Molecular Prussian Blue analogues: synthesis and structure of cubic $Cr_4Co_4(CN)_{12}$ and $Co_8(CN)_{12}$ clusters

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Reactions between $[M(H_2O)_3(tacn)]^{3+}$ (M = Cr, Co) and $[Co(CN)_3(tacn)]$ are demonstrated to produce the molecular box clusters $[Cr_4Co_4(CN)_{12}(tacn)_8]^{12+}$ and $[Co_8(CN)_{12}(tacn)_8]^{12+}$ with core structures consisting of a single cubic unit excised from the Prussian Blue type framework.

The venerable solid pigment Prussian Blue, $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot zH_2O$, is readily prepared by addition of iron(III) ions to an aqueous ferrocyanide solution. This reaction can be generalized to include a variety of octahedral hexaaquo and hexacyano transition metal complexes which combine under similar conditions to form an extensive family of Prussian Blue type compounds:[1,2]

$$x[M(H_2O)_6]^{y+} + y[M'(CN)_6]^{x-} \longrightarrow M_x[M'(CN)_6]_y \cdot zH_2O \qquad (1)$$

The three-dimensional structures adopted by these compounds are based on a simple cubic lattice of alternating metal atoms M and M′ connected *via* linear M′–CN–M linkages. Characteristic of the framework are the cubic cavities demarcated by $M_4M'_4(CN)_{12}$ cages and capable of lodging small neutral molecules or charge-compensating monovalent cations. Such resident species can ordinarily be displaced or exchanged without disrupting the metal–cyanide host framework, giving rise to a range of molecular sieve, ion exchange and catalytic properties.[2–5] In addition, the bridging cyanide ligand is capable of mediating magnetic exchange between neighboring metal centers, and recognition of how the choice of M and M′ can influence the strength of the exchange has enabled the design of bulk magnetic materials with increasingly higher ordering temperatures.[6–9] Recent work has shown how the magnetic properties of these materials can be adjusted electro- and photochemically.[10–11]

In an effort to extend this remarkably diverse chemistry to a molecular level, we have initiated experiments directed toward the preparation of discrete cluster analogues of the cubic cages inherent to the Prussian Blue type structure. Our synthetic approach closely parallels that employed in eqn. (1), relying upon M′–CN–M bridge formation *via* displacement of water by the nitrogen end of cyanide:

$$4[M(H_2O)_3(tacn)]^{y+} + 4[M'(CN)_3(tacn)]^{x-} \longrightarrow [M_4M'_4(CN)_{12}(tacn)_8]^{4(y-x)+} \qquad (2)$$

Now, however, the tridentate ligand 1,4,7-triazacyclononane (tacn) blocks a single face on each of the transition metal reactants, preventing growth of the three-dimensional framework. Rather, it is proposed that the molecules will assemble into a compact cluster, $[M_4M'_4(CN)_{12}(tacn)_8]^{4(y-x)+}$, consisting of a cube of metal atoms with each edge spanned by a cyanide bridge and each corner capped by a tacn ligand. Herein, we report the initial use of this strategy to construct two such molecular Prussian Blue analogues.

A pink equimolar solution of $[Cr(H_2O)_3(tacn)][CF_3SO_3]_3$[12] and $[Co(CN)_3(tacn)]$[13] in water was boiled to dryness to give an orange residue. The residue was dissolved in a 1 : 1 mixture of acetonitrile and ethyl acetate; careful addition of diethyl ether then permitted separation of a pale orange solid suspension from an orange oil. The solid was collected, washed with ether, and dried to give $[Cr_4Co_4(CN)_{12}(tacn)_8][CF_3SO_3]_{12} \cdot 8H_2O$ **1** in 46% yield.‡ The IR spectrum of **1** exhibits a single sharp absorption at ν_{CN} = 2177 cm^{-1}, consistent with the symmetry (T_d, ignoring tacn ligand conformations) of the expected cubic cluster. Furthermore, the direction and magnitude of the shift in energy of this absorption relative to that of the $[Co(CN)_3(tacn)]$ precursor (ν_{CN} 2129 cm^{-1}) is characteristic of M′–CN–M bridge formation,[1] and correlates well with the analogous shift from $K_3[Co(CN)_6]$ (ν_{CN} 2126 cm^{-1}) to $Cr[Co(CN)_6]$ (ν_{CN} 2186 cm^{-1}).[14] The positive ion electrospray mass spectrum of **1** confirms the presence of the $[Cr_4Co_4(CN)_{12}(tacn)_8]^{12+}$ cluster, which displays a fragmentation pattern attributable to successive losses of $[Cr(tacn)]^{3+}$ and/or $[Co(CN)_3(tacn)]$ moieties. Crystals of **1** obtained by numerous different methods invariably produced only very broad X-ray diffraction peaks at low θ angles, indicative of poor long-range ordering (presumably due to the many possible similar-energy configurations for packing twelve triflate anions per cluster cation). In the course of these experiments, a solitary crystal of superior quality was encountered and determined by single crystal X-ray analysis to contain a square cluster of formula $[Cr_2Co_2(CN)_6(Me_2SO)_2(tacn)_4]^{6+}$. Apparently, in this particular preparation, a residual amount of dimethyl sulfoxide lingering from the synthesis of $[Cr(H_2O)_3(tacn)][CF_3SO_3]_3$ served to block two of the Cr sites from further reacting to produce a cube.

Cluster preparations involving anions other than triflate were undertaken in hope that an alternative anion shape might promote formation of more rigorously ordered crystals. The compound $[Co_8(CN)_{12}(tacn)_8][OTs]_{12} \cdot 14H_2O$ **2** was synthesized in 86% yield§ using a procedure similar to that described above. Yellow rectangular plate crystals were grown by allowing a methanol solution of **2** to slowly evaporate. X-Ray analysis¶ revealed the structure of the anticipated cluster with a cubic $Co_8(CN)_{12}$ core (Fig. 1). This cluster, with its novel boxlike geometry,‖ may be regarded as a three-dimensional extension of the above square cluster, as well as previously reported square clusters, such as $[Au_4(CN)_4Pr^n_8]$[18] and the more recent ‘supramolecular’ squares constructed using a variety of neutral bridging ligands.[19] On average, the clusters measure 4.937(7) Å on a cube edge, slightly smaller than the corresponding cage dimensions of 5.083 and 5.105 Å observed in Prussian Blue[16] and $Co^{II}_3[Co^{III}(CN)_6]_2 \cdot 12H_2O$[17] (to our knowledge, there is no known Prussian Blue analogue containing exclusively Co^{III}), respectively, at ambient temperature. The cyanide ligands spanning each edge deviate slightly (but irregularly) from linearity, as reflected in the Co–C–N and Co–N–C angles, which fall within the range 175(1)–180(1)°. Oxygen atoms from a single tosylate anion are positioned over each of the six cube faces in the crystal. No appreciable build-up of electron density was observed inside the cluster cavity; however, in view of the poor quality of the diffraction data, this does not exclude the possibility that a solvent molecule is present. Square openings (Fig. 2) on the cube faces could potentially permit entry by a guest molecule or ion. Based on the van der Waals radii of carbon and nitrogen, the minimum width of these openings is 1.7 Å, and the minimum diameter of the internal cavity is 3.7 Å. The high positive charge associated with the cubic cage should impart a strong preference for anion

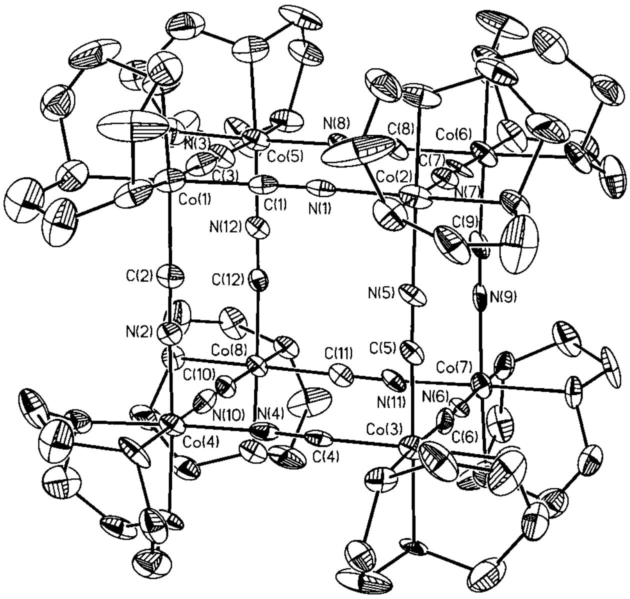

Fig. 1 Structure of the cubic $[Co_8(CN)_{12}(tacn)_8]^{12+}$ cluster in **2** showing 30% probability ellipsoids and the core atom labeling scheme. One orientation of the cyanide ligands is shown;¶ hydrogen atoms are omitted for clarity. Selected mean interatomic distances (Å) and angles (°) (X is a cyanide C or N atom): Co–X 1.89(2), Co–N 1.94(2), X–X 1.15(3), Co···Co 4.937(7); X–Co–X 89.9(7), Co–X–X 178(1), N–Co–X 92.0(9), N–Co–N 86.2(8).

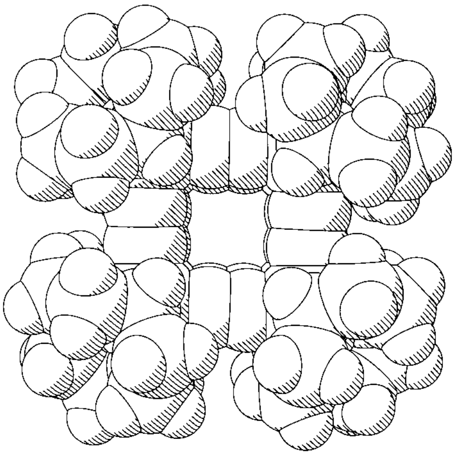

Fig. 2 Space filling model of the $[Co_8(CN)_{12}(tacn)_8]^{12+}$ cluster (including hydrogen atoms) viewed down a cube face

incorporation, as opposed to the cation affinity displayed by Prussian Blue type solids.[2–4]

By varying the metal atoms M and M′ employed in eqn. (2), we hope to produce an array of cubic cluster magnets with a variability in properties comparable to that which has evolved in Prussian Blue type materials.[6–11] The $[Cr_4Co_4(CN)_{12}(tacn)_8]^{12+}$ cluster represents an initial member in this array, possessing four Cr^{III} ions arranged in a tetrahedron over the cube vertices [replacing atoms Co(2), Co(4), Co(5) and Co(7) in Fig. 1] and separated by intervening diamagnetic Co^{III} ions. The temperature dependence of the magnetic susceptibility of **1** was measured using a SQUID magnetometer; a fit of the data to the Curie–Weiss law gives $C = 6.78$ emu K mol^{-1} and $\Theta = 1.21$ K. The effective magnetic moment of 7.5(1) μ_B and associated g value of 1.97 are reasonable for four isolated $S = 3/2$ Cr^{III} ions per cluster molecule.

Investigations further probing the magnetism, electrochemistry, and inclusion properties of these and related molecular Prussian Blue analogues are in progress.

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Notes and References

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‡ Absorption spectrum (H_2O): λ_{max}/nm (ε_M/dm^3 mol^{-1} cm^{-1}) 291 (sh, 970), 367 (740), 476 (330). IR (KBr): ν_{CN} 2177 cm^{-1}. ES$^+$ MS: m/z 1640 ($[\mathbf{1} - 2CF_3SO_3 - 8H_2O]^{2+}$), 1043 ($[\mathbf{1} - 3CF_3SO_3 - 8H_2O]^{3+}$). Anal. Calc. for $C_{72}H_{136}Co_4Cr_4F_{36}N_{36}O_{44}S_{12}$: C, 23.23; H, 3.67; N, 13.55. Found: C, 23.16; H, 3.61; N, 13.05%.

§ Absorption spectrum (H_2O): λ_{max}/nm (ε_M/dm^3 mol^{-1} cm^{-1}) 364 (786), 469 (476). IR (KBr): ν_{CN} 2200 cm^{-1}. ES$^+$ MS: m/z 1118 ($[\mathbf{2} - 3OTs - 14H_2O]^{3+}$), 796 ($[\mathbf{2} - 4OTs - 14H_2O]^{4+}$). Anal. Calc. for $C_{144}H_{232}Co_8N_{36}O_{50}S_{12}$: C, 41.95; H, 5.67; N, 12.23. Found: C, 41.96; H, 5.63; N, 12.05%.

¶ *Crystal data*: $C_{144}H_{224}Co_8N_{36}O_{46}S_{12}$, $M = 4123.82$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 15.1773(2)$, $b = 36.0654(2)$, $c = 34.5918(4)$ Å, $\beta = 91.337(1)°$, $V = 18929.5(3)$ Å^3, $\mu = 0.900$ mm^{-1}. Data ($2 < 2\theta < 46°$) were collected at 135 K using a Siemens SMART diffractometer with graphite monochromated Mo-Kα radiation. The structure was solved by direct methods with the aid of successive difference Fourier maps, and was refined in three overlapping blocks against all data (26910 unique) using SHELXTL 5.0. The clusters are disordered over two externally indistinguishable orientations (one is shown in Fig. 1), in which only the positions of the cyanide C and N atoms are reversed; an occupancy factor of 0.5C + 0.5N was assigned to each of the cyanide atom sites. (In view of the substitutional inertness of Co^{III} and the sharpness of the ν_{CN} peak in the IR spectrum, it is unlikely that the cyanide bridges have reoriented in the individual cluster molecules.) Ten of the twelve tosylate anions are disordered over at least two positions, and were modeled accordingly. The final agreement factors $R_1 = 0.1476$ and $wR_2 = 0.3882$ are high due to the extensive anion disorder present in the crystal and the accompanying poor data quality. CCDC 182/855.

‖ An abstract reporting the synthesis of related $M_8(CN)_{12}$ (M = Co, Rh) clusters capped by cyclopentadienyl ligands recently appeared.[15]

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