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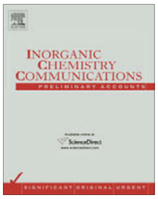

The first anion template cubic cyanometallate cage and its 3,5-dimethyltris(pyrazolyl)methane iron(II, III) tricyanide building blocks

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ABSTRACT

Several 3,5-dimethyltris(pyrazolyl)methane iron(II, III) tricyanide building units have been prepared and characterized. Treatment of $K[(HC(3,5\text{-}Me_2Pz)_3)Fe^{II}(CN)_2](K^+\mathbf{1}^-)$ with $Fe^{II}(H^2O)^6(BF^4)^2$ affords a new anion template cubic cyanometallate cage $[(BF_4) \subset \{Fe^{II}(H_2O)\}_4\{(HC(3,5\text{-}Me_2Pz)_3)Fe^{II}(CN)_3\}_4](BF_4)^3$ **3**.

The Prussian blue (PB) and its analogues which are insoluble polymerics by virtue of the sixfold bridging of the octahedral $[M(CN)_6]^{n-}$ subunits have garnered interest recently because of their electrocatalytic, electrochromic, ion-exchange, ion-sensing, and photomagnetic properties [1,2]. Facially coordinated tripodal ligands were introduced to replace three of these CN groups which block one face of the octahedron [3,4]. Polymerization could be thus inhibited, and a family of cages with a box-like architecture results. Some early examples showed that the reaction of $fac-LM(CN)_3^{n-}$ with $LM(H_2O)_3^{m+}$ or $LM(MeCN)_3^{m+}$ resulted in cyanometallate boxes, $[M_8(CN)_{12}]^{4(n-m+)}$, from the displacement of the labile MeCN or H_2O ligand [5–21]. As part of our interest in this area, we are focusing on the coordination complexes of iron, which have the same components as classic Prussian blue materials and will offer the potential for comparison with classic Prussian blue materials. Surprisingly, despite the prevalence of facile type scorpionate ligands such as tris(pyrazolyl)borates and tris(pyrazolyl)methane in inorganic chemistry, only tris(pyrazolyl)borate iron(II, III) tricyanide and some derived clusters and networks have been described [22–32]. The related tris(pyrazolyl)methane has a framework identical to that of the borate ligands, contains a carbon atom in place of the boron atom, and hence, acts as neutral ligands. In an effort to extend the chemistry of Prussian blue type's complexes, we have chosen 3,5-dimethyltris(pyrazolyl)methane ($HC(3,5\text{-}Me_2Pz)_3$) as a capping ligand to synthesize its cyanometallate complexes and to investigate their reactivity toward cyanometallate cage formation. Herein, we report the preparation and characterization of a new cubic cyanometallate cage containing an anion template and its 3,5-dimethyltris(pyrazolyl)methane iron(II, III) tricyanide building blocks.

The tricyano complex $K[(HC(3,5\text{-}Me_2Pz)_3)Fe^{II}(CN)_3](K^+\mathbf{1}^-)$ was readily prepared by treatment of a methanol solution of $FeCl_2$ with $HC(3,5\text{-}Me_2Pz)_3$ followed by the addition of a slight excess of KCN [33]. The addition of PPh_4Cl to the reaction mixture produced orange microcrystals of $PPh_4^+\mathbf{1}^-$ in an excellent yield [34]. Chemical oxidation of $\mathbf{1}^-$ with iodine or ferrocenium hexaflouorophosphate in acetonitrile produces a yellowish brown precipitate $(HC(3,5\text{-}Me_2Pz)_3)Fe^{III}(CN)_3$ **2** [35]. Infrared spectroscopy performed on an acetonitrile solution of $\mathbf{1}^-$ confirmed the presence of C_{3v} symmetry coordinated with cyanide ligands with strong stretches appearing at 2070 cm^{-1}(s) and 2057 cm^{-1}(vs), which are shifted by 20 and 7 cm^{-1}, respectively, from that of tetraethylammonium cyanide (2050 cm^{-1}). Same tendency also can be observed in **2** which is iron(III) derivatives of $\mathbf{1}^-$. The infrared spectrum of the microcrystalline sample of **2** contains only one peak at 2124 cm^{-1}(s). They are shifted to higher energies relative to $\mathbf{1}^-$, suggesting the presence of oxidation of the iron center that decreases the charge delocalization via π back-bonding. The νCN stretching absorptions of $PPh_4^+\mathbf{1}^-$ and **2** are also found at relatively high energies and are comparable to their borate analogues $[(HB(3,5\text{-}Me_2Pz)_3)\text{-}Fe^{II}(CN)_3]^{2-}$ (2041 cm^{-1}(s), 2017 cm^{-1}(vs)) and $[(HB(3,5\text{-}Me_2Pz)_3)\text{-}Fe^{III}(CN)_3]^-$ (2115 cm^{-1}(s)) [25].

X-ray crystallographic analysis of $PPh_4^+\mathbf{1}^-$, $K^+\mathbf{1}^-$, and **2** revealed that the Fe^{II} or Fe^{III} ions are in an octahedral N_3C_3 coordination sphere with slight deviations of the coordination angles from the

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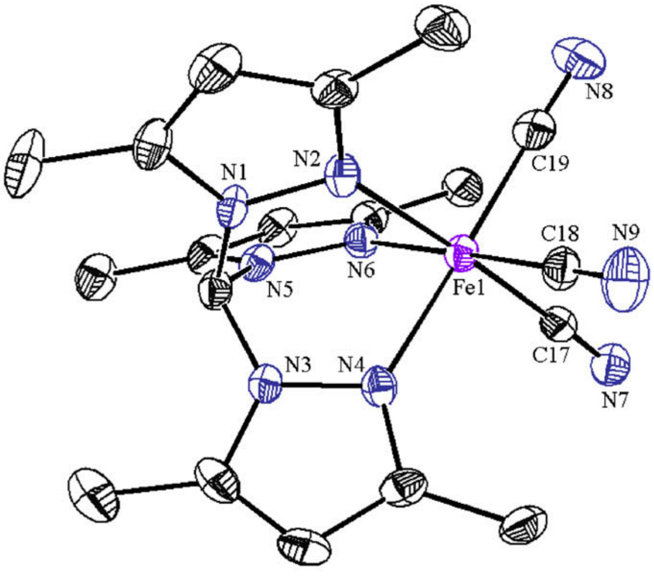

Fig. 1. Thermal ellipsoid plot of the anionic unit in PPh$_4^+$**1**$^-$ with important atom labeled. Hydrogen atoms were omitted for the sake of clarity. Selected bond distances (Å) and bond angles (deg): Fe(1)–N(2) 2.038(5), Fe(1)–N(4) 2.018(5), Fe(1)–N(6) 2.037(5), Fe(1)–C(17) 1.925(7), Fe(1)–C(18) 1.902(7), Fe(1)–C(19) 1.912(7), C(17)–N(7) 1.151(8), C(18)–N(8) 1.166(8), C(19)–N(9) 1.148(7), N(6)–Fe(1)–C(19) 176.1(2), N(4)–Fe(1)–C(18) 177.2(2), N(2)–Fe(1)–C(17) 178.7(2), Fe(1)–C(17)–N(7) 178.5(6), Fe(1)–C(18)–N(8) 178.2(6), Fe(1)–C(19)–N(9) 177.7(6), C(17)–Fe(1)–C(18) 89.5(3), C(17)–Fe(1)–C(19) 89.5(3), C(18)–Fe(1)–C(19) 91.5(3), N(2)–Fe(1)–N(4)86.6(2), N(2)–Fe(1)–N(6) 87.1(2), N(4)–Fe(1)–N(6) 85.9(2).

ideal values (Fig 1 for the anion of PPh$_4^+$**1**$^-$; K$^+$**1**$^-$, and **2** see Supplementary material). The Fe–C bond distances range from 1.902(7) to 1.925(7) Å for PPh$_4^+$**1**$^-$ and 1.817(17) to 1.868(19) Å for K$^+$**1**$^-$. The smallest Fe–C bond distances are found in K$^+$**1**$^-$, while comparatively longer values are exhibited by PPh$_4^+$**1**$^-$ salt, which may be due to the potassium cyanide interaction. The longer Fe–C bond distances range from 1.916(11) to 1.929(10) Å for **2** suggest that Fe^{III} derivatives exhibit less π back-bonding relative to divalent analogues, which also consist of infrared data. Related to known borate analogues $[(HB(3,5\text{-}Me_2Pz)_3)Fe(CN)_3]^{-/2-}$, [25] $[(HC(3,5\text{-}Me_2Pz)_3)Fe(CN)_3]^{0/-}$ (**1**$^-$ and **2**) probably exhibit longer Fe–C bonds and shorter Fe–N bonds, due to a significant difference between the electron charge properties of borate and methane complexes.

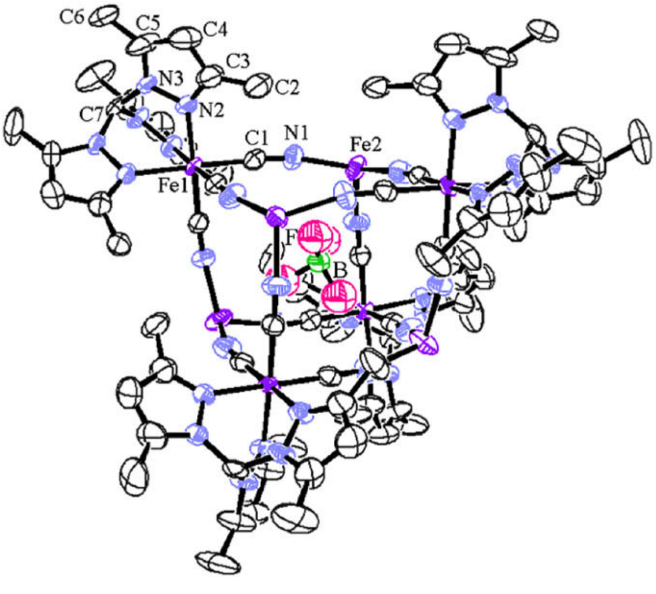

Fig. 2. Thermal ellipsoid plot of the cationic unit in **3** with important atom labeled. Hydrogen atoms and coordinated water molecule (on Fe(2)) were omitted for the sake of clarity. Selected bond distances (Å) and bond angles (deg): Fe(1)–C(1) 1.873(10), Fe(1)–N(2) 2.023(7), Fe(2)–N(1) 2.016(8), Fe(2)–O(1) 2.300(8), C(1)–N(1) 1.175(14), B(1)–F(1) 1.32(2), N(2)–Fe(1)–C(1) 177.8(4), Fe(1)–C(1)–N(1) 176.8(9), C(1)–N(1)–Fe(2) 166.3(9), N(1)–Fe(2)–O(1) 109.6(3).

The reaction of **1**$^-$ with $Fe^{II}(H_2O)_6(BF_4)_2$ leads to the formation of a new anion template cubic cyanometallate cage $[(BF_4)\subset\{Fe^{II}(H_2O)\}_4\{(HC(3,5\text{-}Me_2Pz)_3)Fe^{II}(CN)_3\}_4](BF_4)_3$ **3** [36]. Cage **3** is an air sensitive yellow compound that becomes insoluble green product after exposure to air. Infrared spectroscopy studies on the samples of cage **3** in the solid state revealed only a single *ν*CN band at 2090 cm^{-1}, which are shifted by +20 cm^{-1} compared to the starting material **1**$^-$, consistent with bridging cyanide interaction [32,37]. Using $NaPF_6$ to exchange the anion gives an intractable mixture. The reaction of **1**$^-$ with $Fe^{II}(H_2O)_6(PF_6)_2$ (or $Fe^{II}(H_2O)_6(ClO_4)_2$) also give similar intractable mixtures. Recently, a neutral all iron cubic cyanometallate cage was synthesized, which did not contain any ion inside the cage [31]. The cage **3** reported here is the first cyanometallate cage containing an anion template inside the cage.

Single-crystal X-ray studies revealed that **3** was a distorted cubic box composed of both six and four coordinate eight iron vertices and crystallized in the cubic space group $P23$. $P23$ symmetry was imposed on the box framework (Fig. 2). The $HC(3,5\text{-}Me_2Pz)_3$ ligand was disordered at the threefold symmetry axes. Reflecting the high crystallographic symmetry of the salt, the guest anion BF_4^- is disordered at the three equivalent positions. The refinements indicate that the F atoms are oriented near the four coordination Fe sites about 2.785 Å. The local geometry of four coordination Fe sites is a distorted tetrahedron with CN–Fe–NC angles of about 109.3 ° which were composed of three nitrogen-bound bridging cyanide ligands and one terminal water molecule. Significant distortions of the cage **3** allow for formation of the pseudocubic structure from octahedral and tetrahedral corners; these occur at the 12 unique Fe–N≡C angles around four coordination Fe sites. This distortion is present at each of the four coordination Fe sites to 166.3(9)°. An examination of the cube body diagonals reveals a slight compression along one of the C_3 axes, which lowers the overall symmetry of the cage. Another six coordination Fe sites have NC–Fe–CN angles around 87.7°, and the Fe–C≡N angle is nearly linear (176.8(9)°), which, coming from **1**$^-$, still keeps the slightly distorted octahedral N_3C_3 geometry. The coordination bond lengths of cyanide have a pronounced difference when the Fe–C$_{CN}$ (1.873(10) Å) is compared with the Fe–N$_{CN}$ (2.016(8)Å).

The preparation of 3,5-dimethyltris(pyrazolyl)methane iron tricyanides and their use as building blocks to prepare a new cubic all iron cyanometallate cage have been described. The anion template in the iron cubic cyanometallate cage only works for the BF_4^- anion. Efforts are underway to use 3,5-dimethyltris(pyrazolyl)methane iron tricyanide **1**$^-$ and **2** as building blocks to be incorporated with other transition metal ions in the presence of different anion templates and to investigate the ion-exchange, ion-sensing, and magnetic properties of those cyanometallate cage compounds.

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Appendix. Supplementary. material

CCDC Nos. 693371, 625279, 625280 and 693372 contains the supplementary crystallographic data for K^+1^-, $PPh_4^+\mathbf{1}^-$, **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[33] Synthesis of $[K][(HC(3,5\text{-}Me_2Pz)_3)Fe^{II}(CN)_3]$ K^+1^-: A solution of $HC(3,5\text{-}Me_2Pz)_3$ (1.00 g, 3.36 mmol) in 10 mL of MeCN was added to a solution of $FeCl_2$ (0.426 g, 3.36 mmol) in 20 mL of MeCN. This mixture was stirred at room temperature for 2 h and a solution of KCN (0.76 g, 11.76 mmol) in 50 mL of MeOH was added to stir at room temperature for another 2 hrs. The solvent removed by rotary evaporation to give an yellow solid. This yellow solid was extracted by MeCN (0.5 L × 8) to give an yellow solution. The yellow solution was concentrated by slow rotary evaporation (20 mL) to give yellow microcrystals (0.67 g (85%)). Yellow crystals suitable for X-ray analysis and elementally analysis of complex K^+1^- were grown by allowing an aqueous solution of the product to evaporate slowly. IR (MeCN): νCN 2056 cm^{-1}. IR (KBr): νCN 2050, 2072 cm^{-1}. ESI–MS(−): *m*/*z* 432 $[(HC(3,5\text{-}Me_2Pz)_3)Fe(CN)_3]$. Anal. Calc. for $C_{19}H_{22}FeKN_9.5\ H_2O$ (found): C, 40.64 (40.75); H, 5.74 (5.76); N, 22.45 (22.59).

[34] Synthesis of $[PPh_4][(HC(3,5\text{-}Me_2Pz)_3)Fe^{II}(CN)_3]$ $PPh_4^+\mathbf{1}^-$: A solution of PPh_4Cl (0.63 g, 1.68 mmol) in 10 mL of MeCN was added to a solution of $[K][(HC(3,5\text{-}Me_2Pz)_3)Fe^{II}(CN)_3]$ $K^+\mathbf{1}^-$ (0.79 g, 1.68 mmol) in 20 mL of MeOH. This mixture was stirred at room temperature for 2 hours and the solvent removed by rotary evaporation. The solid was dissolved in CH_2Cl_2 and the solution was then filtered. After reducing the volume of the filtrate to 5 mL, then 50 mL of Et_2O was added to precipitate an orange solid, and dried under vacuum to yield 1.03 g (80%). Single crystals suitable for X-ray analysis and elementally analysis of complex $PPh_4^+\mathbf{1}^-$ were obtained by diffusion of Et_2O into MeCN solution. ^1H NMR(CD_3CN, d): 2.526(s, 9H, CH_3), 2.688(s, 9H, CH_3), 5.932(s, 3H, Pz), 7.663(s, 1H, CH). ^{13}C NMR(CD_3CN, d): 11.028, 15.788, 68.023, 108.554, 142.149, 159.569, 174.723. IR (MeCN): vCN 2058, 2070 cm^{-1}. IR (KBr): vCN 2057, 2071 cm^{-1}. ESI–MS(−): *m*/*z* 432 $[(HC(3,5\text{-}Me_2Pz)_3)Fe(CN)_3]^-$. ESI–MS(+): *m*/*z* 339 PPh_4^+. Anal. Calc. for $C_{43}H_{42}FeN_9P$ (found): C, 66.93 (66.98); H, 5.49 (5.61); N, 16.34 (16.25).

[35] Synthesis of $(HC(3,5\text{-}Me_2Pz)_3)Fe^{III}(CN)_3$ **2**: A solution of ferrocenium hexaflouorophosphate (0.10 g, 0.367 mmol) in 10 mL of MeCN was added to a solution of $[PPh_4][(HC(3,5\text{-}Me_2Pz)_3)Fe^{II}(CN)_3]$ $PPh_4^+\mathbf{1}^-$ (0.283 g, 0.367 mmol) in 20 mL of MeCN and stirred for 2 hours to give an yellow precipitate. The yellow precipitate was filtered washed with 5 mL of MeCN, and dried under vacuum to yield 0.143 g yellow solid (90%). Yellow crystals suitable for X-ray analysis and elementally analysis of complex **2** were grown by by diffusion of Et_2O into DMF solution. IR (KBr): vCN 2124 cm^{-1}. Anal. Calc. for $C_{19}H_{22}FeN_9.DMF$ (found): C, 52.28 (52.35); H, 5.78 (5.77); N, 27.72 (27.69).

[36] Synthesis of $[(BF_4)\subset\{Fe^{II}(H_2O)\}_4\{(HC(3,5\text{-}Me_2Pz)_3)Fe^{II}(CN)_3\}_4](BF_4)_3$ **3**: A solution of $Fe(H_2O)_6(BF_4)_2$ (0.144 g, 0.425 mmol) in 10 mL of MeOH was added to a solution of $[K][(HC(3,5\text{-}Me_2Pz)_3)Fe(CN)_3]$ (0.200 g, 0.425 mmol) in 20 mL of MeOH and stirred for 5 h to give an yellow precipitate. The yellow precipitate was filtered washed with 5 mL of MeOH, and dried under vacuum to yield 0.197 g yellow solid (78%). Yellow crystals suitable for X-ray analysis and elementally analysis of complex **3** were obtained by layering MeOH solutions of the $K^+\mathbf{1}^-$ with MeOH/Et_2O (9:1 v/v) solutions of $Fe(H_2O)_6(BF_4)_2$. IR (KBr): vCN 2090 cm^{-1}. Anal. Calc. for $C_{76}H_{96}B_4F_{16}Fe_8N_{36}O_4$ (found): C, 38.49 (38.69); H, 4.08 (4.25); N, 21.26 (21.17).

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