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Journal:	*ChemComm*
Manuscript ID	CC-COM-05-2019-004151.R1
Article Type:	Communication

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A Co_8 Metallacycle Stabilized by Double Anion-π interactions

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Self-assembly reactions of Co^{II} ions in the presence of the 2,2-bipyrimidine (bpym) ligand produced both a dinuclear and an octanuclear cation with the nuclearity being goverened by hydrogen-bonding versus anion-π interactions between the anions and the ligands .

Supramolecular aggregates[1] have attracted considerable attention over the past few decades due to their elegant architectures[2] and potential applications in both fundamental and applied research.[3] Various approaches have been explored for the synthesis of metallosupramolecular assemblies, with one of the most successful strategiesbeing coordination-driven self-assembly.[2] This convergent strategy capitalizes upon the directionality of transition metal-ligand bonding.[4] Given the wide selection of available metal ions, capping and bridging ligands, this chemistry can be readily tuned to obtain discrete metallacyclic motifs with well-defined sizes and shapes.[2]

Recently, our group has been focusing on extending the aforementioned methodology to include bridging ligands that are capable of existing in both the neutral and radical forms, efforts that led to the isolation of a rare molecular triangle $[Co_3(bptz)_3(dbm)_3]$ and a molecular square $[Co_4(bptz)_4(dbm)_4]$[5] (bptz = 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine and, dbm = 1,3-diphenyl-1,3-propanedionate). In addition, we reported the first lanthanide metallacycle $[Dy_3(bptz)_3(hfac)_6]$[6] (hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate), bearing the radical anion of the bptz ligand.

Apart from the directionality imposed by the precursors, the outcome of the self-assembly process can be controlled by external factors such as the ligand-to-metal ratio, solvent, template effect, and counterions. Anions are known to interact with supramolecular assemblies through non-covalent forces[7] such as hydrogen bonding,[8] π-π stacking,[9] electrostatic,[10] van der Waals,[11] and anion-π interactions.[12] The latter of these forces, defined in the simplest terms, is an attraction between negatively charged species and π-acidic aromatic rings. Extensive studies have revealed that anion–π interactions are governed by electrostatic and anion-induced polarization contributions. Since the early reports of anion-π supramolecular architectures, which focused primarily on small organic molecules and transition metal complexes of π-acidic ligands, the area has emerged as a new branch of supramolecular chemistry and anion-π interactions been discovered in many contexts including proteins[13] and have been used for the design of highly selective anion receptors,[14] transport channels,[15] and calorimetric sensors.[16] Excellent review articles on the topic are available that provide detailed references.[12, 13]

A particularly active line of study vis-à-vis anion-π interactions is their role in the supramolecular chemistry of N-heterocyclic ligands such as derivatives of pyridine, pyrazine,[17] triazine[12c] and cyanuric acid.[18] Our group has extensively explored various π-acidic aromatic systems, including tetrazine[19] and pyridazine[20] derivatives, in which anion-π interactions are the directing elements of the self-assembly process that control the structures of the, typically cyclic, products. For example, we have shown that reactions between solvated Fe^{II} ions and the bptz ligand result in unprecedented $[\{Fe_4(bptz)_4(CH_3CN)_8\}\subset X][X]_7$ ($X^- = [BF_4]^-$, $[ClO_4]^-$) squares and $[\{Fe_5(bptz)_5(CH_3CN)_{10}\}\subset Y][Y]_9$ ($Y^- = [SbF_6]^-$, $[AsF_6]^-$) pentagons, in which the identity of the encapsulated ion dictates the metallacycle nuclearity. Anion-π interactions were found to be critical elements for the metallacycle stability.[19d]

As part of our broad interest in supramolecular chemistry, we have extended our anion-π research to relatively unexplored N-heterocyclic pyrimidine derivatives with various anions. Herein we report self-assembly reactions between Co^{II} metal ions and the neutral ligand 2,2-bipyrimidine (bpym) in the presence of various anions, leading to the high-yield syntheses of $[Co_2(dbm)_2(bpym)(MeOH)_4](NO_3)_2$ (**1**), and, $[Co_8(dbm)_8(bpm)_8](CF_3SO_3)_8$ (**2**). The identity of the anion

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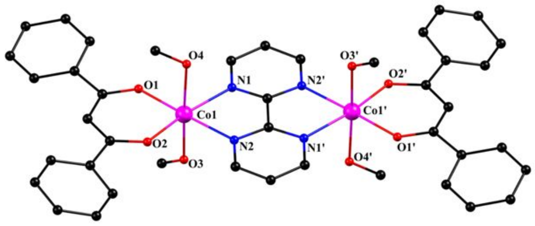
Electronic Supplementary Information (ESI) available: Synthetic, Crystallographic, and Magnetic details. See DOI: 10.1039/x0xx00000x influences weak interactions and, consequently, the structure of the resulting product.

Compound **1** crystallizes in the triclinic space group $P\overline{1}$ with the the $[Co_2(dbm)_2(bpym)(MeOH)_4]^{2+}$ cation residing on a crystallographic center of symmetry. A labeled representation of the cation in **1** as well as selected interatomic distances and angles are presented in Fig. 1 and Table S2. The cation of **1** contains two Co ions bridged by a bis-chelating bpym ligand and further coordinated to one chelating dbm and two methanol ligands. The oxidation state of the Co centers is 2+ as judged by charge balance considerations and bond valence sum (BVS)[21] calculations (Table S3). The pyrimidyl rings are planar, as expected, with deviations less than 0.03 Å from the mean planes. The bpm ligand is planar with the Co^{II} ions being displaced by 0.03 Å from this plane. The unit cell also contains two $[NO_3]^-$ ions that are involved in intermolecular hydrogen bonding interactions with the axial MeOH ligands involving the methanol O atoms, O3, O4, O3', and O 4' as the donors, and the nitrate O atoms, O5, O6, O5', and O6' as the acceptors (Fig. 1). The average hydrogen-bonding distance between the $[NO_3]^-$ ions and the axial methanol ligands is 2.701(2) Å. The intramolecular Co...Co separation is 5.72 Å, with the closest intermolecular Co...Co contact being 8.06 Å.



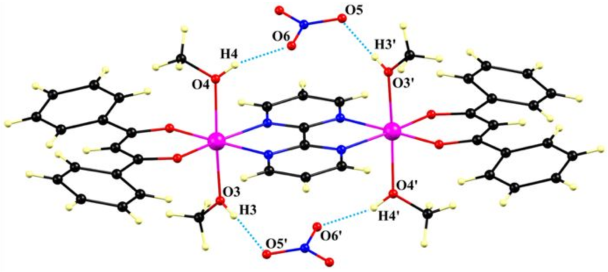


Figure 1. Labeled representation of **1** (top) with H atoms were omitted for the sake of clarity. Hydrogen bonding interactions in **1** (bottom). Color scheme: Co, magenta; O, red; N, blue; C, black, H, yellow. Symmetry operation for the primed atoms in **1**: 1-x, 1-y, 2-z.

Compound **2** crystallizes in the tetragonal space group $I\overline{4}$ with its cation residing on the crystallographic $\overline{4}$ axis and consists of eight pairs of alternating Co^{II} ions and bpym ligands arranged in a molecular polygon which adopts a chair-like conformation. The structure is depicted in Fig. 2 along with a labeled representation of the asymmetric unit $[Co_2(dbm)_2(bpm)_2]^{2+}$. The eight metal ions do not reside in the same plane but are divided into two parallel planes of four Co^{II} moieties at a distance of 3.56 Å. Each divalent Co atom is in a distorted octahedral geometry with four coordination sites being occupied by two chelating bpym N-donor ligands with the other two positions being occupied by one chelating dbm O-donor ligand. The bpym ligands are perpendicular to each other at a dihedral angle of ~ 89.2°). The intramolecular Co...Co cross-ligand separation is 5.71 Å, with the closest intermolecular Co...Co contact being 10.23 Å. To our knowledge, compound **2** is the first metallacycle with bpym and constitutes a unique topology among other reported Co_8 structures.[23]

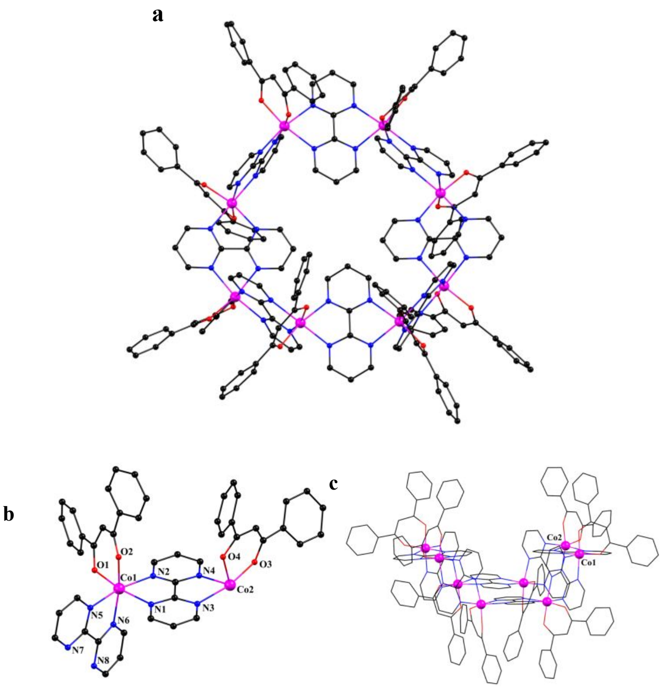


Figure 2. (a) Crystal structure of the cation **2,** (b) its asymmetric unit and, (c) boat-like conformation of the metal atoms in **2**. H atoms were omitted for the sake of clarity. Colors are the same as Fig 1.

A close inspection of the supramolecular interactions in **2** reveals that the $[CF_3SO_3]^-$ ions are not centered in the cavity but, instead, are close to the aromatic rings of bpym ligands. In the asymmetric unit, each anion engages in one short F- or O-pyrimidyl centroid contact (Fig. 3). The distances between the fluoride and the oxygen atoms with the centroid of the pyrimidyl rings are 2.86 Å (F1...C5N2C6C7C8N4) and 2.95 Å (O10...C13N8C14C15C16N6), respectively (Table 1) which are indicative of significant anion-π interactions.

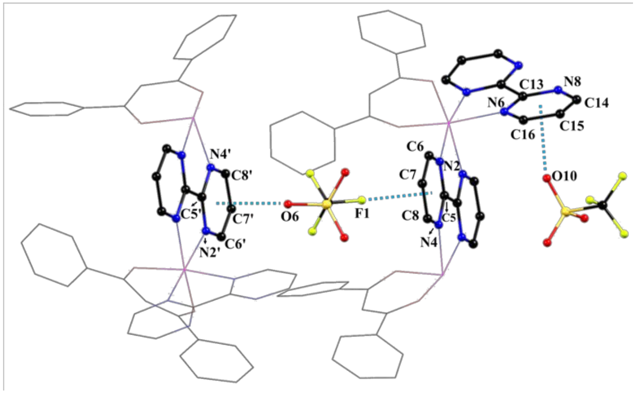


Figure 3. Anion-π interactions between $[CF_3SO_3]^-$ ions and bpym ligands in the asymmetric unit of **2**. Color scheme: Co, magenta; O, red; S, orange, F, green; N, blue; C, black. Symmetry operation for the primed atoms in **2**: 1-x, 1-y, 2-z.

Table 1. Geometry of the anion-π interactions in **2.**

Atom involved	X…C(N) contact / Å	X…centroid distance / Å	X…plane distance / Å	ϕ^a / °
O6	3.202(2) (C5')	2.966(2)	2.964(2)	88.28
F1	3.071(2) (C5) 3.102(2) (C8)	2.863(2)	2.846(2)	89.71
O10	3.162(2) (C13) 3.201(2) (C16)	2.947(3)	2.936(3)	86.13

^{a}Angle of the X…π axis to the plane of the aromatic ring

Also noteworthy is the fact that one of the two $[CF_3SO_3]^-$ anions interact with the pyrimidyl rings of two bpym ligands through both the CF_3 and $[SO_3]^-$ substituents from two different Co_8 cations with relatively short F-ring and O-ring centroid distances (F1…C5N2C6C7C8N4 2.86 Å and O6…C5′N2′C6′C7′C8′N4′ 2.97 Å) (Fig. 4, Table 1). Although there are several reports of short contacts between either the oxygen or the fluorine atoms of $[CF_3SO_3]^-$ anions and aromatic rings,[12e, 22] this is the first system to our knowledge in which they are involved in 'double' anion-π interactions (through both the fluoride and oxygen atoms) with the rings of N-heterocyclic ligands. Similar interactions have been previously observed for aromatic sulfamate anions ($H_2NSO_3^-$) with pyridazine ligands which serve as double receptors for both N- and O- donor atoms of the anion. [24]

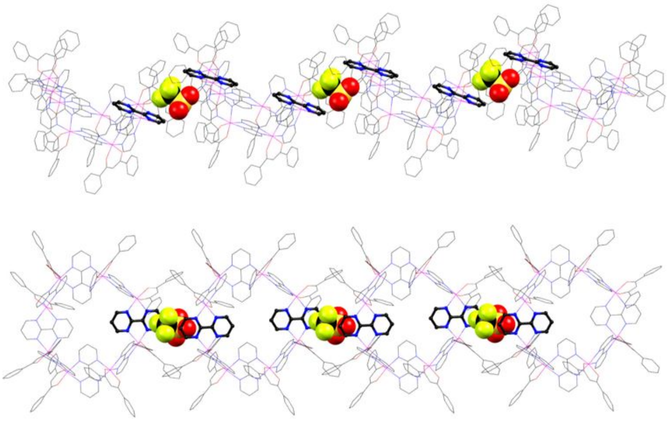


Figure 4. Anion-π interactions between the Co_8 cations and the $[CF_3SO_3]^-$ anions in **2**.

Variable-temperature DC magnetic susceptibility measurements were performed on powdered polycrystalline samples of **1** and **2** in a 0.1 T field from 2.0–300 K. The plots of $\chi_M T$ versus T are depicted in Fig. 5. For **1**, the experimental $\chi_M T$ value of 4.43 cm^3 K mol^{-1} at 300 K is higher than the expected spin-only (g = 2) value of 3.75 cm^3 K mol^{-1} for an uncoupled system, suggesting that the orbital angular momentum is not fully quenched in this complex. Upon cooling, the $\chi_M T$ product steadily decreases to a value of 3.76 cm^3 K mol^{-1} at 100.0 K and then drops sharply to a value of 0.06 cm^3 K mol^{-1} at 2.0 K, an indication of a diamagnetic ground state. Compound **2** exhibits similar behavior, with $\chi_M T$ decreasing from 15.28 cm^3 K mol^{-1} at 300 K to a value of 12.88 cm^3 K mol^{-1} at 100.0 K, and then decreasing more rapidly to 1.52 cm^3 K mol^{-1} at 2.0 K. The value at 300 K is in good agreement with the spin-only (g = 2) value of 15.00 cm^3 K mol^{-1} for eight non-interacting S = 3/2 Co^{II} ions. For both complexes, the shapes of the $\chi_M T$ curves indicate the presence of dominant antiferromagnetic exchange interactions between the metal ions and/or depopulation of the $^4T_{1g}$ ground state of the octahedral Co^{II} ions as well as large zero-field splittings.[27]

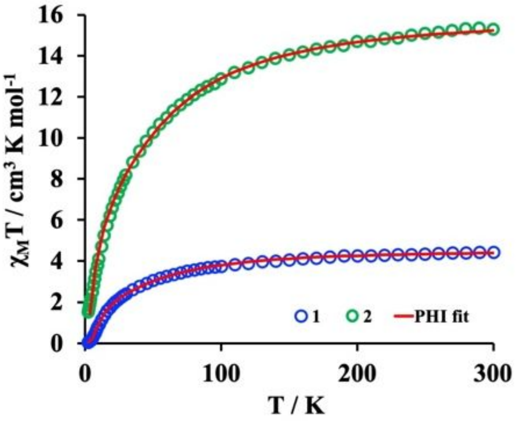


Figure 5. Temperature dependence of $\chi_M T$ for **1** and **2**. Red solid lines are fits to the experimental data.

In order to quantify the strength of the intramolecular magnetic exchange interactions the magnetic susceptibility data for compound **1** were fit using PHI program[25]. We considered only one interaction between the Co^{II} centers (J_1 for **1** and J_2 for **2**) because in both complexes the metal ions are bridged by the same ligands with the same bond distances and torsion angles. In addition, **2** exhibits high crystallographic symmetry. The fit for **1** produced the following parameters: J_1 = - 2.6 cm^{-1}, g = 2.21 and D = + 20.3 cm^{-1}. In the case of **2,** the best fit was obtained with the inclusion of a very small intermolecular coupling constant (zJ = - 0.01 cm^{-1}) and gave: J_2 = - 1.3 cm^{-1}, g = 2.06 and D = + 24.7 cm^{-1}. These results reveal weak antiferromagnetic coupling between the Co^{II} spins and are consistent with the values observed for other compounds with neutral bpym as the bridging ligand.[26] The large and positive D and g > 2 values are typical of octahedral Co^{II} complexes.[27]

In summary, we have shown that anions direct the self-assembly of Co^{II} ions and bipyrimidyl ligands by participating in supramolecular interactions. Intermolecular hydrogen bonding interactions with of the $[NO_3]^-$ anions with coordinated MeOH ligands serve to stabilize the dinuclear compound **1.** In the case of the octanuclear cation in **2**, there is crystallographic evidence of strong anion-π interactions between $[CF_3SO_3]^-$ ions and the centroids of the bpym ligand. The structure of **2** reveals a remarkable unprecedented mode of anion-π interactions for $[CF_3SO_3]^-$ anions between the pyrimidyl rings of the ligand and both the F- and the O- donor atoms of the anion. Moreover, to our knowledge, this is the first time that the bpym ligand has been observed to participate in anion-π interactions with any anion, demonstrating its ability to act as a receptor for both F- or O-donor atoms. Magnetic studies reveal weak magnetic coupling between the Co^{II} spins with coupling constants of J_1 = - 2.6 cm^{-1} and J_2 = - 1.3 cm^{-1} for **1** and **2**, respectively. Work in progress includes the extension of this work with anions similar to $CF_3SO_3^-$ ions such as methanesulfonate ($CH_3SO_3^-$) and sulfamate ($H_2NSO_3^-$) as well the exploration of new reactions of bpym with other 3d metal ions in the presence of a variety of various anions.

We gratefully acknowledge financial support for this work from the National Science Foundation (CHE-1808779) and the Robert A. Welch Foundation (Grant A-1449). The SQUID magnetometer was purchased with funds provided by the Texas A&M University Vice President of Research.

Conflicts of interest

There are no conflicts to declare.

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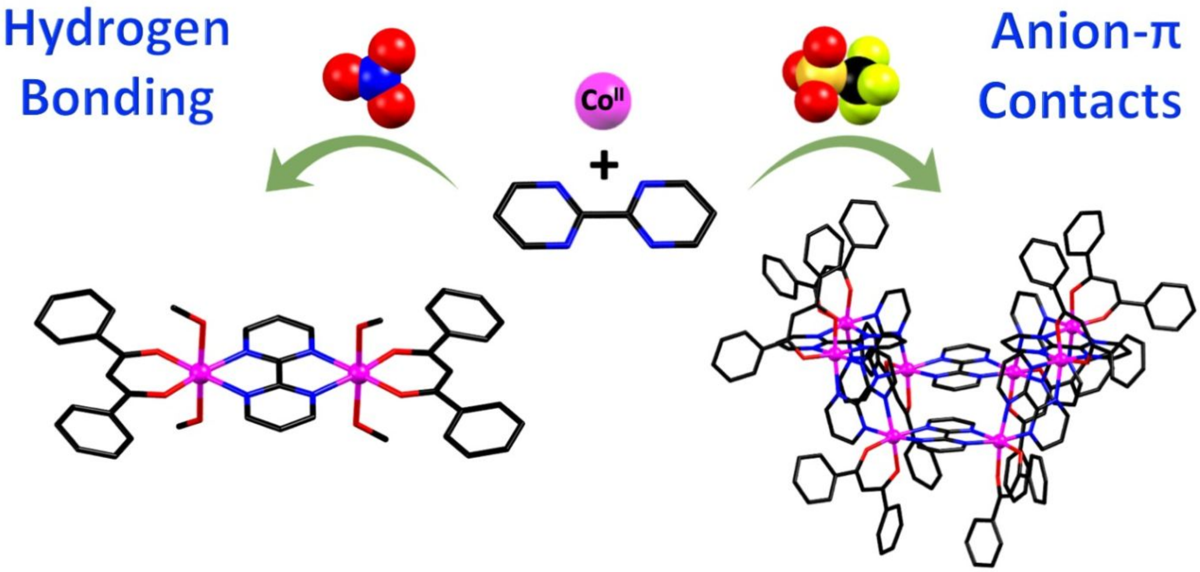

The syntheses, crystal structures and magnetic studies of two new Co^{II} 2,2'-bipyrimidine bridged complexes stabilized by hydrogen bonding versus anion-π interactions are reported.