Å. The intrachain metal–metal separations through the bridging CN ligand are 5.193–5.298 Å. The shortest interlayer separation of the two adjacent metal cations (Mn···Mn) is 8.738(2) Å, whereas the longest separation is 11.719 Å (Fe···Fe).

**FTIR and Raman Spectroscopy.** The FTIR and Raman spectra of complexes recorded in the 4000–5000 cm⁻¹ range are shown in Figure 13. Their spectra show the bands of the imidazole ligand at 3364 cm⁻¹ (υN–H), 3145 cm⁻¹ (υC–H), 1539 cm⁻¹, 1507 cm⁻¹, 1428 cm⁻¹, 1323 cm⁻¹, 1178 cm⁻¹ and 1064 cm⁻¹ (δN–H), 1260 cm⁻¹, 1120 cm⁻¹, 1098 cm⁻¹ (δC–H), and 756 cm⁻¹ (υC–H), comparable to the data reported for imidazole complexes of the type [M(Him)₆](NO₃) and [M(Him)₆](ClO₄)₂ (M = Co, Ni, Fe, and Zn). The bridging by the CN⁻ ligands in the mixed metal systems presented here is confirmed by variation observed in the CN⁻ stretching frequencies in the range of 2200–2000 cm⁻¹ (Table 5). In the FTIR spectra of the complexes, absorptions are observed at 2153 and 2115 cm⁻¹ (1), 2154 and 2075 cm⁻¹ (2), 2167 cm⁻¹ (3), and 2146 and 2116 cm⁻¹ (4). Overall, the absorptions are at higher wave-numbers than the cyano stretching vibrations of (Ph₄P)₂-[Fe(CN)₅imidazole]·2H₂O (2104 and 2122 cm⁻¹). The higher frequencies of υCN that appear at 2153, 2145, 2167, and 2169 cm⁻¹ for complexes 1, 2, 3, and 4, respectively, are assigned to the stretching vibration of the equatorial CN⁻ ligands that form the M–CN–M’ bridges. Since the CN⁻ stretching frequencies of these CN groups depend on the electronegativity, crystal field stability, oxidation number,


and coordination number of the metal ion,\(^{34,35}\) then \(\nu_{\text{CN}}\) of Fe\(^{III}\)–CN–Zn\(^{II}\) > \(\nu_{\text{CN}}\) of Fe\(^{III}\)–CN–Co\(^{II}\) > \(\nu_{\text{CN}}\) of Fe\(^{III}\)–CN–Mn\(^{II}\) > \(\nu_{\text{CN}}\) of Fe\(^{III}\)–CN. The frequencies at 2115 cm\(^{-1}\) (1) and 2116 cm\(^{-1}\) (4) are assigned as the nonbridging CN stretching vibrations by comparison with the complex (PPh\(_4\))\(_2\)[Fe(CN)\(_5\)imidazole]).

The trends observed in the FTIR absorption spectra are observed also in the powder Raman spectra of the materials. In all cases, the Raman CN bands are at higher wavenumbers than those of the parent complex (PPh\(_4\))\(_2\)[Fe(CN)\(_5\)imidazole].


**Table 5.** FTIR and Raman CN Stretching Bands

<table>
<thead>
<tr>
<th></th>
<th>FTIR</th>
<th>Raman</th>
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<tbody>
<tr>
<td>1 (CoFe)</td>
<td>2151, 2145(sh), 2076</td>
<td>2169, 2151(sh)</td>
</tr>
<tr>
<td>2 (MnFe)</td>
<td>2143, 2070</td>
<td>2163, 2141 (sh)</td>
</tr>
<tr>
<td>3 (ZnFe)</td>
<td>2165, 2094</td>
<td>2186, 2168</td>
</tr>
<tr>
<td>4 (Mn(bpy)(_2)Fe)</td>
<td>2145, 2128, 2116, 2053</td>
<td>2160, 2116</td>
</tr>
<tr>
<td>5 (LiFe)</td>
<td>2138(sh), 2129</td>
<td>2128, 2122, 2116, 2108</td>
</tr>
</tbody>
</table>

**Figure 13.** ATR-FTIR (upper) and Raman (\(\lambda_{\text{exc}}\) 785 nm, lower) spectra of the CN stretching region (left) and full spectrum (right) for 1–4 and Li\(_2\)[Fe(CN)\(_5\)imidazole]] (Li\(^{+}\)).
the imidazole is oriented with its plane bisecting the \(x/y\) plane formed by the equatorial cyano ligands resulting in pseudo \(C_{3v}\) local symmetry. For the corresponding \(\text{PPh}_4^+\) salt of \([\text{Fe(CN)}_5(\text{imidazole})]^{2-}\), the imidazole is oriented such that the plane is coincident with the \(x/z\) molecular axis (and hence has \(C_{2v}\) local symmetry). For 4, additional bands are observed corresponding to the 2-2’-bipyridine ligand coordinated to the manganese center.

**UV/Vis**–**NIR Spectroscopy.** The UV/vis–NIR diffuse reflectance spectra of all of the compounds as intimate mixtures in BaSO₄ are shown in Figure 14. \((\text{Ph}_4\text{P})_2[\text{Fe(CN)}_5\text{(imidazole)}]\cdot 2\text{H}_2\text{O}\) shows absorption bands in the solid state with maxima at 268, 356, and 415 nm and a shoulder at 528 nm. In the NIR region (1400–2500 nm), overtone IR absorption bands of cyano and \(\text{PPh}_4\) moieties are observed. The absorption at ca. 400 nm is assigned as a LMCT band of the \([\text{Fe(CN)}_5\text{(imidazole)}]^{2-}\) by comparison with the solution spectrum of the complex. The spectra of the bimetallic complexes all show an absorption band at longer wavelengths compared to that of the \((\text{Ph}_4\text{P})_2[\text{Fe(CN)}_5\text{(imidazole)}]\cdot 2\text{H}_2\text{O}\). In the visible region, a broad intense band is centered at 250 nm is assigned as a LMCT band of the \([\text{Fe(CN)}_5\text{(imidazole)}]^{2-}\) by comparison with the solution spectrum of the complex. The spectra show a rapid increase at an ordering temperature of 25 K indicative of a magnetic transition. This ordering temperature is higher than that reported so far for \(\text{Co}^{II}-\text{Fe}^{III}\) complexes of the type \(\text{A}_2\text{Co}^{II}[(\text{CN})_6\text{Fe}^{III}\text{H}_2\text{O}]\), where \(\text{A}\) is an alkali metal ion.\(^{(36)}\) The temperature dependence of the magnetic susceptibility \(\chi_M(T)\) as well as \(\chi^{-1}(T)\) plots are shown in Figure 17. The \(\chi_M(T)\) value at 300 K is 3.22 cm\(^3\) K mol\(^{-1}\) \((\mu_{\text{eff}} = 4.9 \mu_B)\) for ferromagnetic coupling between one \(\text{Co}^{II}\) high-spin and one \(\text{Fe}^{III}\) low-spin center. Upon cooling, \(\chi_M(T)\) remains constant until 25 K, where it suddenly increases to reach a maximum value of 1445 cm\(^3\) K mol\(^{-1}\) \((\mu_{\text{eff}} = 107.51 \mu_B)\) at 18 K and then decreases to 97.08 cm\(^3\) K mol\(^{-1}\) \((\mu_{\text{eff}} = 27.86 \mu_B)\) at 2 K. This is in accord with the Currie–Weiss Law plot (based on \(1/\chi_M = C(T - \theta)\)) in the temperature range of 45–300 K, where a straight line with a positive Weiss constant is observed.

The ferromagnetic behavior may be enhanced by the orthogonality of the half-filled orbitals of Fe(III) \((t_{2g})^1\) and Co(II) \((e_g)^2\). The decrease of \(\chi_M T\) below 18 K is assigned to an antiferromagnetic interlayer interaction since the interlayer distance \((7.6-8.3\text{ Å})\) is less than 10 Å.38

The field-dependent magnetization performed on \(1\) at 2 K (Figure 18) shows ferromagnetic behavior. Compound \(1\) reaches a saturation value of magnetization \((3.21\text{ NµB})\) close to the theoretical value of \(4\text{ NµB}\) for a bimetallic system of high-spin Co(II) and low-spin Fe(III). This is consistent with the parallel alignment of the interacting spins. The spectrum presents a hysteresis loop at 2 K with a coercive field \((H_c)\) and a remnant magnetization \((M_r)\) of 81 Oe and 2.81 NµB, respectively. The high ordering temperature may be assigned to the dimensionality of the material, which facilitates cooperativity between metal centers along the planes compared to other reported Co/Fe bimetallics that crystallize as 3D systems in which defects in the structure serve to interrupt the cooperativity between metal centers. On the other hand, the position of the imidazole ligand in the structure is such that the superposition of different planes allows imidazoles from adjacent planes to orient parallel to each other to engage in \(\pi-\pi\) stacking. The distance between the imidazoles rings is 3.683 Å, and hence \(\pi-\pi\) interactions are not expected to be significant.

The temperature dependence of the magnetization of \(1\) between 50 and 1000 Oe is shown in Figure 16. Similar behavior is observed at all field strengths with a sudden increase in the magnetization below 25 K up to a field-dependent maximum value between 3000 and 9600 emu mol\(^{-1}\) from 50 to 1000 Oe. The abrupt increase in the magnetization below 25 K confirms magnetic ordering arising from ferromagnetic coupling within each layer.

The role of water of crystallization in determining the magnetic properties of \(1\) was studied using dehydrated samples. The thermal dependence of the magnetic susceptibility \(\chi_M T\) and \(1/\chi\) for the dehydrated sample of \(1\) are shown in Figure 16. The ordering temperature is increased to 30 K from 25 K (for \(1\)). The positive Weiss constant for the dehydrated sample \((\theta = +12.26\text{ K})\) obtained between 50 and 300 K) is close to that of the hydrated sample \((\theta = +15.3\text{ K})\) and is indicative of ferromagnetic behavior. However, the zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements of dehydrated \(1\) (Figure 17) show a sharp rise below 30 K, indicative of a magnetic transition. The increase in the ordering temperature is tentatively assigned to a decrease in the interlayer separation due to the loss of water.

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**Figure 15.** Temperature dependence of \(\chi_M T\) of \(1\).

**Figure 16.** Temperature dependence of the magnetization of \(1\). Upper graph: Field-cooled (FC, squares) and zero field-cooled (ZFC, circles) magnetization at 100 Oe. Middle graph: Under 50, 250, 500, and 1 kOe magnetic fields. Lower graph: Temperature dependence of the magnetization of dehydrated \(1\). Field-cooled (FC, open circles) and zero-field-cooled (ZFC, black squares) magnetization at 100 Oe.
of water of crystallization. A bifurcation of the curves is observed at 25 K, and the ZFC magnetization curve after reaching a maximum at 20 K rapidly decreases, which is indicative of domain wall freezing.39

Figure 19 shows the temperature dependence of the molar susceptibility \( \chi_M T \) and \( 1/\chi_M \) of 2. At room temperature, \( \chi_M T \) is 3.79 cm\(^3\) K mol\(^{-1}\) (\( \mu_{\text{eff}} = 5.50 \mu_B \)), which is lower than the theoretical value for noncoupled high-spin (HS) Mn\(^{II}\) and low-spin (LS) Fe\(^{III}\) 4.75 cm\(^3\) K mol\(^{-1}\) (\( \mu_{\text{eff}} = 6.16 \mu_B \)) assuming \( g = 2 \). Upon cooling, \( \chi_M T \) decreases slightly to the minimum value of 3.20 cm\(^3\) K mol\(^{-1}\) (\( \mu_{\text{eff}} = 5.06 \mu_B \)) at 30 K and then abruptly increases to 97.75 cm\(^3\) K mol\(^{-1}\) (\( \mu_{\text{eff}} = 27.96 \mu_B \)) at 4 K and then rapidly decreases to 59.83 cm\(^3\) K mol\(^{-1}\) (\( \mu_{\text{eff}} = 21.86 \mu_B \)) at 2 K. The magnetic behavior shows that, above 30 K, the complex shows antiferromagnetic interaction between

the metal centers, whereas below 30 K, the metal ions \{HS Mn(II) and LS Fe(III)\} couple ferromagnetically. In accordance with this, the Currie–Weiss plots in the temperature ranges of 50–300 K and 5–18 K show a negative and a positive Weiss constant of $\theta = -9.7$ K and $+4.8$ K, respectively. This metamagnetic behavior can be assigned to the combination of intralayer ferromagnetic and interlayer antiferromagnetic interactions, with the interlayer separations being less than 10 Å.

Figure 20 shows the temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization, $M(T)_{ZFC}$ and $M(T)_{FC}$, respectively, of 2 at an applied field of 100 G. A magnetic ordering temperature of 4.5 K is observed, at which the field-cooled and the zero-field-cooled curves diverge. $M(T)_{ZFC}$, after reaching a maximum at 4 K, gradually decreases, possibly due to domain wall freezing, as observed for K$_3$Co[Fe(CN)$_6$]$_3$·2H$_2$O.\(^{(41)}\) The $M(T)_{FC}$ rises upon further cooling and has a bifurcation at 5 K, suggesting considerable irreversibility. The field dependence of the magnetization of 2 was measured in the field range of $-10000$ to $+10000$ Oe at 5 K (Figure 21). The curve is sigmoidal, and above 1000 Oe, it gradually increases without reaching the saturation value within the range of the measurement field. However, the curve shows a small hysteresis with a coercive field and a remnant magnetization value of 47 Oe and $0.26 \ N_m$, respectively. This is indicative of some ferromagnetic interaction.

In order to confirm the metamagnetic transition, the magnetization was determined as a function of the external magnetic field at 5 and 10 K (Figure 22). As was observed at lower field strengths, the dependence at 5 K shows a rapid increase below 250 G and then increases gradually at higher fields to approach a saturation value of 3.9 N$_m$ at 50 KOe, which is an indication of a phase transition to a ferromagnetic state. This phase transition is not observed at 10 K. Overall, however, it is important to note that although the data support assignment of the material as being metamagnetic, it is also possible that the phenomena observed are due to spin glass behavior.

The temperature-dependent molar magnetic susceptibility, $\chi_M$, of the single crystal of 3 between 5 and 300 K is shown as $\chi_M(T)$ and $\chi^{-1}(T)$ in Figure 23. $\chi_M(T)$ at room temperature is 0.375 cm$^3$ K mol$^{-1}$ ($\mu_{eff} = 1.73 \mu_B$), which is similar to that obtained for the (Ph$_4$P)$_2$[Fe$^{III}$]($\text{CN})_5$imidazol]-2H$_2$O and is expected for a low-spin iron(III) compound with regard to the diamagnetic nature of Zn(II). The $\chi^{-1}(T)$ curve is linear and intercepts the axis almost through zero, indicative of a paramagnetic compound. As the temperature is lowered, the value of $\chi_M(T)$ remains constant until 45 K, then steadily decreases to 0.320 cm$^3$ K mol$^{-1}$ ($\mu_{eff} = 1.6 \mu_B$) at 5 K, which indicates weak intramolecular antiferromagnetic (AF) coupling between isolated low-spin iron(III) centers through the -CN–Zn–NC– bonding system; the Fe$^{III}$$\ldots$Fe$^{III}$ distance in the structure of 3 is 9.943 Å.

The plot of $\chi_M(T)$ for 4 is shown in Figure 24. The $\chi_M(T)$ value (4.06 cm$^3$ K mol$^{-1}$, 5.70 $\mu_B$) at 300 K is lower than the expected value 4.75 cm$^3$ K mol$^{-1}$ ($\mu_{eff} = 6.16 \mu_B$; calculated assuming $g = 2$) for the noncoupled HS Mn$^{II}$ ($S = 5/2$) and LS Fe$^{III}$ ($S = 1/2$). The slightly lower value of $\chi_M(T)$ than that calculated indicates that the solid sample used for the magnetic measurement contains dinuclear species of the form HS Mn$^{III}$ ($S = 2$)/LS Fe$^{III}$ ($S = 0$). With decreasing temperature, $\chi_M(T)$ decreases smoothly to a minimum value of 3.22 cm$^3$ K mol$^{-1}$ ($\mu_{eff} = 5.075 \mu_B$) at 15 K, then sharply increases to reach a maximum of 15.76 cm$^3$ K mol$^{-1}$ ($\mu_{eff} = 11.23 \mu_B$) at 3.5 K, and rapidly decreases to 5.88 cm$^3$ K mol$^{-1}$ ($\mu_{eff} = 6.86 \mu_B$) at 2 K, indicative of short-range antiferromagnetic interaction. This is confirmed by the $\chi^{-1}(T)$ value, in which the plot above 20 K obeys the Currie–Weiss law (Figure 24) showing a negative Weiss constant of $\theta = -6.5$ K. The highly distorted structure precludes alignment of the spins of the metal centers.

**Conclusions**

We have described a series of new bimetallic materials based on the [Fe$^{III}$]($\text{CN})_5$imidazole]$^{2-}$ building block. The single crystal of a paramagnetic 3D network for Zn$^{II}$/Fe$^{III}$ was obtained with the Zn$^{II}$ ions pentacoordinated to cyano ligands through nitrogen and forming a square pyramidal structure around the zinc ions. By contrast, the Co$^{II}$/Fe$^{III}$ and Mn$^{II}$/Fe$^{III}$ systems crystallize as 2D networks. The preference of the latter bimetallic complexes to crystallize in a 2D network is ascribed to the effect of the nonbridging imidazole ligand, the $\pi$ acceptor ability of which results in a trans effect, reducing the $\sigma$-donor strength of the axial cyano


\(^{(41)}\) Kumar, A.; Yusuf, S. M. Physica B 2005, 362, 278.
The layers are made up of deformed square grids from tetrameric $[-\text{M}^{\text{II}}-\text{CN}-\text{Fe}^{\text{III}}-]_2^-$ (M = Mn or Co) units. The metal centers are in an octahedral geometry with the equatorial cyano ligands through nitrogen atoms, and bind two solvent molecules in a trans fashion (water in the case of 1 and methanol in the case of 2). The coordination of the imidazole to the iron ion results in a significant trans effect on the axial cyanide ligand, which reduces its ability to bridge a second metal ion. The magnetic studies carried out on these compounds reveal ferromagnetic behavior for 1 and 2 and a weak antiferromagnetic property for the MnII/FeIII system 4. The deviation of the layer structure from planarity (less pronounced for 1) induces non-collinearity of the metal centers and hence spins, enhancing the disorder of spins and thereby increasing the paramagnetic character of the materials formed. In this study, we demonstrate that the building block $[\text{Fe}^{\text{III}}(\text{CN})_5(\text{imidazole})]^2-$ is a versatile component in the preparation of new materials exhibiting a diverse range of magnetic properties. Furthermore, it shows that the imidazole ligand, while not forming a bridge between metal centers itself, has a profound influence on the bridging ability of the CN$^-$ ligands. In principle, the use of substituted imidazoles offers a considerable handle on tuning the solid state properties. However, it should be noted that the synthetic route used to make the building block does not allow for this. Nevertheless, the preparation of the Mn(bpy)-based bimetallic material does indicate that further tuning of, for example, the properties of 4 is a worthwhile direction in which to proceed in obtaining new materials in this class.

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**Supporting Information Available:** Selected bond lengths and angles for 1–4. This material is available free of charge via the Internet at http://pubs.acs.org.