

Article

Use of Pyrazole Hydrogen Bonding in Tripodal Complexes to Form Self Assembled Homochiral Dimers

Greg Brewer ^{1,*}, Raymond J. Butcher ²  and Peter Zavalij ³¹ Department of Chemistry, Catholic University, Washington, DC 20064, USA² Department of Chemistry, Howard University, Washington, DC 20059, USA; rbutcher@howard.edu³ Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA; pzavaliv@umd.edu

* Correspondence: brewer@cua.edu

Received: 5 March 2020; Accepted: 25 March 2020; Published: 31 March 2020



Abstract: The 3:1 condensation of 5-methyl-1H-pyrazole-3-carboxaldehyde (MepyrzH) with tris(2-aminoethyl)amine (tren) gives the tripodal ligand tren(MePyrzH)₃. Aerial oxidation of a solution of cobalt(II) with this ligand in the presence of base results in the isolation of the insoluble Co(tren)(MePyrz)₃. This complex reacts with acids, HCl/NaClO₄, NH₄ClO₄, NH₄BF₄, and NH₄I to give the crystalline compounds Co(tren)(MePyrzH)₃(ClO₄)₃, {[Co(tren)(MePyrzH_{0.5})₃](ClO₄)_{1.5}]₂ {[Co(tren)(MePyrzH_{0.5})₃](BF₄)_{1.5}]₂ and [Co(tren)(MePyrzH)₃][Co(tren)(MePyrzH)₃]₂. The latter three complexes are dimeric, held together by three N_{pyrazole}–H⋯N_{pyrazolate} hydrogen bonds. The structures and symmetries of these homochiral dimers or pseudodimers are discussed in terms of their space group. Possible applications of these complexes by incorporation into new materials are mentioned.

Keywords: supramolecular; dimer; pyrazole; hydrogen bonding; crystal structure; cobalt

1. Introduction

Tripodal ligands (see Figure 1) discussed in this report are formed from the Schiff base condensation of tris(2-aminoethyl)amine (tren), with three moles of an imidazole-2-carboxaldehyde, imidazole-4-carboxaldehyde or 5-methyl-1H-pyrazole-3-carboxaldehyde. The imidazole rings may have methyl substituents (not illustrated) in the 1,2 or 4 positions, which does not drastically affect reactivity [1,2]. The ligands are triprotic, H₃L, and can coordinate to a metal(II) or metal(III) to give mononuclear complexes [MH₃L]²⁺, [MH₃L]³⁺ or [ML] in the presence of base [3–7]. The resultant imidazole and imidazolate complexes have been extensively studied in terms of proton coupled electron transfer (PCET) [8–13], tunable redox potentials, spin crossover (SC) between spin(HS) low spin(LS) electronic ground states [14–16] and formation of double salts which exhibit size recognition properties [17,18]. The properties of the metal complexes of the fully protonated (H₃L) or fully deprotonated ligands (L³⁻) are certainly important as they have far ranging applications to materials research including switches [19,20], memory storage [21], and magnets [22,23]. The complexes are also chiral as the three arms of the tren ligand can wrap around the metal in a clockwise or counter clockwise fashion to give Δ (delta) or Λ (lambda) complexes.

The supramolecular [24–26] properties of the complexes of partially deprotonated or hemideprotonated ligands (H₂L⁻, HL²⁻, H_{1.5}L^{-1.5}) are perhaps more important in potential materials science applications. These complexes self assemble to give extended molecular arrays that exhibit very different topologies and preference for homo vs heterochirality.

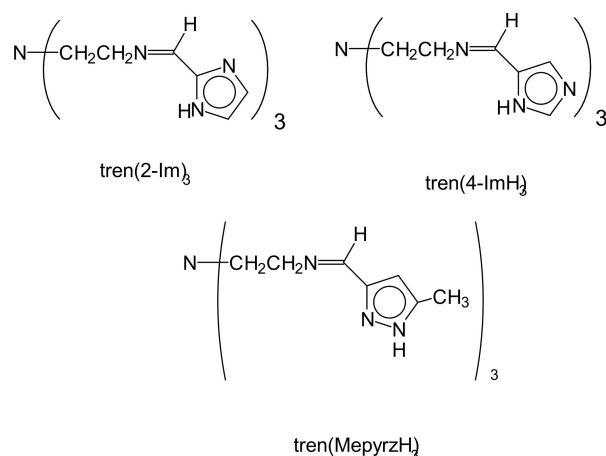


Figure 1. Line drawings of tripodal azole ligands.

The driving force is the formation of an extensive network of hydrogen bonding interactions between a protonated azole and a deprotonated azole, $\text{N}_{\text{azole}}\text{-H} \cdots \text{N}_{\text{azolate}}$. Examples of complexes of H_2L^- and HL^{2-} ligands that give 1D linear and zig-zag chains are illustrated below in Figure 2 [27].

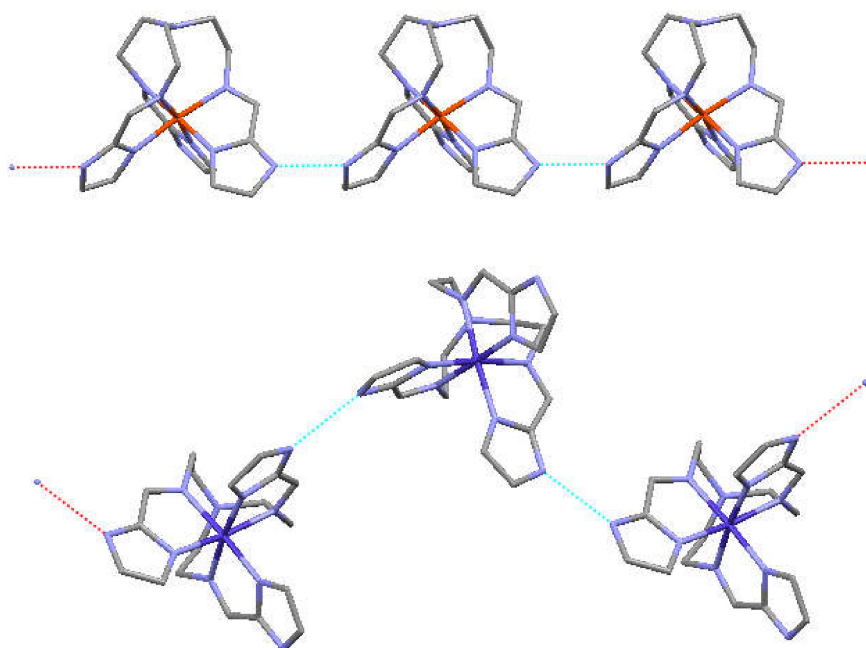


Figure 2. Partially deprotonated complexes have been observed for $[\text{Fetren}(2\text{-Im})_2(2\text{-ImH})]^+$ (linear, top) and $[\text{Cotren}(2\text{-ImH})_2(2\text{-Im})]^{2+}$ (zig-zag, bottom) that give 1D hydrogen bound chains. Please see [27] from preceding paragraph.

The greatest number of supramolecular complexes are those of the hemideprotonated ligand with iron(II), iron(III), cobalt(II) or cobalt(III) as the metal. The hemideprotonated state can be achieved if each of the three N1 azole nitrogen atoms has a hydrogen atom at half occupancy, $\text{NH}_{0.5}$, $\text{tren}(\text{azoleH}_{0.5})_3^{-1.5}$ or if the metal complexes average out to 1.5 hydrogen atoms per complex as in a 50:50 compound of $[\text{Mtren}(\text{azoleH})_3]^{+2 \text{ or } +3}$ and $[\text{Mtren}(\text{azole})_3]$. The hemideprotonated $\text{tren}(2\text{-ImH}_{0.5})_3^{-1.5}$ and $\text{tren}(4\text{-ImH}_{0.5})_3^{-1.5}$ systems exhibit a 2D hexagonal sheet structure, which exhibit extensive hydrogen bonding between neighboring complexes [28]. Each hemideprotonated complex is hydrogen bound to three neighboring structures, which give an extended 2D sheet. There is little or no interaction between adjacent layers [29,30]. Examples of these are depicted in Figure 3 [31].

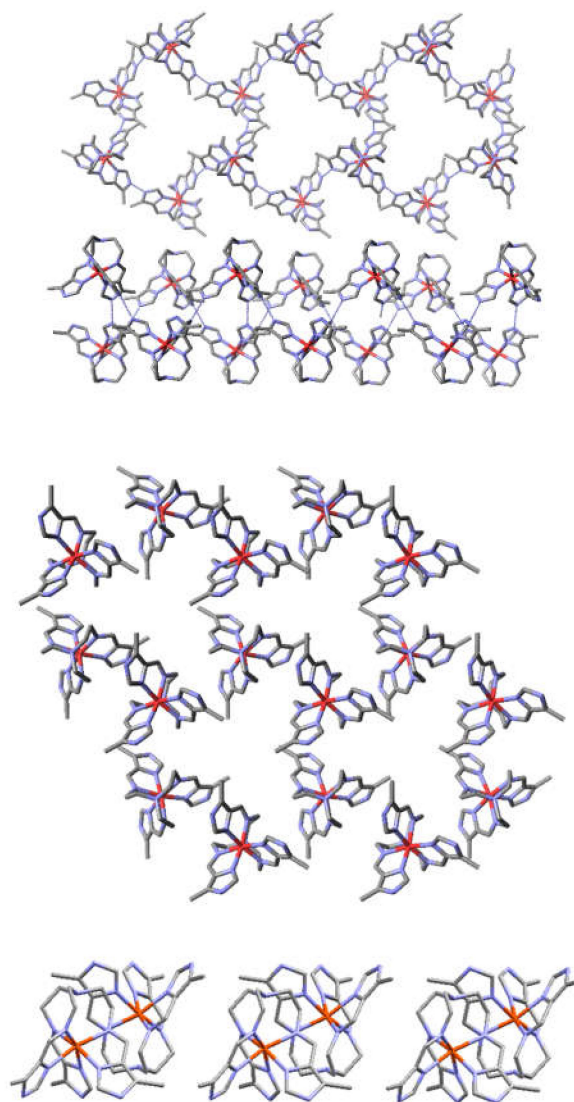


Figure 3. Face on upper and sideways lower views of extended 2D sheet structures for trigonal $\text{Fetren}(4\text{-MeImH}_{0.5})_3^{+1.5}$ (top) and hexagonal $[\text{Fetren}(4\text{-MeImH}_{0.5})_3]^{+1.5}$ (bottom). Please see [31] from preceding paragraph.

This work describes the preparation and structures of the cobalt complexes of the $\text{tren}(\text{MepyrzH})_3$ ligand.

2. Experimental

2.1. General Information

Tris(2-aminoethyl)amine (tren), cobalt(II) tetrafluoroborate hexahydrate, cobalt(II) perchlorate hexahydrate, ammonium perchlorate, ammonium tetrafluoroborate, ammonium iodide and 0.10 M potassium hydroxide in methanol were obtained from Aldrich (Milwaukee, WI, USA). 5-Methyl-1H-pyrazole-3-carboxaldehyde was obtained from ChemBridge (San Diego, CA, USA). All solvents were of reagent grade and used without further purification. IR spectra were obtained as KBr pellets on a 1600 FT IR spectrometer (Perkin Elmer, Waltham, MA, USA).

2.2. Synthesis

$[\text{Co}(\text{tren}(\text{MepyrzH})_3)(\text{ClO}_4)_3]$ A solution of HCl (1.32 mL of 0.1 M HCl in methanol, 0.132 mmol) was added to a slurry of the previously prepared [32] $\text{Co}(\text{tren}(\text{MepyrzH})_3)$ (0.021 g, 0.044 mmols) in

methanol (40 mL) in a 100 mL round bottom flask. The mixture was refluxed for an hour and filtered while hot. An excess of NaClO_4 in a few mL of methanol was added. Orange-red crystals precipitated overnight.

$\{[\text{Cotren}(\text{MepyrzH}_{0.5})_3](\text{ClO}_4)_{1.5}\}_2 \text{NH}_4\text{ClO}_4$ (0.034 g, 0.29 mmol) was added as a solid to a slurry of $\text{Cotren}(\text{Mepyrz})_3$ (0.023 g, 0.048 mmol) in methanol (30 mL) in a 100 mL round bottom flask. There was no immediate change. The mixture was refluxed for 2 h to give a clear, orange solution. The reaction mixture was filtered while hot and set aside to concentrate. After several hours small red crystals were produced. They were recrystallized from DMF to produce crystals suitable for crystallography.

$\{[\text{Cotren}(\text{MepyrzH}_{0.5})_3](\text{ClO}_4)_{1.5}\}_2 \text{NH}_4\text{BF}_4$ (0.029 g, 0.28 mmol) was added as a solid to a slurry of $\text{Cotren}(\text{Mepyrz})_3$ (0.021 g, 0.044 mmol) and methanol (30 mL) in a 100 mL round bottom flask. There was no immediate change. The mixture was refluxed for 2 h to give a clear, orange solution. The reaction mixture was filtered while hot and set aside to concentrate. After several hours small red crystals were produced. Two different types of crystals, the title compound and a hydrate) were produced and analyzed

$[\text{Cotren}(\text{MepyrzH})_3][\text{Cotren}(\text{Mepyrz})_3]_2 \text{NH}_4\text{I}$ (0.047 g, 0.32 mmol) was added as a solid to a slurry of $\text{Cotren}(\text{Mepyrz})_3$ (0.032 g, 0.067 mmol) and methanol (10 mL) in a 100 mL round bottom flask. There was no immediate change. The mixture was refluxed for 2 h to give a clear, orange solution. The reaction mixture was filtered while hot and set aside to concentrate. After several hours small red crystals were produced.

$\{[\text{Cotren}(\text{MepyrzH}_{0.5})_3 (\text{C}_6\text{H}_6) \text{CH}_3\text{CN}]\}_2(\text{ClO}_4)_3$. This complex was isolated in an attempt to repeat the synthesis of $[\text{Cotren}(\text{MepyrzH})(\text{Mepyrz})_2](\text{ClO}_4)$ [33]. Tren (0.077 g, 0.53 mmol) and absolute ethanol (~16 mL) were added to a 25 mL round bottom flask. 5-Methyl-1H-pyrazole-3-carbaldehyde (0.174 g, 1.6 mmol) was added as a solid. The reaction mixture was refluxed for 2 h and filtered. $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.193, 0.53 mmol) was added as a solid to the filtrate. The reaction mixture was refluxed a further 2 h and was set aside to concentrate. Over a week a large quantity of solid had formed. It was filtered, washed sparingly with absolute ethanol and placed in a dessicator over CaCl_2 to dry. After several days the solid (0.110 g) was dissolved in 15–20 mL acetonitrile with warming. The solution was filtered into a beaker. The beaker was set in a sealed jar with a few mL benzene in jar to allow for slow diffusion of benzene into the acetonitrile solution. Large brown blockish crystals formed over several days.

2.3. Structure Determinations

Crystal data were collected on a SMART 1000 CCD area2 detector Apex II system (Bruker, Madison, WI, USA), or on an Oxford Gemini diffractometer (Oxford, UK). All structures were solved using the direct methods program SHELXS-97 (Univ. of Gottingen, Germany) [34]. All nonsolvent heavy atoms were located using subsequent difference Fourier syntheses. The structures were refined against F^2 with the program SHELXL [35,36], in which all data collected were used including negative intensities. In several of the complexes the perchlorate or tetrafluoroborate anions were conformationally disordered. In these cases each conformation was tetrahedrally idealized and the multiplicities of the conformations were constrained to unity. All nonsolvent heavy atoms were refined anisotropically. All hydrogen atoms were located by Fourier difference. Complete crystallographic details are summarized in Table 1. Selected bond distances and angles are given in Table 2 and hydrogen bonding data is in Table 3. Crystallographic data for all complexes can be obtained free of charge from the Cambridge Crystallographic Data Center. The deposition numbers for the complexes are provided. $[\text{Cotren}(\text{MepyrzH})_3] (\text{ClO}_4)_3$ 973179, $[\text{Cotren}(\text{MepyrzH}_{0.5})_3]_2 (\text{ClO}_4)_3$ 973180, $[\text{Cotren}(\text{MepyrzH}_{0.5})_3]_2 (\text{BF}_4)_3$ 973182, $[\text{Cotren}(\text{MepyrzH})_2(\text{Mepyrz})] [\text{Cotren}(\text{Mepyrz})_2(\text{MepyrzH})] (\text{BF}_4)_3 \cdot 3.81 \text{H}_2\text{O}$ 973183, $\{[\text{Cotren}(\text{MepyrzH}_{0.5})_3 (\text{C}_6\text{H}_6) \text{CH}_3\text{CN}]\}_2(\text{ClO}_4)_3$ 973181 (123 K), $\{[\text{Cotren}(\text{MepyrzH}_{0.5})_3 (\text{C}_6\text{H}_6) \text{CH}_3\text{CN}]\}_2(\text{ClO}_4)_3$ 973178 (150 K), $[\text{Cotren}(\text{MepyrzH})_3][\text{Cotren}(\text{Mepyrz})_3]_2$ 973177.

Table 1. a) [Cotren(MepyrzH)₃](ClO₄)₃·3.5 H₂O, b) [Cotren(MepyrzH_{0.5})₃]₂(ClO₄)₃, c) [Cotren(MepyrzH_{0.5})₃]₂(BF₄)₃, d) [Cotren(MepyrzH)₂(Mepyrz)] [Cotren(MepyrzH)(Mepyrz)₂](BF₄)₃·3.81 H₂O, e) {[Cotren(MepyrzH_{0.5})₃]₂ (ClO₄)₃·(C₆H₆)₂ (CH₃CN)₂ @123K, f) {[Cotren(MepyrzH_{0.5})₃]₂ (ClO₄)₃·(C₆H₆)₂·(CH₃CN)₂ @150K, g) [Cotren(MepyrzH)₃][Cotren(Mepyrz)₃] I₂.

	a)	b)	c)	d)	e)	f)	g)
Empirical formula	C ₂₁ H ₃₇ Cl ₃ Co N ₁₀ O _{15.5}	C ₄₂ H ₅₇ Cl ₃ Co ₂ N ₂₀ O ₁₂	C ₄₂ H ₅₇ B ₃ Co ₂ F ₁₂ N ₂₀	C ₄₂ H _{64.62} B ₃ Co ₂ F ₁₂ N ₂₀ O _{3.81}	C ₅₈ H ₇₅ Cl ₃ Co ₂ N ₂₂ O ₁₂	C ₅₈ H ₇₅ Cl ₃ Co ₂ N ₂₂ O ₁₂	C ₄₂ H ₅₇ Co ₂ N ₂₀ I ₂
M/g mol ⁻¹	842.89	1258.28	1220.37	1292.43	1496.61	1496.61	1213.74
Temperature/K	295(2)	123(2)	123(2)	150(2)	123(2)	150(2)	150(2)
λ/Å	0.71073	0.71073	1.54178	0.71073	0.71073	0.71073	0.71073
Crystal System	Monoclinic	Trigonal	Trigonal	Monoclinic	Tetragonal	Tetragonal	Monoclinic
Space group	P21/c	R32	R32	Cc	P4 ₃ 2 ₁ 2	P4 ₃ 2 ₁ 2	Cc
Unit cell dimensions	a = 12.9005(9) Å b = 17.8994(10) Å c = 15.5785(11) Å α = 90° β = 99.931(7)° γ = 90°	a = 16.7663(2) Å b = 16.766(3) Å c = 20.0641(3) Å α = 90° β = 90° γ = 120°	a = 16.6003(3) Å b = 16.6003(3) Å c = 20.0513(6) Å α = 90° β = 90° γ = 120°	a = 16.268(2) Å b = 17.394(2) Å c = 20.188(3) Å α = 90° β = 106.941(2)° γ = 90°	a = 11.82570(10) Å b = 11.82570(10) Å c = 48.5723(11) Å α = 90° β = 90° γ = 90°	a = 11.8445(18) Å b = 11.8445(18) Å c = 48.694(8) Å α = 90° β = 90° γ = 90°	a = 21.1716(10) Å b = 12.3416(6) Å c = 19.6850(9) Å α = 90° β = 93.1640(10) ° γ = 90°
Volume/Å ³	3543.3(4)	4884.55(14)	4785.25(19)	5464.7(13)	6792.70(17)	6831.4(18)	5135.7(4)
Z	4	3	3	4	4	4	4
Abs. Coeff./mm ⁻¹	0.791	0.697	4.776	0.710	0.682	0.679	1.900
F(000)	1740	1950	1878	2664	3112	3112	2436
Crystal size/mm ³	0.53 × 0.47 × 0.08	0.47 × 0.43 × 0.28	0.26 × 0.24 × 0.19	0.295 × 0.05 × 0.045	0.39 × 0.39 × 0.32	0.21 × 0.30 × 0.44	0.22 × 0.135 × 0.11
Theta range/°	5.05 to 26.37	5.164 to 32.828	5.33 to 75.57	1.76 to 22.50	3.05 to 35.17	2.13 to 25.00	1.91 to 27.50
Index ranges	-15 ≤ h ≤ 16 -22 ≤ k ≤ 19 -18 ≤ l ≤ 19	-24 ≤ h ≤ 25 -25 ≤ k ≤ 25 -30 ≤ l ≤ 30	-20 ≤ h ≤ 20 -19 ≤ k ≤ 20 -14 ≤ l ≤ 25	-17 ≤ h ≤ 17 -18 ≤ k ≤ 18 -21 ≤ l ≤ 21	-19 ≤ h ≤ 18 -18 ≤ k ≤ 18 -76 ≤ l ≤ 51	-14 ≤ h ≤ 13 -14 ≤ k ≤ 14 -57 ≤ l ≤ 57	-27 ≤ h ≤ 27 -16 ≤ k ≤ 16 -25 ≤ l ≤ 25
Reflections Collected	20,906	31,672	11,282	15,317	99,409	57,503	36,049
Independent Reflections	7193	3862	2195	6970	14,527	6006	11,652
R1	0.0853	0.0294	0.0814	0.0775	0.0724	0.0537	0.0371
WR2	0.2031	0.0847	0.2203	0.1913	0.1515	0.1189	0.0774
GOF on F ²	1.031	1.123	1.075	1.074	1.194	1.000	1005

Table 2. Selected bond distances (Å) and angles (°) for a) [Cotren(MepyrzH₃)(ClO₄)₃·3.5 H₂O], b) [Cotren(MepyrzH_{0.5})₃]₂(ClO₄)₃ [a], c) [Cotren(MepyrzH_{0.5})₃]₂(BF₄)₃, [a] d) [Cotren(MepyrzH)₂(Mepyrz)]₂[Cotren(MepyrzH)(Mepyrz)₂](BF₄)₃·3.81 H₂O [b], e) {[Cotren(MepyrzH_{0.5})₃]₂(ClO₄)₃·(C₆H₆)₂·(CH₃CN)₂} @123K [c], f) {[Cotren(MepyrzH_{0.5})₃]₂(ClO₄)₃·(C₆H₆)₂·(CH₃CN)₂} @150K, [c] g) [Cotren(MepyrzH)₃][Cotren(Mepyrz)₃]₂ [d].

	a)	b)	c)	d) [CoH ₂ L] ²⁺ and [CoHL] ⁺		e)	f)	g) [CoH ₃ L] ²⁺ and [CoL]			
SG and sym	P2 _{1/c} C _{2h}	R32 D ₃	R32 D ₃	Cc, Cs		P4 ₃ 2 ₁ 2 D ₄	P4 ₃ 2 ₁ 2 D ₄	Cc, Cs			
T(K)	295(2)	123(2)	123(2)	150(2)		123(2)	150(2)	150(2)			
Co-N _{ap} non-bonded	3.339	3.468	3.468	3.432	3.462	3.492	3.492	3.306	3.300		
M-M' non-bonded	NA	5.853	5.853	5.773		5.861	5.872	5.847			
Co-N1(imine)	1.954(2)	1.9591(14)	1.962(4)	1.954(18)	1.947(18)	1.951(2)	1.963(4)	2.031(8)	2.060(7)		
	1.955(2)			1.940(17)	1.982(17)			1.961(2)	1.951(4)	2.049(7)	2.067(8)
	1.970(3)			1.974(18)	1.921(18)			1.924(2)	1.962(4)	2.064(9)	2.038(10)
average	1.960	1.9591	1.9624	1.956	1.950	1.945	1.959	2.048	2.055		
Co-N2(pyrazole)	1.908(3)	1.9141(15)	1.910(4)	1.896(15)	1.918(15)	1.908(2)	1.928(4)	1.979(7)	2.017(8)		
	1.919(2)			1.893(16)	1.8959(16)			1.917(2)	1.913(4)	2.019(8)	2.048(7)
	1.928(2)			1.954(17)	1.883(17)			1.924(2)	1.915(4)	2.145(5)	1.865(5)
average	1.918	1.9141	1.910	1.914	1.899	1.916	1.919	2.048	1.977		
N1-Co-N2 (bite)	81.32(10)	81.66(6)	81.52(17)	81.6(8)	83.6(8)	82.16(10)	80.94(15)	77.3(3)	80.0(3)		
	81.53(11)			82.5(7)	81.3(7)			81.32(10)	82.00(15)	78.3(3)	80.6(3)
	81.46(11)			80.2(8)	80.1(7)			81.25(9)	81.17(16)	76.1(3)	82.2(3)
average	81.44	81.66	81.52	81.4	81.7	81.58	81.37	77.2	80.9		
N1-Co-N2'(trans)	175.82(11)	175.23(6)	175.43(17)	175.0(7)	176.0(8)	174.95(11)	173.78(17)	174.2(4)	175.8(3)		
	175.22(11)			174.0(8)	177.5(8)			174.19(10)	174.71(17)	170.6(3)	176.2(3)
	175.19(11)			172.6(8)	173.7(8)			175.16(10)	175.12(16)	171.4(3)	172.9(3)
average	175.4	175.23	175.43	173.9	175.7	174.77	174.54	172.1	174.97		
C1-N _{ap} -C1	118.6(3)	119.991(5)	119.996(14)	121(2)	130(2)	120.0(2)	120.3(4)	119.6(80)	116.2(8)		
	120.8(3)	119.990(6)	119.991(12)	114(2)	116.0(19)	120.6(2)	120.0(4)	121.1(8)	120.7(7)		
	119.1(3)	119.984(5)	119.995(14)	123(2)	114(2)	119.4(3)	119.7(4)	116.6(8)	119.1(9)		
average	119.5	119.988	119.994	119.3	120.0	120.0	120.0	119.1	118.7		

[a] There is only one Co and one arm of tren in the asymmetric unit. [b] There are two Co atoms each with three tren arms in the asymmetric unit, [CoH₂L]²⁺ (listed first) and [CoHL]⁺ listed second. [c] There is one Co atom and three tren arms in the asymmetric unit. [d] There are two Co atoms each with three tren arms in the asymmetric unit, [CoH₃L]²⁺ (listed first) and [CoL] listed second.

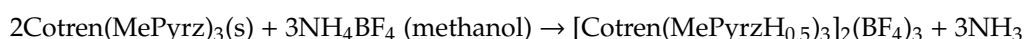
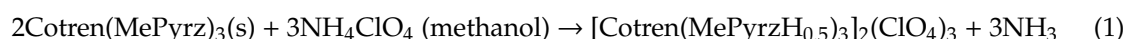
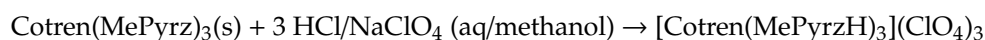
Table 3. Pyrazole hydrogen bond distances (Å) and angles (°) for, [Cotren(MepyrzH_{0.5})₂ (ClO₄)₃, [Cotren(MepyrzH_{0.5})₂ (BF₄)₃, [Cotren(MepyrzH)₂(Mepyrz)][Cotren(MepyrzH)(Mepyrz)₂](BF₄)₃·3.81 H₂O, {[Cotren(MepyrzH_{0.5})₃]₂(ClO₄)₃·(C₆H₆)₂·(CH₃CN)₂ @123K, {[Cotren(MepyrzH_{0.5})₃]₂(ClO₄)₃·(C₆H₆)₂·(CH₃CN)₂ @150K, [Cotren(MepyrzH)₃][Cotren(Mepyrz)₃] I₂.

Compound	Interaction	d(D-H)	d(H ... A)	d(D ... A)	<(DHA)
[Cotren(MepyrzH _{0.5}) ₂ (ClO ₄) ₃ T = 123(2)K	N-H ... N' (three)	0.88	1.83	2.670(3)	160.1
Average		0.88	1.83	2.670	160.1
[Cotren(MepyrzH _{0.5}) ₂ (BF ₄) ₃ T = 123(2)K	N-H ... N' (three)	0.88	1.83	2.674(8)	158.9
Average		0.88	1.83	2.67	158.9
[Cotren(MepyrzH) ₂ (Mepyrz)] [Cotren(MepyrzH)(Mepyrz) ₂] (BF ₄) ₃ ·3.81 H ₂ O T = 150(2) K	N-H ... N' N-H ... N' N-H ... N'	0.88 0.88 0.88	1.88 1.87 1.87	2.73(2) 2.72(3) 2.714(10)	162 161 160.
Average		0.88	1.87	2.72	161
{[Cotren(MepyrzH _{0.5}) ₃] ₂ (ClO ₄) ₃ ·(C ₆ H ₆) ₂ ·(CH ₃ CN) ₂ @123K T = 123(2) K	N-H ... N' N-H ... N' N-H ... N'	0.88 0.88 0.88	1.83 1.83 1.80	2.679(3) 2.679(3) 2.643(4)	161.9 161.5 160.5
Average		0.88	1.82	2.667	161.3
{[Cotren(MepyrzH _{0.5}) ₃] ₂ (ClO ₄) ₃ ·(C ₆ H ₆) ₂ ·(CH ₃ CN) ₂ @150K, T = 150(2) K	N-H ... N' N-H ... N'(twice)	0.88 0.88	1.81 1.84	2.655(7) 2.685(5)	160.0 161.0
Average		0.88	1.83	2.675	160.7
[Cotren(MepyrzH) ₃][Cotren(Mepyrz) ₃] I ₂ T = 150(2) K	N-H ... N' N-H ... N' N-H ... N'	0.88 0.88 0.88	1.98 1.89 1.90	2.819(12) 2.744(12) 2.754(8)	160. 162 162
Average		0.88	1.92	2.772	152

3. Results and Discussion

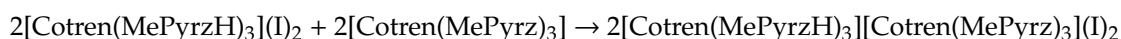
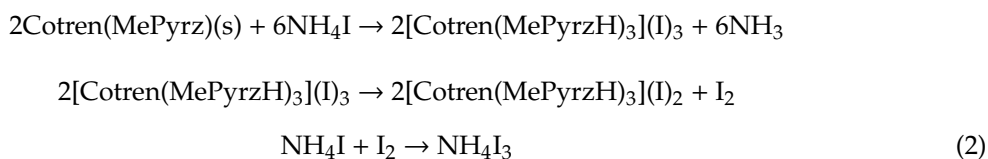
3.1. Synthesis and Initial Characterization

The syntheses of [Cotren(MePyrzH)₃](ClO₄)₃, [Cotren(MePyrzH_{0.5})₃]₂(ClO₄)₃ and [Cotren(MePyrzH_{0.5})₃]₂(BF₄)₃ were achieved by the reaction of the previously prepared insoluble Co(tren)(MePyrz)₃, [37] with Lewis acids as illustrated below. The insolubility of this species is not understood in comparison to analogous complexes of similar ligands, but does not appear to hinder its reactivity. Lewis acid base reactions can be conducted by adding a solution of a suitable Lewis acid to a slurry of [Cotren(MePyrz)₃] which acts as a Lewis base due to its three deprotonated pyrazolate rings. The resulting solution of both reactants is left to stand and the products crystallize from the reaction mixture.



The tetrafluoroborate salt crystallizes as both an anhydrous and a hydrated form and both were structurally characterized. The synthesis of the analogous iodide salt is complicated by the fact that the iodide ion can reduce the cobalt(III) to cobalt(II). The product is a cobalt(II)-cobalt(III) mixed valence species [38], [Cotren(MePyrzH)₃][Cotren(MePyrz)₃]I₂. The likely sequence of reactions is protonation

of the cobalt complex by the ammonium cation, followed by reduction of this species by iodide and the formation of the pseudo dimer as illustrated below:



For completeness an attempt was made to prepare the previously synthesized [33] and structurally characterized $[\text{Cotren}(\text{MepyrzH})(\text{Mepyrz})_2](\text{ClO}_4)$ by following the literature preparation which grew crystals by infusion of benzene into an acetonitrile solution of the reaction product. The present work resulted in the isolation of $\{[\text{Cotren}(\text{MepyrzH}_{0.5})_3(\text{C}_6\text{H}_6)\text{CH}_3\text{CN}]_2(\text{ClO}_4)_3\}$ despite careful attempts to reproduce the previously reported synthesis. The present inability to isolate the reported $[\text{Cotren}(\text{MepyrzH})(\text{Mepyrz})_2](\text{ClO}_4)$ is not understood, but it is possible that in the earlier work the purification produced both $[\text{Cotren}(\text{MepyrzH})(\text{Mepyrz})_2](\text{ClO}_4)$ (which was reported) and $\{[\text{Cotren}(\text{MepyrzH}_{0.5})_3(\text{C}_6\text{H}_6)\text{CH}_3\text{CN}]_2(\text{ClO}_4)_3\}$ which was not reported or observed earlier. However, it is isolated and structurally characterized as part of this work.

The initial characterization of complexes was carried out by IR spectroscopy. The most useful regions for examination in the IR were the N-H, C=N, and perchlorate Cl-O, and tetrafluoroborate B-F. The IR spectra of the $[\text{Cotren}(\text{MepyrzH})_3](\text{ClO}_4)_3$ mononuclear complex shows the characteristic absorption bands attributable to the pyrazole $\nu_{\text{N-H}}$ ($3100\text{--}3300\text{ cm}^{-1}$), imine $\nu_{\text{C=N}}$ at $\sim 1640\text{ cm}^{-1}$ and perchlorate $\nu_{\text{Cl-O}}$ ($1147\text{--}1154$ and 625 cm^{-1}). The position of the imine absorption for the cobalt complexes increases with the protonation state of the ligand [39]. For $[\text{Cotren}(\text{Mepyrz})_3]$ the absorption appears close to 1600 cm^{-1} , consistent with deprotonation of the ligand. This peak shifts to higher wavenumbers for the dimers/pseudodimers. The $[\text{Cotren}(\text{MePyrzH})_3][\text{Cotren}(\text{MePyrz})_3]\text{I}_2$ pseudo-dimer exhibit two imine $\nu_{\text{C=N}}$ absorptions in the IR spectrum corresponding to the Co(II) and Co(III) components. In addition to the expected $\nu_{\text{N-H}}$ and $\nu_{\text{C=N}}$ absorptions, the IR spectra of all the pseudo-dimers exhibit broad bands at $\sim 2100\text{--}1800$ and $\sim 2375\text{ cm}^{-1}$, which are not observed in the IR spectra of the mononuclear complexes. These bands have been observed previously in similar hydrogen bound complexes and are attributed to intermolecular azole-azole hydrogen bonding [40–42].

3.2. Structures of the Complexes, General Features

All of the cobalt species reported here are six coordinate distorted octahedral complexes bound to three facial pyrazole nitrogen atoms and three facial imine nitrogen atoms. The apical nitrogen atom (N_{ap}) of the tren caps the three facial imine nitrogen atoms. In these complexes the Co to N_{ap} distance is too large to be considered a bond. However in related complexes the distance is short enough that the geometry is the seven coordinate capped octahedron [43]. The complexes are chiral, Λ or Δ , as determined by the twist orientation of the three tren arms. Relevant bond distance and angles are given for all complexes in Table 2. The above features are illustrated for $[\text{Cotren}(\text{MepyrzH})_3](\text{ClO}_4)_3$ in Figure 4. This is the only mononuclear complex reported here and the remaining complexes are dimeric or pseudodimeric species held together by three $\text{N}_{\text{pyrazole-H}} \cdots \text{N}_{\text{pyrazolate}}$ hydrogen bonds as described below. There are earlier reports of mononuclear tren pyrazole complexes [44–47].

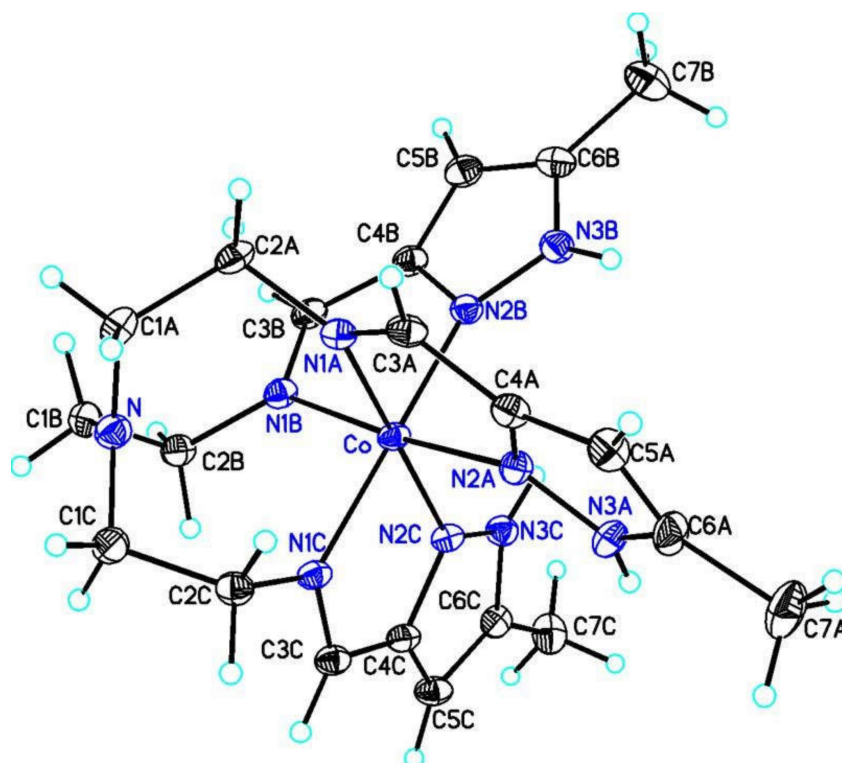


Figure 4. Structure of the $[\text{Co}(\text{tren}(\text{MepyrzH})_3)]^{3+}$ cation. Note that the apical nitrogen atom, labelled N above, caps the face of the three imine nitrogen atoms, N1A, N1B and N1C.

3.3. General Structure of the Dimers/Pseudodimers

Structures of several tren pyrazolate dimers or pseudodimers, $[\text{Fetren}(\text{MepyrzH})_3\text{-Fetren}(\text{Mepyrz})_3]^{2+}$, $[\text{Mntren}(\text{MepyrzH})_3\text{-Fetren}(\text{Mepyrz})_3]^{2+}$, $[\text{Fetren}(\text{MepyrzH})_3\text{-Cotren}(\text{Mepyrz})_3]^{2+}$, $[\text{Mntren}(\text{MepyrzH})_3\text{-Cotren}(\text{Mepyrz})_3]^{2+}$ have been reported previously [32,37]. The term dimer is used if there is a single metal complex in the asymmetric unit, meaning that it is a true dimer, made of two identical halves. Even in a dimer that contains two different metals, M and M', or the same metal in two different oxidation states the symmetry imposed by the space group may average these which manifests as a $\text{M}_{0.5}\text{M}'_{0.5}$ bound to a hemideprotonated ligand, $\text{tren}(\text{MepyrzH}_{0.5})_3^{-1.5}$. The term pseudodimer is used if there are two metal complexes in the asymmetric unit. This too is determined by the symmetry imposed by the space group. In this case the two metal complexes are different, either because the metals are different, in different oxidation states or the levels of protonation on the two ligands are different, such as $\text{tren}(\text{MepyrzH})_3$, $\text{tren}(\text{Mepyrz})_3^{3-}$. Regardless of this distinction between dimer and pseudodimer both complexes exhibit three structural features in common. 1) The dimers have three $\text{N}_{\text{pyrazole}}\text{-H}\cdots\text{N}_{\text{pyrazolate}}$ hydrogen bonds that link the two halves of the dimer/pseudodimer together. 2) The dimers exhibit π - π stacking of the three pairs of pyrazole rings. The pyrazole rings are not perfectly eclipsed. There is slippage between the two rings but their small interplanar angle ($<2^\circ$) and a short centroid to centroid distance (~ 3.4 Å) supports the π - π interaction. And 3) homochirality of both metal complexes of the dimer/pseudodimer, either both Δ or both Λ . These features are illustrated in Figure 5 for $[\text{Cotren}(\text{MepyrzH})_3][\text{Cotren}(\text{Mepyrz})_3]^{2+}$ cation. This homochirality feature is required for the formation of both the hydrogen bonding and the π - π stacking. There are other examples of complexes that exhibit some of these features individually. A copper Schiff base dimer is held together by hydrogen bonding but lacks the other structural elements [48]. The π - π stacking feature is observed in imidazole based supramolecular complexes of manganese(II) and cobalt(II) [49]. The intervalence and hydrogen bonding features of the Co(II)-Co(III) pseudodimer were observed in a ferrocene derivative [50]. The structures of the present cobalt complexes exhibit these same features but these new systems exhibit previously

unobserved symmetry characteristics due to the crystallization of the complex in Sohncke [51] space groups as discussed in the descriptions that follow.

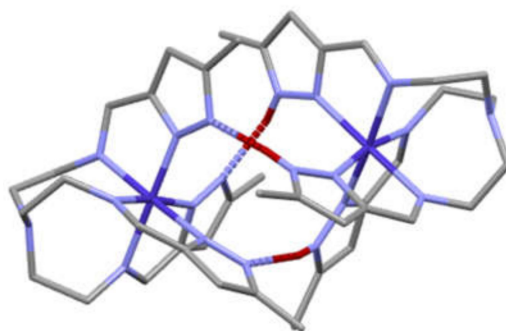


Figure 5. Structure of the $[\text{Cotren}(\text{MepyrzH})_3][\text{Cotren}(\text{Mepyrz})_3]^{2+}$ cation. All the hydrogen atoms except for the bridging hydrogen atoms, shown in red, have been deleted. Note the three $\text{N}_{\text{pyrazole}}\text{-H}\cdots\text{N}_{\text{pyrazolate}}$ hydrogen bonds, shown as dashed blue red bonds, holding the two homochiral halves of cation together and the alignment of the three pairs of pyrazole rings to promote π - π stacking. The apical nitrogen atoms of the tren units are in light blue at the bottom left and upper right of figure. The two octahedral cobalt atoms are in dark blue, the cobalt(III) on left and cobalt(II) on right.

In the case of the tren pyrazole dimers both halves of the dimer must be of the same chirality either delta or lambda in order for the hydrogen bonding and π - π stacking to occur. Another example of polynucleation that must select for homochirality is the tetrahedral tetranuclear complex, $\{[\text{Cotren}(4\text{-MeImH})(4\text{-MeIm})_2]_3[\text{Cotren}(4\text{-MeImH})_3]\}(\text{ClO}_4)_6$, which is averaged as $[\text{Cotren}(4\text{-MeImH}_{0.5})_3]_4(\text{ClO}_4)_6$, and pictured in Figure 6 [52]. In the case of both the dinuclear and tetranuclear complex homochirality within the polynuclear unit, dimer or tetramer, is required to form the three (dimer) or six hydrogen bonds (tetramer) that hold the polynuclear unit together. In both cases each monomer forms three hydrogen bonds. In the dimer the three hydrogen bonds are to the same molecule and in the tetramer the three hydrogen bonds are to three different complexes. Extension of homochirality throughout the entire crystal can only occur in a Sohncke space group which is non-centrosymmetric and contains a single enantiomer.

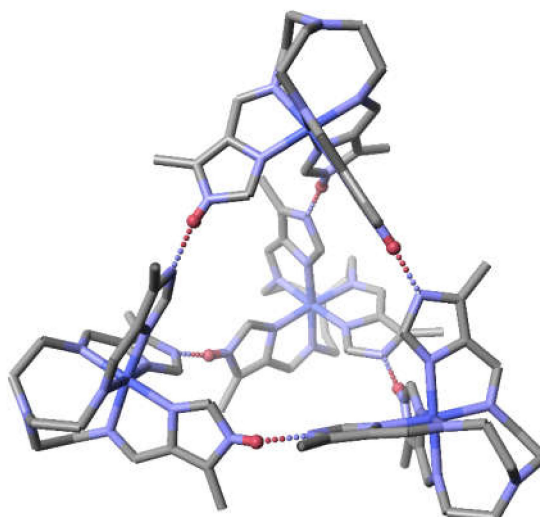


Figure 6. Structure of $[\text{Cotren}(\text{4MeImH}_{0.5})_3]_4(\text{ClO}_4)_6$ (average level of protonation per Co) showing the tetrahedral array of cobalt complexes and the six hydrogen bonds folding the cluster together. All hydrogen atoms, except for the hydrogen bond bridging hydrogen atoms, shown in red, and the perchlorate anions have been omitted for clarity. Note that there are twelve hydrogen bond imidazole atoms which require six hydrogen atoms to link all the imidazoles together. Each cobalt complex forms three hydrogen bonds (through its three arms) to each of the other three cobalt complexes.

Broadly speaking there are two types of symmetry elements that could be observed in these $\text{Mtren}(\text{Mepyrz})_3$ dimers/pseudodimers. A three-fold axis along the apical tren nitrogen atom and the metal atom (making the three tren arms identical) or a symmetry element that interchanges the two metal sites such as a two fold rotation axis. The former would result in a single tren arm per metal complex in the asymmetric unit and the latter would give three tren arms but an average metal site, $[\text{M}_{0.5} \text{M}_{0.5}'\text{L}]$. The presence of both symmetry elements would give a single tren arm and a single metal atom in the asymmetric unit. Some previously prepared dimers/pseudodimers crystallized in $\text{C}_{2/c}$ (C_{2h}) and P_{bcn} (D_{2h}). These space groups are centrosymmetric, contain both enantiomers and exhibit one metal and three tren arms in the asymmetric unit due to a two fold proper rotation axis. Others crystallize in C_c (C_s) (non centrosymmetric, both enantiomers) and Pbar1 (C_i) (centrosymmetric, both enantiomers). The dimers in these groups exhibit two metal sites and three tren arms/metal in the asymmetric unit. None of these space groups are of the Sohncke classification. In the present collection of homonuclear cobalt complexes Sohncke space groups are observed for three of the dimers which alters the symmetry considerations significantly.

$[\text{Cotren}(\text{MepyrzH}_{0.5})_3]_2 \text{X}_3$ ($\text{X} = \text{ClO}_4^-$ and BF_4^-). The structures of $[\text{Cotren}(\text{MepyrzH}_{0.5})_3]_2 \text{X}_3$ ($\text{X} = \text{ClO}_4^-$ and BF_4^-) dimers are isomorphous in Sohncke space group $\text{R}32$ which has D_3 symmetry. There is a single cobalt(III) ion and a three fold rotation axis (shown in red) that runs through the apical tren nitrogen and the cobalt atoms. They also possess three two fold rotation axis (shown in blue) that bisects the cobalt-cobalt non bonded axis. This is illustrated in Figure 7.

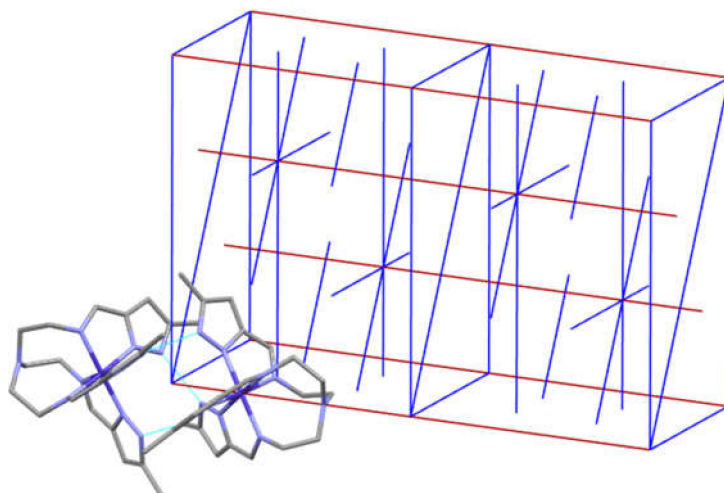


Figure 7. The unit cell (space group R32) of $[\text{Cotren}(\text{MepyrzH}_{0.5})_3]_2^{3+}$ is depicted above with one of the dimers (all H atoms and counterions omitted for clarity) that it contains. The red line is a three fold rotation axis and also an axis of the cell. Note that the three fold axis (red) runs through the apical tren nitrogen and cobalt atoms which result in a single tren arm in the asymmetric unit. R32 (D_3) requires a three fold rotation axis (red) and three perpendicular two fold rotation axis (blue). The two fold rotation (blue) bisects the non bonded cobalt-cobalt axis and is perpendicular to a $\text{N}_{\text{pyrazole}}-\text{H} \cdots \text{N}_{\text{pyrazolate}}$ hydrogen bond. This results in a single cobalt atom in the asymmetric unit by a two fold rotation. The effect of both of these symmetry elements is that the asymmetric unit contains a single cobalt atom (not two) and a single tren arm (not three).

There are no mirror planes or glide planes as R32 is a Sohncke space group that allows for the crystallization of a single enantiomer of a chiral molecule. A mirror plane is equivalent to an improper axis of rotation which a chiral molecule cannot have. This type of symmetry, imposed by a Sohncke space group, has not been observed previously in the earlier pyrazole dimers/pseudodimers. The entire crystal is homochiral (resolved at the level of the crystal) but the entire sample is likely achiral as it contains equal numbers of molecules of opposite chirality (racemic conglomerate). Crystals of this type could be separated by hand into the lambda and delta isomers as was done by Pasteur for tartrate salts.

$[\text{Cotren}(\text{MepyrzH}_{0.5})_3]_2 (\text{BF}_4)_3$ also crystallizes as a hydrate, $[\text{Cotren}(\text{MepyrzH})_2(\text{Mepyrz})][\text{Cotren}(\text{Mepyrz})_2(\text{MepyrzH})] (\text{BF}_4)_3 \cdot 3.81 \text{H}_2\text{O}$, in Cc. It is neither isomorphous or a polymorph of $[\text{Cotren}(\text{MepyrzH}_{0.5})_3]_2$. In this case the space group requires that the two metal sites be distinct and that there is no three fold axis along the apical tren nitrogen and cobalt atoms. These differences are achieved by having different levels of protonation on the two pyrazolate rings of the two ligands in the pseudodimer to give the $\{[\text{Cotren}(\text{MepyrzH})_2(\text{Mepyrz})][\text{Cotren}(\text{MepyrzH})(\text{Mepyrz})_2]\}^{3+}$ cation.

$[\text{Cotren}(\text{MepyrzH}_{0.5})_3 (\text{C}_6\text{H}_6 \text{CH}_3\text{CN})_2 (\text{ClO}_4)_3$. This complex resulted from the attempt to repeat the earlier synthesis of $[\text{Cotren}(\text{MepyrzH})(\text{Mepyrz})_2]\text{ClO}_4$. This attempt resulted in the preparation of a new compound that crystallized in $P4_32_12$ which has D_4 symmetry. In this dimer the two cobalt complexes are equivalent as a two-fold rotation axis bisects a $\text{N}_{\text{pyrazole}}-\text{H} \cdots \text{N}_{\text{pyrazolate}}$ hydrogen bond axis and the non-bonded cobalt-cobalt axis as shown in Figure 8. The three tren arms are not equivalent. The four fold rotation axis is a screw axis of the cell (not the molecule) There are no mirror planes as this is a Sohncke space group that allows for crystallization of a single enantiomer as was discussed earlier for $[\text{Cotren}(\text{MepyrzH}_{1.5})_3]_2 \times_3$ ($X = \text{ClO}_4^-$ and BF_4^-) that crystallizes in R32 (racemic conglomerate). The situation here is more complicated as $P4_32_12$ is an entaniomorphous (chiral) space group which means that if one enantiomer crystallizes in $P4_32_12$ the other enantiomer cannot crystallize in the same space group and must crystallize in the enantiomorphous space group, $P4_12_12$ in this case. This could result in total spontaneous resolution. While it was not possible to examine each crystal a structural determination was made of another crystal from the same batch and it was identical to the first. Both results are reported here.

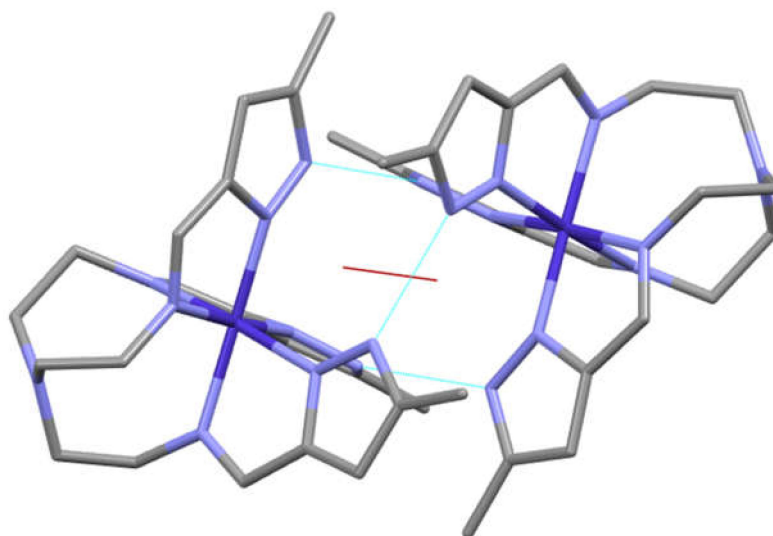


Figure 8. Structure of the pyrazole dimer in $P4_32_12$. The unit cell axes are not depicted here. The hydrogen atoms and counterions have been omitted for clarity. Note the three hydrogen bonds (dashed blue) connecting the two pairs of pyrazole rings and the alignment of rings for π - π stacking. The red line is a C_2 proper rotation axis that bisects one of the three hydrogen bonds and the non-bonded cobalt-cobalt axis. This two fold rotation axis (the only symmetry element in the molecule) means that there is a single cobalt atom and three tren arms in the asymmetric unit. This contrasts with the previous molecule in $R32$ in that it lacks a three fold rotation axis on the molecule. The four fold rotation axis in this space group (D_4 symmetry) is not a rotation axis of the molecule itself but a screw axis of the cell. Clearly a tripodal ligand could not have a fold fold proper rotation axis.

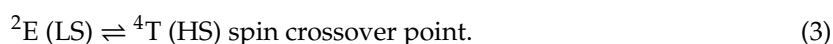
$[\text{Cotren}(\text{MePyrzH})_3][\text{Cotren}(\text{MePyrz})_3]_2$. This compound was prepared by the same method as were $[\text{Cotren}(\text{MePyrzH}_{0.5})_3]_2 X_3$ ($X = \text{ClO}_4^-$ and BF_4^-). The reaction was simply adding a solution of ammonium iodide (rather than perchlorate or tetrafluoroborate) to the insoluble $\text{Cotren}(\text{MePyrz})_3$. The result in this case was different as the product was the mixed valent cobalt(II)-cobalt(III) pseudodimer in Cc (C_s symmetry). There are two cobalt complexes in the asymmetric unit each with three unique tren arms. In this case one complex has all three pyrazolates protonated and the other has all three deprotonated. These are assigned as cobalt(II) and cobalt(III) respectively due to the fact that reduction is easier for a positively charged species over a neutral assuming other factors are unchanged. This species is an intervalence compound as it contains a cobalt(II) and a cobalt(III) or an average oxidation state of $\text{Co}^{+2.5}$. In this case the rate of electron transfer between the two cobalt atoms would be slow as this is a Class I intervalence compound as the metals are not in identical structural fields. However a small change in crystallization conditions (presence of a two-fold rotation axis) would mean that the compound was a Class III intervalence system with a non-localized electron.

3.4. Correlation of Spin State with Structural Parameters

Structural signatures of high spin (HS) and low spin (LS) iron(II) and iron(III) [53] tripodal tren imidazole complexes have been investigated previously from experimental and computational approaches [54,55]. The signatures are 1) the $\text{Fe-N}_{\text{imidazole}}$ and $\text{Fe-N}_{\text{imine}}$ bond distances 2) the $\text{N}_{\text{imidazole}}\text{-Fe-N}_{\text{imine}}$ bite angle 3) the $\text{N}_{\text{imidazole}}\text{-Fe-N}_{\text{imine'}}$ trans angle 4) the Fe-N_{ap} distance and 5) the N_{ap} conformation. In general the HS state correlates with long $\text{Fe-N}_{\text{imidazole}}$ and $\text{Fe-N}_{\text{imine}}$ bond distances ($> 2.10 \text{ \AA}$), $\text{N}_{\text{imidazole}}\text{-Fe-N}_{\text{imine}}$ bite angles of $\sim 76^\circ$, $\text{N}_{\text{imidazole}}\text{-Fe-N}_{\text{imine'}}$ trans angles of $\sim 166^\circ$, short M-N_{ap} distances ($< 3.1 \text{ \AA}$) and the conformation of the apical nitrogen atom of the tren bent in ("Nin") towards the iron atom. In contrast the LS state correlates with short $\text{Fe-N}_{\text{imidazole}}$ and $\text{Fe-N}_{\text{imine}}$ bond distances ($< 2.00 \text{ \AA}$), $\text{N}_{\text{imidazole}}\text{-Fe-N}_{\text{imine}}$ bite angles of $\sim 81^\circ$, $\text{N}_{\text{imidazole}}\text{-Fe-N}_{\text{imine'}}$ trans angles of $\sim 175^\circ$, long Fe-N_{ap} distances ($> 3.1 \text{ \AA}$) and "N out" or planar conformation of the apical tren nitrogen atom. The above structural signatures are so pronounced that LS structures of iron(II) and iron(III) are

essentially identical with these ligands as are HS structures. In other words the effect of oxidation state is minor relative to spin state on structural parameters.

Comparison of the above structural parameters of iron(III) (d^5) and iron(II) (d^6) with the analogous values for all of the cobalt(III) (d^6) complexes in Table 2 clearly suggests that all of the cobalt(III) complexes are LS. This is hardly surprising as all but a few cobalt(III) complexes are LS. This does not mean that structural data is a true measurement of the electronic ground state but it does suggest that the above parameters correlate extremely well with spin state selection in this class of complexes. The [Cotren(MePyrzH)₃][Cotren(MePyrz)₃]I requires further comment as it contains both a cobalt(II) and a cobalt(III). The Co-pyrazole bond distance is the longest (2.048 Å) and the bite (77.2°) and trans (172.1°) angles are the smallest for Cotren(MePyrzH)₃ of all the complexes listed in Table 2. The lengthening of the Co-pyrazole bond distance can be explained on the fact that pyrazolate is a stronger binder than a pyrazole. The bite and trans angles are not completely in the LS regime but have moved in that direction. More definitive comments on the spin state of the Co(II) in this complex requires a separate investigation to synthesize, isolate and magnetostructurally characterize a mononuclear [Cotren(MePyrzH)₃]²⁺ species. It is possible that the Co(II) d^7 species is LS or close to the equilibrium:



4. Summary

One aspect of materials science work is to incorporate features into a molecular system that have potential for applications. Two aspects that may be desirable to incorporate into a molecular system are spin crossover (SC) and intervalence (IV). A SC molecule can switch between two electronic states with different magnetic properties due to a change in temperature, pressure, optical stimulation or other environmental features such as pH. Such molecules can be thought of as a switch or memory storage device. A metal(II)-metal(III) intervalence molecule has a non integral average oxidation state and can serve as a storage site for an electron or could be used to promote rapid electron transfer. If the symmetry of the intervalence compound resulted in a single metal in the asymmetric unit then the compound would be a Class III intervalence species in which the electron is not localized and the metal ions are in an average non integral oxidation state. Well known examples of these are magnetite, Fe₃O₄, basic iron acetate, Fe₃O(OAc)₆(H₂O)₃, and the Creutz Taube ion, [(NH₃)₅Ru(pyrazine)Ru(NH₃)₅]⁵⁺. The pyrazole dimers/pseudodimers discussed here have the features of SC and IV. In addition they have the ability to self-assemble through a stereochemical (chiral) molecular recognition process which means that one tren pyrazole complex can bind selectively to only the same enantiomer of a racemic mixture. If these molecules were incorporated into a material then the door is open to fully exploit the stereochemical and symmetry features as well as the SC and IV aspects. An example of how this incorporation could be achieved is as follows. The central nitrogen atom of the tren can be alkylated by reaction with an alkyl iodide, RI, or other agent. A silicon (or other) based material, which had incorporation of this functionalization, -Si-Si-C(I)-Si-Si- could be reacted with tren to give -Si-Si-C(N(CH₂CH₂NH₂)₃)-Si-Si-. Further reaction of this with MepyrzH followed by a metal would incorporate half of the dimer (monomer) into the material. The other half of the dimer can self-assemble onto the first half by chiral recognition and formation of hydrogen bonds to give dimer/pseudodimer attached to the original material. Incorporation of the dimer/pseudodimer into the original material allows for possible exchange reactions such as selective removal of a single enantiomer from solution. There are many potential uses of such a material that could exploit the SC and IV properties. The complexes presented here and in earlier work show that subtle variations in reaction and or crystallization conditions have a profound effect on the molecular symmetry by altering the space group that is exhibited. Any of these features could be exploited by incorporating these molecules into a new material.

Author Contributions: G.B. was responsible for the conceptual development of the project, design of experimental synthesis and obtaining crystals of the desired compounds; R.J.B. and P.Z. independently carried out the single crystal structure determinations; G.B. wrote the manuscript but discussion of the crystallographic information was dependent upon the expertise of the crystallographers; Clearly this report would not be possible without the experimental work and structural expertise of R.J.B. and P.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was in part funded by NASA under the coop NASAM13A administered through the Goddard Space Flight center.

Acknowledgments: The contribution of C.T. Brewer to the discussion if this work is gratefully acknowledged.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Brewer, C.T.; Brewer, G.; Luckett, C.; Marbury, G.S.; Viragh, C.; Beatty, A.M.; Scheidt, W.R. Proton control of oxidation and spin state in a series of iron tripodal imidazole complexes. *Inorg. Chem.* **2004**, *43*, 2402–2415. [[CrossRef](#)] [[PubMed](#)]
2. Lambert, F.; Policar, C.; Durot, S.; Cesario, M.; Yuwei, L.; Korri-Youssoufi, H.; Keita, B.; Nadjo, L. Imidazole and imidazolate iron complexes: on the way for tuning 3D-structural characteristics and reactivity. *Redox Inorg. Chem.* **2004**, *43*, 4178–4188. [[CrossRef](#)] [[PubMed](#)]
3. Sunatsuki, Y.; Ikuta, Y.; Matsumoto, N.; Ohta, H.; Kojima, M.; Iijima, S.; Hayami, S.; Maeda, Y.; Kaizaki, S.; Dahan, F.; et al. An unprecedented homochiral mixed-valence spin-crossover compound. *Angew. Chem. Int. Ed.* **2003**, *42*, 1614. [[CrossRef](#)] [[PubMed](#)]
4. Ikuta, Y.; Ooidemizu, M.; Yamahata, Y.; Yamada, M.; Osa, S.; Matsumoto, N.; Iijima, S.; Sunatsuki, Y.; Kojima, M.; Dahan, F.; et al. A New Family of Spin Crossover Complexes with a Tripod Ligand Containing Three Imidazoles: Synthesis, Characterization, and Magnetic Properties of $[\text{Fe}^{\text{II}}\text{H}_3\text{L}^{\text{Me}}](\text{NO}_3)_2 \cdot 1.5\text{H}_2\text{O}$, $[\text{Fe}^{\text{III}}\text{L}^{\text{Me}}] \cdot 3.5\text{H}_2\text{O}$, $[\text{Fe}^{\text{II}}\text{H}_3\text{L}^{\text{Me}}][\text{Fe}^{\text{II}}\text{L}^{\text{Me}}]\text{NO}_3$, and $[\text{Fe}^{\text{II}}\text{H}_3\text{L}^{\text{Me}}][\text{Fe}^{\text{III}}\text{L}^{\text{Me}}](\text{NO}_3)_2$ ($\text{H}_3\text{L}^{\text{Me}} = \text{Tris}[2-((2\text{-methylimidazol-4-yl)methylidene)amino]ethyl]amine$). *Inorg. Chem.* **2003**, *42*, 7001–7017. [[PubMed](#)]
5. Yamada, M.; Ooidemizu, M.; Ikuta, Y.; Osa, S.; Matsumoto, N.; Iijima, S.; Kojima, M.; Dahan, F.; Tuchagues, J.P. Interlayer Interaction of Two-Dimensional Layered Spin Crossover Complexes $[\text{Fe}^{\text{II}}\text{H}_3\text{L}^{\text{Me}}][\text{Fe}^{\text{II}}\text{L}^{\text{Me}}]\text{X}$ ($\text{X}^- = \text{ClO}_4^-$, BF_4^- , PF_6^- , AsF_6^- , and SbF_6^- ; $\text{H}_3\text{L}^{\text{Me}} = \text{Tris}[2-((2\text{-methylimidazol-4-yl)methylidene)amino]ethyl]amine$). *Inorg. Chem.* **2003**, *42*, 8406. [[CrossRef](#)]
6. Sunatsuki, Y.; Ohta, H.; Kojima, M.; Ikuta, Y.; Goto, Y.; Matsumoto, N.; Iijima, S.; Akashi, H.; Kaizaki, S.; Dahan, F.; et al. Supramolecular Spin-Crossover Iron Complexes Based on Imidazole–Imidazolate Hydrogen Bonds. *Inorg. Chem.* **2004**, *43*, 4154–4171. [[CrossRef](#)]
7. Ohta, H.; Sunatsuki, Y.; Ikuta, Y.; Matsumoto, N.; Iijima, S.; Akashi, H.; Kambee, T.; Kojima, M. Spin crossover in a supramolecular Fe(II)-Fe(III) system. *Mater. Sci.* **2003**, *21*, 191.
8. Slattery, S.J.; Blaho, J.K.; Lehn, J.; Goldsby, K.A. pH-Dependent metal-based redox couples as models for proton-coupled electron transfer reactions. *Coord. Chem. Rev.* **1998**, *174*, 391–416. [[CrossRef](#)]
9. Hays, A.A.; Vassiliev, I.R.; Golbeck, J.H.; Debus, R.J. Role of D1-His190 in Proton-Coupled Electron Transfer Reactions in Photosystem II: A Chemical Complementation Study. *Biochemistry* **1998**, *37*, 11352–11365. [[CrossRef](#)] [[PubMed](#)]
10. Aedelroth, P.; Paddock, M.L.; Tehrani, A.; Beatty, J.T.; Feher, G.; Okamura, M.Y. Identification of the Proton Pathway in Bacterial Reaction Centers: Decrease of Proton Transfer Rate by Mutation of Surface Histidines at H126 and H128 and Chemical Rescue by Imidazole Identifies the Initial Proton Donors. *Biochemistry* **2001**, *40*, 14538–14546. [[CrossRef](#)]
11. Carina, R.F.; Verzegnassi, L.; Bernardinelli, G.; Williams, A.F. Modulation of iron reduction potential by deprotonation at a remote site. *Chem. Comm.* **1998**, 2681–2682. [[CrossRef](#)]
12. Bond, A.M.; Haga, M. Spectrophotometric and voltammetric characterization of complexes of bis(2,2'-bipyridine)(2,2'-bibenzimidazole)ruthenium and -osmium in oxidation states II, III, and IV in acetonitrile/water mixtures. *Inorg. Chem.* **1986**, *25*, 4507–4514. [[CrossRef](#)]

13. Haga, M.; Ano, T.; Kano, K.; Yamabe, S. Proton-induced switching of metal-metal interactions in dinuclear ruthenium and osmium complexes bridged by 2,2'-bis(2-pyridyl)bibenzimidazole. *Inorg. Chem.* **1991**, *30*, 3843–3849. [[CrossRef](#)]
14. Real, J.A.; Gasper, A.B.; Muñoz, M.C. Thermal, pressure and light switchable spin-crossover materials. *Dalton Trans.* **2005**, *12*, 2062–2079. [[CrossRef](#)] [[PubMed](#)]
15. Ohta, H.; Sunatsuki, Y.; Kojima, M.; Iijima, S.; Akashi, H.; Matsumoto, N. A Tripodal Ligand Containing Three Imidazole Groups Inducing Spin Crossover in Both Fe(II) and Fe(III) Complexes; Structures and Spin Crossover Behaviors of the Complexes. *Chem. Lett.* **2004**, *33*, 350–351. [[CrossRef](#)]
16. Sunatsuki, Y.; Sakata, M.; Matsuzaki, S.; Matsumoto, N.; Kojima, M. Thermal and Pressure Induced Spin Crossover of a Novel Iron(III) Complex with a Tripodal Ligand Involving Three Imidazole Groups. *Chem. Lett.* **2001**, 1254. [[CrossRef](#)]
17. Brewer, G.; Butcher, R.J.; Viragh, C.; White, G. Supramolecular assemblies prepared from an iron(II) tripodal imidazole complex. A molecular scaffolding for the self assembly of icosahedral complexes of K⁺, Rb⁺, Cs⁺ and NH₄⁺ cations. *Dalton Trans.* **2007**, 4132–4142. [[CrossRef](#)]
18. Alvarado, L.; Brewer, C.; Brewer, G.; Butcher, R.J.; Straka, A.; Viragh, C. Supramolecular assemblies prepared from an iron(II) tripodal complex, tetrafluoroborate, and alkali metal cations. The effect of cation size on coordination number, anion disorder and hydrogen bonding. *Cryst. Eng. Comm.* **2009**, *11*, 2297–2307. [[CrossRef](#)]
19. Ohba, M.; Yoneda, K.; Agusti, G.; Munoz, M.C.; Gasbar, A.B.; Real, J.A.; Yamasaki, M.; Ando, H.; Nakao, Y.; Sakaki, S.; et al. Bidirectional Chemo-Switching of Spin State in a Microporous Framework. *Angew. Chem. Int. Ed.* **2009**, *48*, 4767. [[CrossRef](#)]
20. Hauser, A.; Jeftic, J.; Romstedt, H.; Hinek, R.; Spiering, H. Cooperative phenomena and light-induced bistability in iron(II) spin-crossover compounds. *Coord. Chem. Rev.* **1999**, *190*, 471–491. [[CrossRef](#)]
21. Kahn, T.O.; Jay-Martinez, C. Spin-Transition Polymers: From Molecular Materials Toward Memory Devices. *Science* **1998**, *279*, 44–48. [[CrossRef](#)]
22. Miller, T.J.S. Magnetically ordered molecule-based assemblies. *Dalton Trans.* **2006**, 2742–2749. [[CrossRef](#)]
23. Batten, S.R.; Murray, K.S. Structure and magnetism of coordination polymers containing dicyanamide and tricyanomethanide, *Coord. Chem. Rev.* **2003**, *246*, 103–130. [[CrossRef](#)]
24. Steed, J.W.; Atwood, J.L. *Supramolecular Chemistry*; John Wiley and Sons: Weinheim, Germany, 2000.
25. Saalfrank, R.W.; Demleitner, B.; Sauvage, J.P. *Transition Metals in Supramolecular Chemistry*; Sauvage, J.P., Ed.; John Wiley and Sons: Weinheim, Germany, 1999.
26. Dodziuk, H. *Introduction to Supramolecular Chemistry*; Kluwer Academic Publishers: Boston, MA, USA, 2001.
27. Alvarado, L.; Brewer, G.; Carpenter, E.E.; Viragh, C.; Zavalij, P. Use of acid–base and redox chemistry to synthesize cobalt(III) and iron(III) complexes of a partially deprotonated triprotic imidazole-containing Schiff base ligand: Hydrogen bound 1D linear homochiral and zig-zag heterochiral supramolecular complexes. *Inorg. Chim. Acta* **2010**, *363*, 817–822. [[CrossRef](#)]
28. Brewer, G.; Alvarado, L.; Lear, S.; Viragh, C.; Zavalij, P. Synthesis, Structure and Supramolecular Features of Heteronuclear Iron(III)-Copper(II) Complexes of a tripodal imidazole containing ligand. *Inorg. Chim. Acta* **2016**, *439*, 111–116. [[CrossRef](#)]
29. Garcia-Terán, J.P.; Castillo, O.; Luque, A.; Garcia-Couceiro, U.; Beobide, G.; Román, P. Supramolecular architectures assembled by the interaction of purine nucleobases with metal-oxalato frameworks. Non-covalent stabilization of the 7H-adenine tautomer in the solid-state. *Dalton Trans.* **2006**, 902–911.
30. Maurizot, V.; Yoshizawa, M.; Kawano, M.; Fujita, M. Control of molecular interactions by the hollow of coordination cages. *Dalton Trans.* **2006**, 2750–2756. [[CrossRef](#)]
31. Brewer, G.; Alvarado, L.J.; Brewer, C.T.; Butcher, R.J.; Cipresi, J.; Viragh, C.; Zavalij, P.Y. Synthesis, structure and supramolecular features of homonuclear iron(III) and heteronuclear iron(III)–cobalt(III) complexes, [FeH₃L][ML](ClO₄)₃ (M = Fe(III) or Co(III)). 2D sheet and tetrahedral arrays. *Inorg. Chim. Acta* **2014**, *421*, 100–109. [[CrossRef](#)]
32. Brewer, C.T.; Brewer, G.; Butcher, R.J.; Carpenter, E.E.; Schmiedekamp, A.M.; Schmiedekamp, C.; Straka, A.; Viragh, C.; Yuzafpolskiy, Y.; Zavalij, P. Synthesis and Characterization of Homo- and Heterodinuclear M(II)-M(III)' (M(II) = Mn or Fe, M(III)' = Fe or Co) Mixed Valence Supramolecular Pseudo-dimers. The Effect of Hydrogen Bonding on Spin State Selection of M(II). *Dalton Trans.* **2011**, *40*, 181. [[CrossRef](#)]

33. Paul, S.; Barik, A.K.; Peng, S.M.; Kar, S.K. Novel Copper(II) Induced Formation of a Porphyrinogen Derivative: X-ray Structural, Spectroscopic, and Electrochemical Studies of Porphyrinogen Complexes of Cu(II) and Co(III) Complex of a Trispyrazolyl Tripodal Ligand. *Inorg. Chem.* **2002**, *41*, 5803–5809. [[CrossRef](#)]
34. Sheldrick, G.M. Phase Annealing in SHELX-90: Direct Methods for Larger Structures. *Acta Crystallogr.* **1990**, *A46*, 467–473. [[CrossRef](#)]
35. Sheldrick, G.M. *SHELXL-97: FORTRAN Program for Crystal Structure Refinement*, 1997; Göttingen University: Göttingen, Germany, 2001.
36. Sheldrick, G.M. *SHELXL-97: FORTRAN Program for Crystal Structure Analysis*, Göttingen University, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400; Göttingen University: Göttingen, Germany, 1998.
37. Brewer, C.T.; Brewer, G.; Butcher, R.J.; Carpenter, E.E.; Schmiedekamp, A.M.; Viragh, C. Synthesis and characterization of a spin crossover iron(II)–iron(III) mixed valence supramolecular pseudo-dimer exhibiting chiral recognition, hydrogen bonding, and π – π interactions. *Dalton Trans.* **2007**, *21*, 295–298. [[CrossRef](#)] [[PubMed](#)]
38. Clark, R.J.H. The Chemistry and spectroscopy of Mixed-Valence complexes. *Chem. Soc. Rev.* **1984**, *13*, 219. [[CrossRef](#)]
39. Katsuki, I.; Motoda, Y.; Sunatsuki, Y.; Matsumoto, N.; Nakashima, T.; Kojima, M. Spontaneous Resolution Induced by Self-Organization of Chiral Self-Complementary Cobalt(III) Complexes with Achiral Tripod-Type Ligands Containing Three Imidazole Groups. *J. Am. Chem. Soc.* **2002**, *124*, 629–640. [[CrossRef](#)]
40. Mimura, M.; Matsuo, T.; Motoda, Y.; Matsumoto, N.; Nakashima, T.; Kojima, M. Deprotonated Copper(II) Complex with a Tripod Ligand Involving Three Imidazole Groups: A Two-Dimensional Chiral Honey-Comb Structure Made by Hydrogen Bonds. *Chem. Lett.* **1998**, 691. [[CrossRef](#)]
41. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; John Wiley and Sons: New York, NY, USA, 1978.
42. Novak, A. Hydrogen bonding in solids correlation of spectroscopic and crystallographic data. *Struc. Bond.* **1973**, *18*, 177–216.
43. Brewer, G.; Brewer, C.; White, G.; Butcher, R.J.; Viragh, C.; Carpenter, E.E.; Schmiedekamp, A. Synthesis and Characterization of Iron(II) and Iron(III) Complexes Derived from Tris(2-aminoethyl)methane. *Inorg. Chim. Acta* **2009**, *362*, 4158. [[CrossRef](#)]
44. Hardie, M.J.; Kilner, C.A.; Halcrow, M.A. Tris[4-(1H-pyrazol-3-yl)-3-azabut-3-enyl]amine iron(II) diperchlorate monohydrate. *Acta Crystallogr. Sect. C.* **2004**, *C60*, m177. [[CrossRef](#)]
45. Sczepanik, J.; Kaminsky, E.B.K.W.; Dechert, S.; Meyer, F. Non-Macrocyclic Schiff Base Complexes of Iron(II) as ParaCEST Agents for MRI. *Eur. J. Inorg. Chem.* **2019**, *2019*, 2404–2411. [[CrossRef](#)]
46. Lazar, H.C.; Barrett, T.F.S.A.; Kliner, C.A.; Letard, J.F.; Halcrow, M.A. Thermal and light-induced spin-crossover in salts of the heptadentate complex [tris(4-[pyrazol-3-yl]-3-aza-3-butenyl)amine]iron(II). *Dalton Trans.* **2007**, 4276–4285. [[CrossRef](#)]
47. Paul, S.; Barik, A.K.; Butcher, R.J.; Kar, S.K. Synthesis and characterisation of nickel(II) complexes with tripodal ligand tris[4-(3-(5-methylpyrazolyl)-3-aza-3-butenyl) amine (MPz3tren): X-ray crystal structure of [Ni(MPz3tren)](BF₄)₂·0.5H₂O. *Polyhedron* **2000**, *19*, 2661. [[CrossRef](#)]
48. Plass, W.; Pohlmann, A.; Rautengarten, J. Magnetic Interactions as Supramolecular Function: Structure and Magnetic Properties of Hydrogen-Bridged Dinuclear Copper(II) Complexes. *Angew. Chem. Int. Ed.* **2001**, *40*, 4207. [[CrossRef](#)]
49. Yi, J.; Che, Y.X.; Zheng, J.M. Magnetic Interactions as Supramolecular Function: Structure and Magnetic Properties of Hydrogen-Bridged Dinuclear Copper(II) Complexes. *J. Coord. Chem.* **2007**, *60*, 2067.
50. Sun, H.; Steeb, J.; Kaifer, A.E.J. Efficient Electronic Communication between Two Identical Ferrocene Centers in a Hydrogen-Bonded Dimer. *Am. Chem. Soc.* **2006**, *128*, 2820–2821. [[CrossRef](#)]
51. Lenartson, A. Absolute Asymmetric Synthesis. Ph.D. Thesis, University of Gothenberg, Gothenberg, Sweden, 2009.
52. Brewer, G.; Butcher, R.J.; Lear, S.; Noll, B.; Zavalij, P.Y. Synthesis, Structure and Supramolecular Features of Cobalt(III) and Cobalt(II) Complexes, [CoHxL](ClO₄)_y ($x = 3, 2, 1.50, 1.45, 1$ and 0) and $x = 3, y = 2$) of a Triprotic Imidazole Containing Schiff Base Ligand. Effect of protonation state on supramolecular structure. *Inorg. Chim. Acta* **2014**, *410*, 94–105.

53. Brewer, C.; Brewer, G.; Butcher, R.J.; Carpenter, E.E.; Cuenca, L.; Noll, B.C.; Scheidt, W.R.; Viragh, C.; Zavalij, P.Y.; Zielaski, D. Synthesis and characterization of manganese(II) and iron(III) d^5 tripodal imidazole complexes. Effect of oxidation state, protonation state and ligand conformation on coordination number and spin state. *Dalton Trans.* **2006**, *28*, 1009–1019. [[CrossRef](#)]
54. Brewer, G.; Olida, M.J.; Schmiedekamp, A.M.; Viragh, C.; Zavalij, P.Y. A DFT Computational Study of Spin Crossover in Iron(III) and Iron(II) Tripodal Imidazole Complexes. A Comparison of Experiment with Calculations. *Dalton Trans.* **2006**, 5617–5629. [[CrossRef](#)]
55. Brewer, G.; Olida, M.J.; Schmiedekamp, A.M.; Viragh, C.; Zavalij, P.Y. A DFT Computational Study of Spin Crossover in Iron(III) and Iron(II) Tripodal Imidazole Complexes. A Comparison of Experiment with Calculations, 2nd printing. *Dalton Trans.* **2007**, 697. [[CrossRef](#)]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).