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Anion−π−π Interactions in a Dinuclear M_2L_2 Metallocycle

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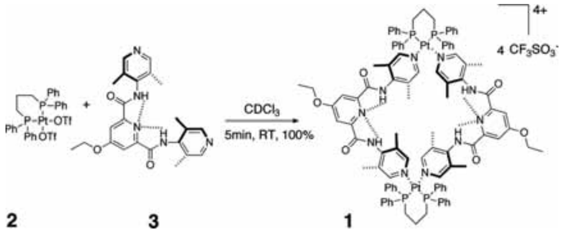
The combination of the square-planar cis-protected [Pt(dppp)$(O_3SCF_3)_2$] (M) with the ditopic *N*,*N'*-bis(3,5-dimethyl-4-pyridinyl)-4-ethoxy-2,6-pyridinedicarboxamide ligand (L) leads both in solution and in the solid state to the quantitative self-assembly of a M_2L_2 metallocycle. We also report crystallographic evidence derived from the solid-state structure of the dinuclear metallocycle in support of the existence of anion−π−π interactions.

Recently, experimental and theoretical studies have confirmed the existence of attractive anion−π interactions involving simple and multiatomic anions and π-acidic systems.[1] Initial experimental evidence of anion−π−π interactions has emerged from crystallographic studies of synthetic coordination compounds based on the electron-deficient 1,3,5-triazine moiety. Detailed theoretical studies have suggested that the strength of the anion−π interaction could possibly be enhanced through the involvement of the π-acidic system in additional π−π-stacking interactions.[2] The understanding of all noncovalent interactions, including this new anion−π−π proposal, is of fundamental importance for structural predictions and the design of artificial receptors.

Scheme 1. Different Types of Noncovalent Interactions Observed for Complex **1**

Scheme 2. Formation of Metallocycle **1**



Because many of the estimates of the binding geometry and binding strength of anion−π interactions are only available from theoretical studies, we present herein a crystallographic example of the new anion−π−π interaction. The reported anion−π−π interaction is established between the multiatomic triflate anion and a pyridine ring as the π-acidic system, which, in turn, is involved in a π−π-stacking interaction with a phenyl substituent (Scheme 1).

The metallocycle **1**[3] (M_2L_2) was obtained in quantitative yield by simply mixing **2** with **3** in a 1:1 ratio at room temperature in $CHCl_3$-*d* (Scheme 2). The M_2L_2 metallocycle was characterized by multinuclear NMR spectroscopy and X-ray analysis. The ^{31}P NMR spectrum exhibits a sharp singlet at δ −14.01 ppm, with appropriate platinum satellites, indicative that all phosphorus atoms are chemically equivalent.

Single crystals suitable for X-ray diffraction analysis of the structure of **1** were obtained upon slow evaporation

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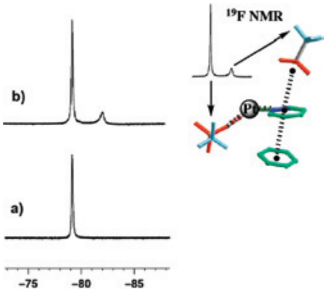

Figure 1. Selected region of ^{19}F NMR spectrum ($CDCl_3$) of macrocycle **1** at two different temperatures: (a) 293 K (δ −79.14 ppm); (b) 223 K (δ −78.89 and −81.63 ppm).

at room temperature of a $CHCl_3$ solution containing an equimolecular mixture of components **2** and **3**. The X-ray structure confirmed the formation of metallocycle **1** in the solid state and revealed the presence of two triflate anions located inside the cavity, while the other two were positioned at a distance of 3.179 Å from the platinum(II) centers.

In order to investigate the existence in solution of nonchemically equivalent triflate anions in the metallocyle **1**, we performed variable-temperature ^{19}F NMR experiments. We first acquired the ^{19}F NMR spectra of **2** and **1** at 293 K. In both cases, we observed a single signal for the fluorine atoms of the triflates, centered at δ −78.80 ppm for **2** and at δ −79.14 ppm for **1**. Most likely, at room temperature the "in and out" exchange process in which the triflates of **1** may be involved is fast on the ^{19}F NMR chemical shift time scale, rendering the two types of triflates indistinguishable. Upon lowering of the temperature to 223 K, we observed in the ^{19}F NMR spectrum of **1** the appearance of two fluorine resonances at δ −78.89 and −81.63 ppm with an intensity ratio of 3:1[4] (Figure 1). The observation of two separate fluorine signals for the triflate counterions in **1** can be explained by the existence of nonchemically equivalent triflates in solution that are involved in a slow chemical exchange regime at this temperature (cooling of the sample below 223 K induced precipitation). Simply on the basis of the chemical shift values, we assigned the signal resonating at δ −81.63 ppm to triflate ions interacting with the pyridyl rings. We determined the coalescence temperature to be 263 K and the difference in the chemical shift ($\Delta\nu$) of the two signals close to that temperature as 776.30 Hz. With these data, we quantified the free-energy barrier of the exchange process $\Delta G^{\ddagger} = 11.43$ kcal mol^{-1}.

In the crystal lattice of **1**, we observed that each of the two triflate anions that are found inside the aromatic cavity of the macrocycle is hydrogen-bonded to three water molecules[5] (Figure 2).

Two of these water molecules, acting as doubly hydrogen-bonded donors, connect two adjacent triflate anions included in the cavity: O1W−H1WB···O2B = 1.903(3) Å; O1W−H1WA···O3B = 1.987(3) Å. The third water molecule is hydrogen-bonded to the C=O group of a neighboring macrocycle, O2W−H2Wa···O1 = 2.061(3) Å, and supplies the third hydrogen-bond acceptor group for the included triflates, O2W−H2Wa···O1B = 2.148(3) Å.

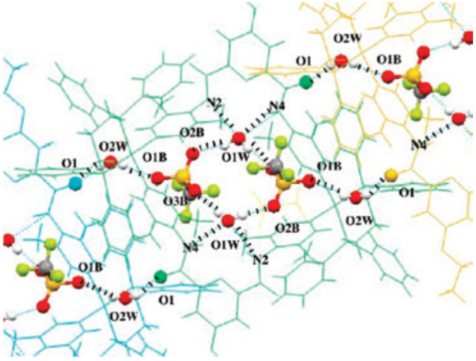

Figure 2. Crystal packing of **1** showing the intermolecular hydrogen-bridging interactions of the in-$CF_3SO_3^-$ anions and the water ligands, anchored to both NH groups and to C=O1 of the neighboring macrocycle.

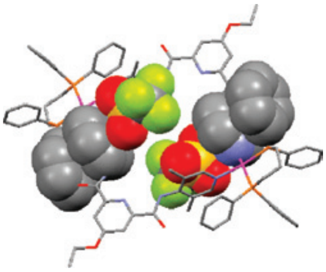

Figure 3. Detailed crystal packing of **1** showing the triflate−π−π binding motif. The bridging water molecules responsible for the interaction of the $CF_3SO_3^-$ anions with the metallocycle have been omitted for clarity.

Each water molecule that bridges two adjacent triflates also acts as a hydrogen-bond acceptor for two amide NHs of **1**. In short, each triflate is doubly hydrogen-bonded to the metallomacrocycle, which is included through the intermediacy of two water molecules.[6] As a result, an intermolecular hydrogen-bonding network, mediated by water molecules, of infinite chains of anion triflates oriented above the π systems exists in the crystal lattice (Figure 2).

A detailed analysis of the crystal structure also reveals the presence of triflate (anion)−π−π interaction binding motifs (Figure 3). This interaction geometry is observed for both triflate anions positioned inside the cavity.

The pyridine and phenyl rings are π−π-stacked in a face-to-face geometry with an angle between the two aromatic planes of 16.34(1)°. The distance between the centroids of the two stacked rings is 3.53(2) Å (Figure 4a). It is known that the distance between π−π planes involved in strong interactions is around 3.28 Å, whereas when weak interactions π−π are operative, the intermolecular distance increases above 3.6 Å. The maximum contact distance accepted for π−π interaction is approximately 3.08 Å.[7]

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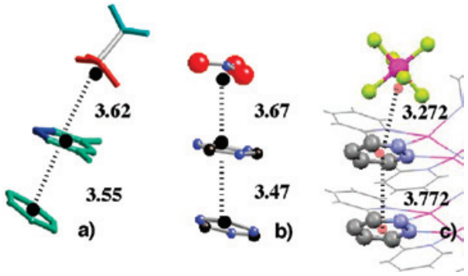

Figure 4. Examples of anion−π−π interactions. (a) Anion−π interaction between the multiatomic $CF_3SO_3^-$ and the pyridine ring, π−π stacking between the pyridine and arene rings, **1**. (b) Anion−π interaction between the multiatomic NO_3^- and the triazine ring, π−π stacking between the triazine rings.[2a] (c) Anion−π interactions between the hexafluorophosphate and the pyrazine ring, π−π stacking between the pyrazine rings[2b] and refcodes LIBPUI and IMIHIV.[9b] Centroid distances are in angstroms.

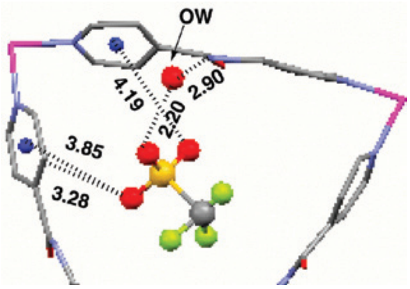

Figure 5. Molecular structure of the complex $Pt_3(4\text{-}NC_5H_4CO)NH\text{-}4\text{-}C_5H_4N)_3$ containing an encapsulated anion triflate.[8h]

The oxygens on the triflate (O1B, O2B, and O3B) and the pyridine ring have an angle between their planes of 27.43(1)°, and the centroid-to-centroid distance of these planes is 3.62 Å (Figure 4a). This interaction geometry is indicative that one oxygen (O2b) is predominantly interacting with the electron-deficient pyridine ring at 3.07 Å.

Pyridyl derivatives are widely used as ligands in metallosupramolecular systems.[8] In order to find structures related to the one described here for the triflate−π−π interaction, we searched the Cambridge Structure Database (CSD) for crystallographic files containing *cis*-Pt-(dppp)(OTf)$_2$ pyridyl fragments; however, we were unable to find precedents for this type of interaction in the database. The closest evidence we found was reported by Puddephatt et al.[8h] (Figure 5), and the authors claimed that the close fit of the triflate ion inside the cavity is the main driving force for the interaction. Most likely, the hydrogen-bonding sites of the amide groups in **1** should also be considered for the final orientation of the anion in the structure reported here.

The triflate (anion)−π−π interaction reported here is geometrically similar to those observed in metal-mediated triazine and pyridazine supramolecular systems[2a,b] (Figure 4b,c). Nevertheless, triazine and pyridazine contain a higher number of heteroatoms in the aromatic ring. On the contrary, in the three cases triazine−triazine, pyridazine−pyridazine, and pyridine−arene π−π interactions, the two aromatic rings are forced to stack closely as a consequence of the coordination of the molecular units to a common metal ion copper(II), silver(I), and platinum(II), respectively.

A second search of the CSD for short contacts between one oxygen atom of a triflate and the centroid of a pyridine ring gave us 129 hits. Among them, 7 refcodes describe the existence of short contacts between one of the oxygen atoms of the triflate and pyridyl fragments coordinated to platinum(II).[9a]

The finding of a triflate (anion)−π−π interaction described here increases the utility of the pyridine ring as a π-acidic center. The influence of the number of heteroatoms, in the π-acidic systems, has already been examined.[10] Not unexpectedly, it was concluded that fewer π-acidic systems, having fewer numbers of heteroatoms, are involved in weaker anion−π interactions. However, in the case at hand, the heteroatom (N) in the pyridyl ring is directly involved in the formation of a N−Pt^{II} coordination bond. The results obtained here are also consistent with the importance that coordinated transition metals have in the polarization of heterocycles with low π acidity to which they are bound.[1j]

In summary, we presented crystallographic evidence of a triflate (anion)−π−π interaction in the solid state. This type of interaction requires aromatic systems with sufficient π acidity. The presence of platinum(II) as the Lewis acid and the dppp ligand, in combination with the π−π-stacking pyridyl−phenyl contribution, could be determining factors for control of the geometry of the final anion−π−π interaction. We also want to highlight that the hydrogen-bonding network in which the triflates are involved when interacting with **1** is probably responsible for the existence of dynamic processes between different triflates that we have observed in solution.

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Supporting Information Available: Spectroscopic and crystallographic data (CIF). This material is available free of charge via Internet at http://pubs.acs.org.

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