

Understanding the Forces That Govern Packing: A Density Functional Theory and Structural Investigation of Anion- π -Anion and Nonclassical C-H \cdots Anion Interactions

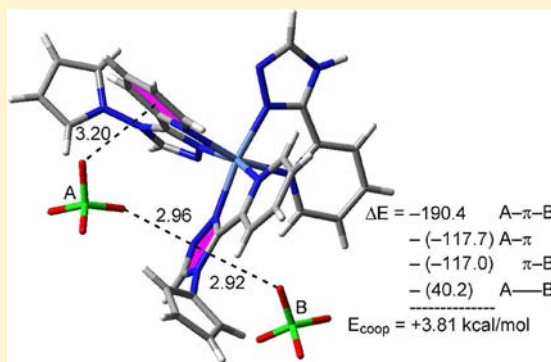
Sally Brooker,^{*,†} Nicholas G. White,[†] Antonio Bauzá,[‡] Pere M. Deyà,[‡] and Antonio Frontera^{*,‡}

[†]Department of Chemistry and MacDiarmid Institute for Advanced Materials and Nanotechnology, University of Otago, P.O. Box 56, Dunedin 9054, New Zealand

[‡]Department de Química, Universitat de les Illes Balear, Crta de Valldemossa km 7.5, Palma de Mallorca, 07122 Palma (Balears), Spain

S Supporting Information

ABSTRACT: The ability of Ni(II) coordinated 4-pyrrolyl-3,5-di(2-pyridyl)-1,2,4-triazole (**pldpt**) to establish multiple anion- π interactions is analyzed. Experimentally, such complexes were previously shown to form strong anion- π interactions, including “ π -pocket” and “ π -sandwiched” motifs, in the crystal lattice. In the latter, the triazole ring is “sandwiched” by two anions forming a ternary anion- π -anion assembly (π -sandwich) which, surprisingly, gave about 0.2 Å shorter anion- π distances than in binary assemblies (where only one side of the triazole participates in the anion binding), indicating the possibility of cooperativity. In depth analysis, using dispersion-corrected density functional theory (DFT, BP86-D/def2-TZVP level of theory), shows that this ternary anion- π -anion interaction is slightly less energetically favorable than the binary anion- π interactions in isolation. Hence, the sandwich interaction is not cooperative (E_{coop} is positive), but, as E_{coop} contributes less than 1.5% of the total interaction energy (which is dominated by the strong electrostatic attraction of the anions to the highly π -acidic Ni(II)-coordinated triazole ring), the presence of nonclassical C-H \cdots anion hydrogen bonds can offset this, making the short anion- π sandwich interactions the most favorable solid state conformation.



INTRODUCTION

The emergence of supramolecular chemistry has had a great impact on how efficiently chemists prepare structures of different sizes and shapes.¹⁻³ The components of these structures are held together by a variety of noncovalent forces. Some of these (e.g., π -stacking,⁴⁻⁶ cation- π ,^{7,8} and C-H/ π ^{9,10} contacts¹¹) are very common and well accepted among supramolecular chemists. The recent appearance of anion- π interactions¹²⁻¹⁴ has added a new dimension to the supramolecular chemistry of anions and, in particular, has emerged as a new concept for anion-transport, anion-sensing, and anion-recognition chemistry.¹⁵⁻²⁴ For decades, these areas relied on hydrogen bonding interactions²⁵⁻²⁹ and anion coordination chemistry.³⁰ By analogy with cation- π interactions^{7,8} (the interaction between a cation and an electron-rich π -system with a negative quadrupole moment), noncovalent interactions between anions and electron-deficient π -systems with positive quadrupole moments are broadly defined as anion- π interactions.¹²⁻¹⁴ Energetically, the interaction of cations with electron rich arenes is stronger than the interaction of anions with electron deficient arenes because the van der Waals radii of anions are larger than cations and consequently the equilibrium distances are longer.³¹ Since the forces that govern the ion- π

interactions are very dependent on distance, cations are better able to interact with arenes than anions. A good strategy to overcome this drawback is the coordination of transition metal ions to heteroaromatic rings, as this strongly increases the π -acidity of the ring, significantly increasing the binding energy of the anion- π interactions.³²⁻³⁴

Recently, some of us published a systematic crystallographic investigation of the anion-binding ability of the five-membered 1,2,4-triazole ring in a new family of mononuclear nickel(II) complexes of **pldpt** (4-pyrrolyl-3,5-di(2-pyridyl)-1,2,4-triazole, Figure 1) with four different anions, BF_4^- , ClO_4^- , PF_6^- , and SbF_6^- .³⁵ In all four complexes, two types of anion- π interactions were observed: one where one anion interacts with only one triazole ring, and another where the other anion is situated in a π -pocket provided by two triazole rings and one pyridine ring (vide infra). The anion is the only moiety in this pocket, and so should be free to adopt the most energetically favorable conformation for anion- π bonding: surprisingly, the anion forms its shortest interaction with the triazole ring that is already interacting with an anion (range, average for F-triazole

Received: July 6, 2012

Published: September 13, 2012

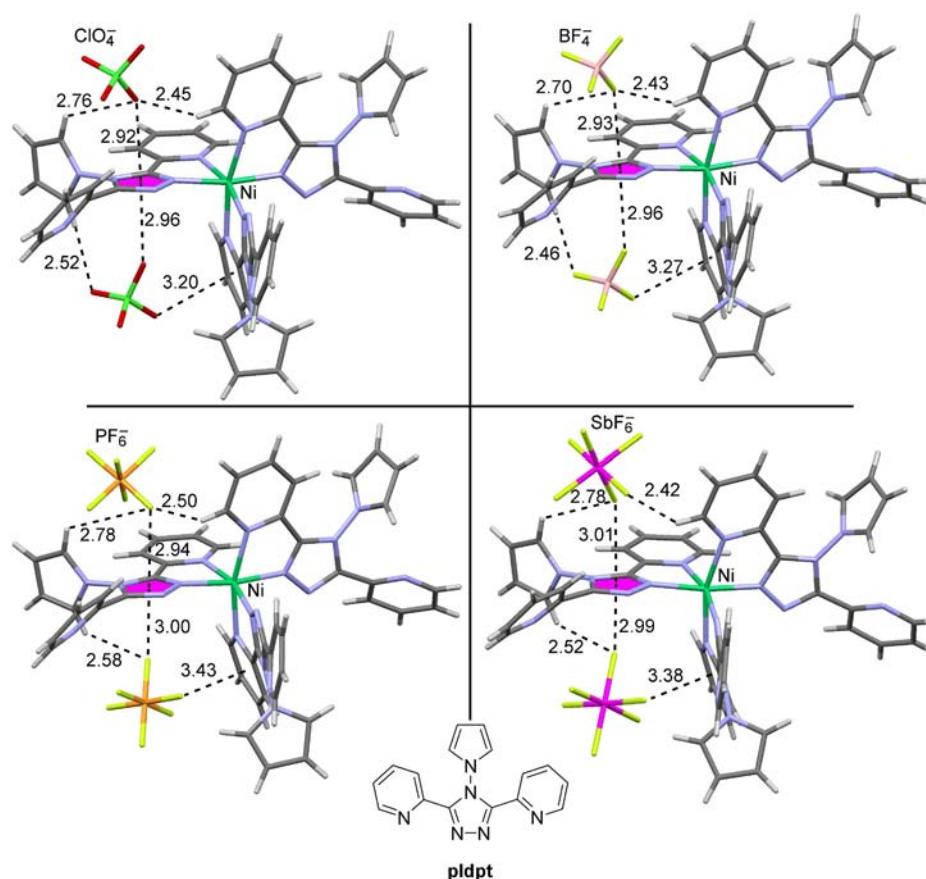


Figure 1. Partial views of the single crystal X-ray structures published by White et al.,³⁵ showing the experimentally observed anion- π -anion sandwich and C-H \cdots anion interactions (distances in Å).

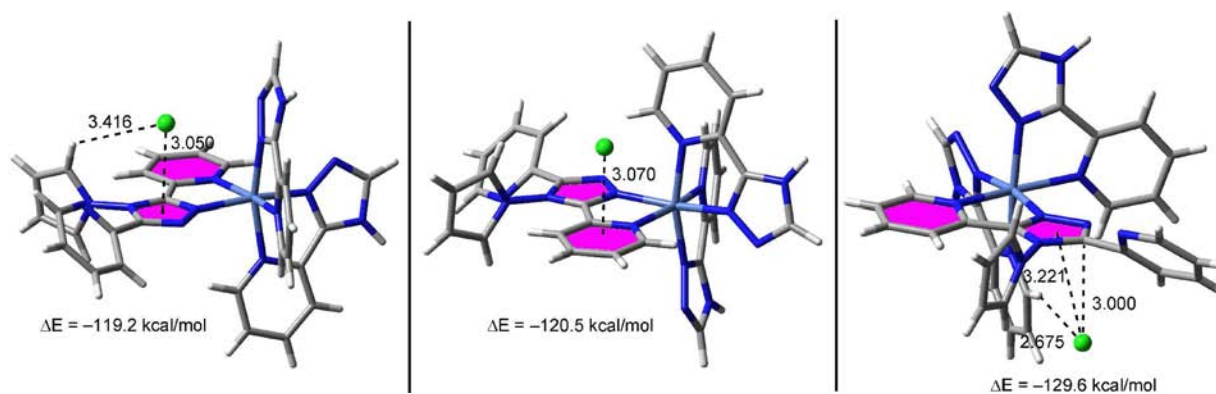


Figure 2. Geometries of the optimized binary anion- π assemblies and the interaction energies in the model system (distances in Å).

centroid: binary 3.090(9)–3.492(9) Å, 3.28 Å; ternary/sandwich 2.926(5)–3.005(4) Å, 2.97 Å,³⁵ which is suggestive of cooperativity. This ternary anion- π -anion arrangement occurs for all four complexes, even when the size and shape of the anion is varied substantially (Figure 1). To shed light on this unexpected observation, and to further understanding of the intricate balance of supramolecular interactions that govern packing, we have performed a high level density functional theory (DFT) study. The results of this analysis of several aspects of the anion- π interaction and the different forces that are important in this system, along with consideration of the possibility of cooperativity between the anion- π interactions involving the triazole ring, are presented herein.

RESULTS AND DISCUSSION

The theoretical study is presented in two parts. In the first part the position of a spherical anion is optimized in a model of the system, to analyze possible synergistic effects in the ternary anion- π -anion assembly. The second part is devoted to the study of the real crystal structure, using the crystallographic coordinates. We show that nonclassical hydrogen bonds in conjunction with anion- π and electrostatic interactions determine the overall packing arrangement observed.

Anion- π -Anion: Cooperative or Noncooperative?

The focus here is on analyzing whether cooperative, synergistic ternary anion- π -anion interactions are possible. For this reason a simplified system (Figure 2 and Supporting

Information, Figure S1) has been used: one **pldpt** ligand is completely conserved (that which is involved in the π -sandwich) and the other two ligands have been simplified, eliminating the rings that are not coordinated to the Ni(II) cation. The system was further simplified by using chloride in place of the polyatomic monoanions.

The interaction energies and optimized distances of the three relevant binary anion– π assemblies are shown in Figure 2. In addition to the anion– π interaction, two of them also exhibit C–H...anion hydrogen bonding interactions.³⁶ The interaction energies are all very large and negative ($\Delta E = -119$ to -130 kcal mol⁻¹) because of the strong electrostatic attraction between the anion and the highly π -acidic Ni(II)-coordinated aromatic rings. The slightly larger, more favorable interaction energy in the right-hand assembly is due to a stronger hydrogen bond. These large interaction energies between charged aromatic rings and anions have been described before in charged systems.^{37,38} For instance the interaction energies between chloride anion and either quinolizinium or tropylium cations range from -86 to -89 kcal mol⁻¹. Moreover, similar interaction energies (~ 130 kcal mol⁻¹) have been recently published for anion– π complexes involving Co(II) malonate anions and protonated 2-aminopyridine.³⁹

To analyze possible cooperative effects, the binding energy of the ternary assembly (Figure 3) was calculated and is very

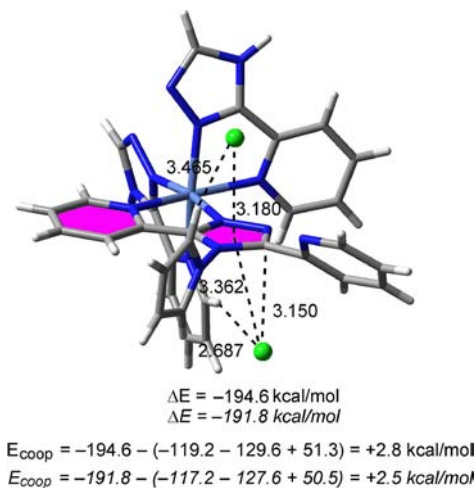


Figure 3. Ternary anion– π –anion sandwich assembly (distances in Å), and cooperativity energy (E_{coop}) obtained at the BP86-D/def2-TZVP level of theory. The values in *italics* correspond to the BP86-D/def2-TZVPD level of theory.

favorable ($\Delta E = -194.6$ kcal mol⁻¹). The cooperativity energy, E_{coop} , was then calculated by subtracting from this the interaction energies of the two binary assemblies (Figure 2, left and right assemblies) and the repulsive interaction energy between the two chloride anions (without the ligand) at the distance that they are at in the ternary assembly (see eq 1, Experimental Section). The resulting **positive** E_{coop} value, $+2.8$ kcal mol⁻¹, demonstrates that the interplay between the pair of anion– π interactions is **unfavorable**, as would be intuitively expected for an interaction involving two negatively charged anions. In contrast, when one anion is replaced by a cation, that is, anion– π –cation assembly, favorable cooperativity effects occur.^{40,41} However, the important point is that E_{coop} is **extremely small**. In fact, it is less than 1.5% of the total interaction energy of the ternary anion– π –anion assembly,

explaining why, when other weak interactions are considered (*vide infra*), the anion-sandwiching arrangement does occur in the solid state. At this point we analyzed the influence of the utilization of diffuse functions in the basis set upon the computed interaction energies. The calculated values using the def2-TZVPD basis set are included in Figure 3 in *italics* and in Supporting Information, Table S1. These values are very similar to those obtained using the def2-TZVP basis set, indicating that this basis set is of sufficient quality to study these systems.

As previously discussed, the interaction energies are large and negative because of the strong electrostatic interaction between the very π -acidic Ni(II)-coordinated aromatic rings and the anion. To know the contribution of the “genuine” anion– π interaction, we have also computed a model of the system that is neutral (Figure 4), by replacing one **pldpt** by two chloride ions to balance the Ni(II) charge. The interaction energy of this neutral system with the chloride anion is considerably lower, but still favorable ($\Delta E = -12.5$ kcal mol⁻¹, Figure 4, left).

However, this includes the contribution of a nonclassical hydrogen bond with a C–H of the pyrrole ring. Hence another model, in which the pyrrole ring is replaced by a hydrogen atom, thus removing the hydrogen bond, was used to investigate the “genuine” anion– π interaction alone (Figure 4, central); the resulting interaction energy for this “pure” anion– π assembly is -8.5 kcal mol⁻¹, very similar to that of the anion-pyridine interaction (-8.7 kcal mol⁻¹, Figure 4, right). Simple subtraction shows that the interaction energy of the pyrrole-chloride hydrogen bond is -4.0 kcal/mol, which is approximately half that of the anion– π interaction.

Anion– π versus Nonclassical C–H...Anion Interactions. The above results clearly demonstrate that the simultaneous interaction of two anions with opposite faces of a single aromatic ring coordinated to Ni(II), is favorable energetically but is slightly unfavorable in terms of cooperativity (i.e., it is slightly more favorable to have two independent binary interactions than one ternary interaction). Despite this, the anion– π distances are experimentally observed to be about 0.2 Å shorter in the ternary anion– π –anion assemblies than in the binary assembly (Figure 1), which appears to disagree with the results presented in the first part of this study. The anion in the π -pocket, A, makes three π -interactions, the shortest of which is to the triazole simultaneously interacting with the other anion, B (Supporting Information, Figure S2). To probe this complex situation, several calculations using the whole system, as well as several parts of the system, and some neutral models, have been carried out using the crystallographic coordinates.

As in the first part of this study, the calculated interaction energies of several *binary* assemblies (Figure 5) are very large and negative because of the electrostatic contribution. Since the values are dominated by this large component, the influence of the other interactions, such as anion– π , is only small. Nevertheless, the slightly larger binding energies do correspond to the shorter anion– π distances (Figure 5). Re-evaluation of these interaction energies using neutral models (where one **pldpt** ligand is replaced by two chloride ions, as above) again leads to significantly reduced, but still favorable, ΔE values, of about -16 kcal/mol.

The calculated ΔE (-190 kcal mol⁻¹) and E_{coop} ($+3.8$ kcal mol⁻¹) for the *ternary* anion– π –anion assembly observed in the crystal structure (Figure 6) are in agreement with the values obtained for the optimized model systems, which validates the model used in the first part of this study (Figure 3). Again the

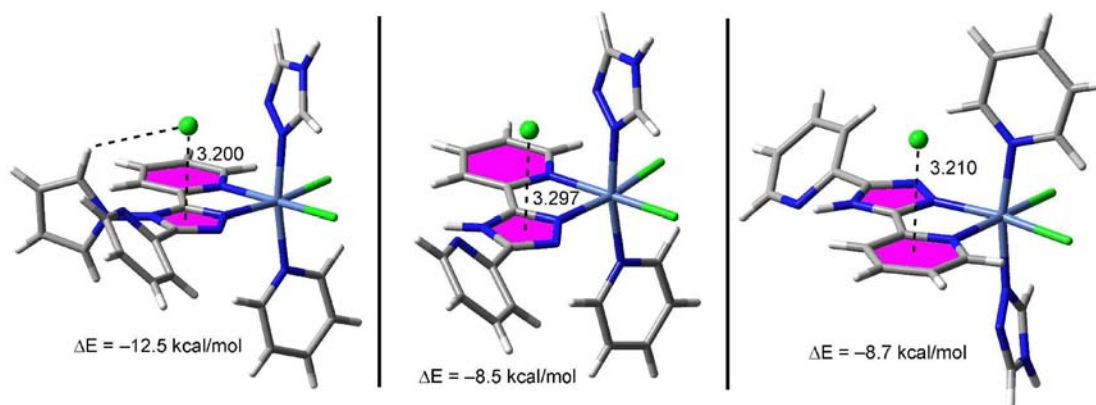


Figure 4. Anion- π assemblies for the neutral model systems (in which one pldpt ligand has been replaced by two chloride ions), and their interaction energies (distances in Å). Left: includes pyrrole C-H hydrogen bond. Center: pyrrole replaced by H to remove hydrogen bond. Right: anion-pyridine interaction.

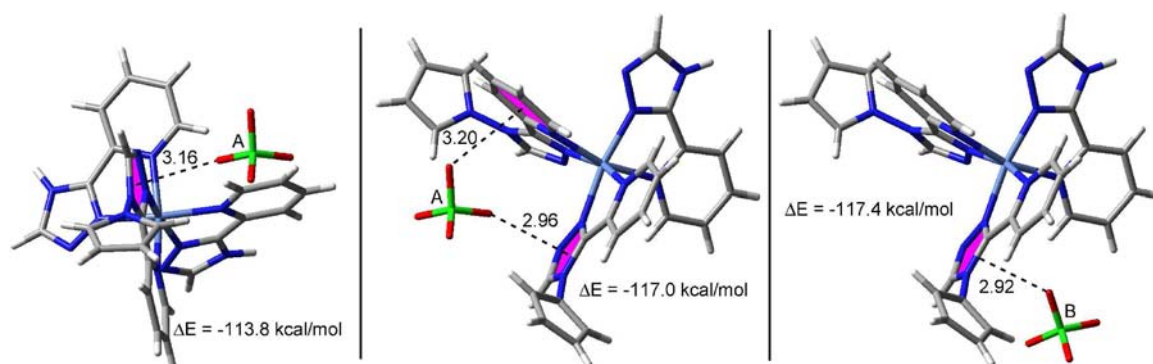


Figure 5. Interaction energies calculated for three binary anion- π assemblies identified in the X-ray structure of the ClO_4^- salt.

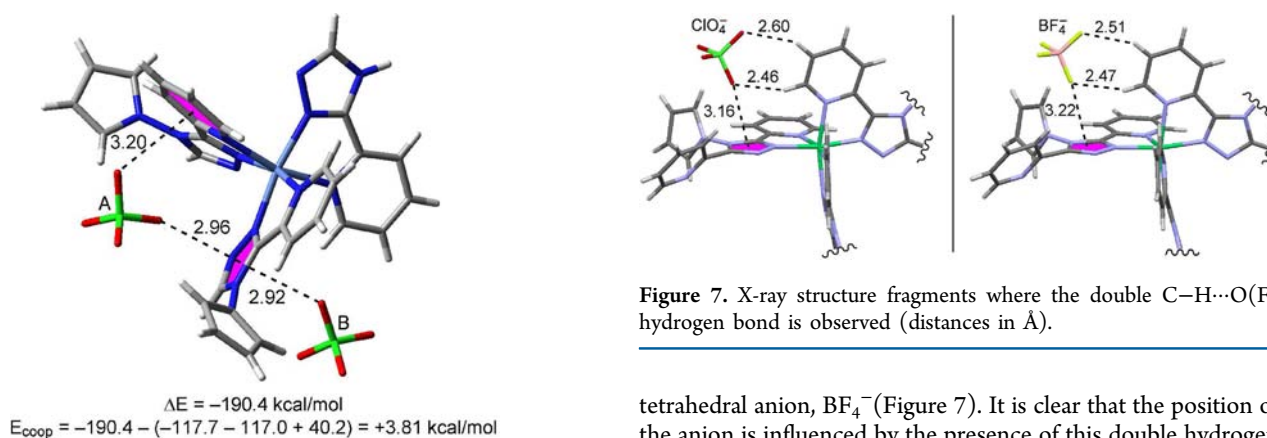


Figure 6. Ternary anion- π -anion sandwich assembly (distances in Å), and cooperativity energy (E_{coop}) for this crystal fragment.

ΔE of the ternary assembly is very large and negative, and the E_{coop} is small but unfavorable, and so anion- π interactions alone cannot explain the observed structural parameters for ternary/sandwiching vs binary anion- π interactions. It is clear, therefore, that additional factors must also contribute.

Closer examination of the part of the crystal structure where the anion- π distance is longer, that is, a binary interaction involving anion A (Supporting Information, Figure S2) that does not involve anion- π -anion sandwiching, reveals two nonclassical, directional, C-H \cdots O bonds (Figure 7). The same arrangement is seen in the crystal structure of the other

Figure 7. X-ray structure fragments where the double C-H \cdots O(F) hydrogen bond is observed (distances in Å).

tetrahedral anion, BF_4^- (Figure 7). It is clear that the position of the anion is influenced by the presence of this double hydrogen bond that clearly affects the anion- π distance. The energy associated with these double H-bonds was calculated to be $-4.2 \text{ kcal mol}^{-1}$ for ClO_4^- and $-5.2 \text{ kcal mol}^{-1}$ for BF_4^- . In the other part of the crystal structure where the sandwich assembly is formed, this double C-H \cdots O(F) bond is not observed. Instead, several single H-bonds are present that help to shorten the anion- π distance (Figure 8) because of the directionality of the C-H groups of the pyrrole ring.

For the octahedral anions, additional interactions with neighboring molecules are present that complicate the analysis. For these anions a larger theoretical model should be used, increasing the size of the system and decreasing the suitability of the calculations. Therefore such calculations have not been undertaken. In any case, the observation of short distances in the anion- π -anion assembly for PF_6^- and SbF_6^- anions is

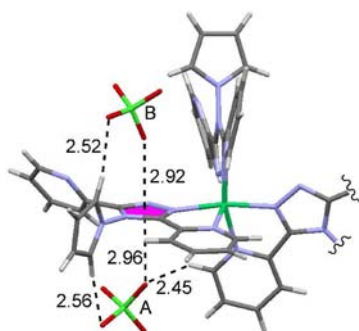


Figure 8. X-ray fragment showing the hydrogen bonds that shorten the anion– π interaction (distances in Å).

likely due to the participation of an intricate combination of intermolecular interactions that influence the final location of the anion in the solid state structure.

Finally, we have used the Bader's theory of "atoms in molecules" (AIM),⁵² which provides an unambiguous definition of chemical bonding, to further describe the anion– π and hydrogen bonding interactions described above for the ternary anion– π –anion sandwich assembly (see Figure 6). The AIM theory has been successfully used to characterize and understand a great variety of interactions including the ones studied herein.³¹ In Figure 9 we show the representation of

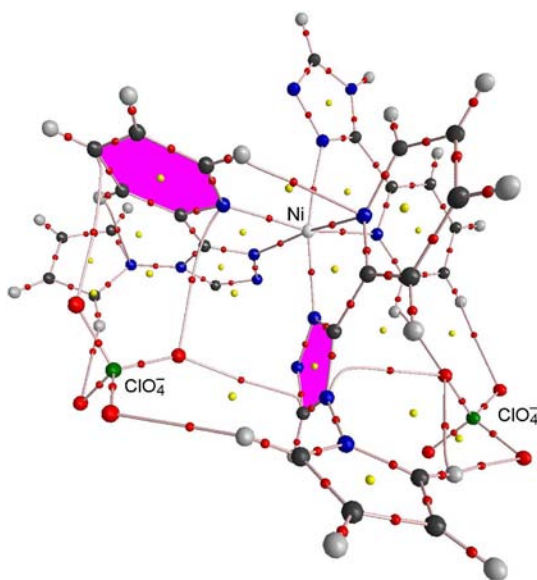


Figure 9. Representation of Bond (in red) and Ring (in yellow) Critical Points observed in the ternary anion– π –anion sandwich assembly. The bond paths connecting bond critical points and atomic nuclei are also represented.

critical points and bond paths computed for the assembly. For the sake of clarity, the aromatic rings involved in anion– π interactions are highlighted in pink in the figure. The interaction involving the six-membered ring is characterized by the presence of two bond critical points that connect two oxygen atoms of the anion with one carbon and one nitrogen atom of the pyridine ring. Both anion– π interactions involving the triazole ring are characterized by the presence of a single bond critical point. In one case it connects the anion with one carbon atom of the ring and in the other case it connects the anion with a nitrogen atom of the ring (see Figure 9). In

addition, a number of bond critical points connect both anions with several hydrogen atoms belonging to either pyridine or pyrrole rings confirming the existence of additional C–H...O hydrogen bonding interactions that influence the final position of the anion in the X-ray structure.

CONCLUSIONS

DFT calculations indicate that, despite the shorter distances observed, there is no favorable cooperativity in crystallographically observed anion–triazole–anion sandwich interactions. However the unfavorable cooperativity energy is small, and the interaction energy of the ternary anion– π –anion assembly is very large and negative, because of the coordinated Ni(II) cation that strongly increases the π -acidity of the aromatic rings. To evaluate the different forces that contribute to the binding (purely electrostatic, hydrogen bonding, and anion– π), the contributions from the anion– π and hydrogen bonding interactions have been estimated using neutral models. This study reveals that nonclassical C–H...X interactions offset the slightly unfavorable cooperativity, "pulling" the anion away from the ideal location for anion– π interactions and leading to the shorter anion– π distances observed experimentally in the ternary anion– π –anion assembly than in the binary anion– π assembly. This work demonstrates the delicate balance of noncovalent interactions that controls packing.

EXPERIMENTAL SECTION

All calculations were carried out using TURBOMOLE version 5.9⁴² using density-functional theory calculations including an empirical correction for dispersion (DFT-D). In particular, we have used the BP86-D/def2-TZVP level of theory, which is a good compromise between the accuracy of the results and the size of the system. For comparison purposes some model complexes have also been computed at the BP86-D/def2-TZVPD level of theory that includes diffuse functions. We have also used the resolution of the identity approximation, since it is considerably faster than DFT itself, and geometries are almost identical for both methods.⁴³ The basis set superposition error (BSSE) correction has been performed using the Boys and Bernardi counterpoise method.⁴⁴ We have used the crystallographic coordinates for the calculations and have optimized only the position of the anion, to estimate the contributions of the noncovalent interactions observed in the solid state. Other possible conformations of the crystal fragments have not been considered because the ultimate aim of this study is to analyze the binding properties of the noncovalent interaction in the geometry that they have in the solid state. This approximation has been successfully used by some of us^{45–47} and others^{48–50} to evaluate noncovalent interactions in the solid state.

In the anion– π –anion assembly, where two different anion– π interactions coexist, we have studied their interplay by computing the cooperativity energy E_{coop} using eq 1:

$$E_{\text{coop}} = E_{\text{BSSE}}(\text{A}-\pi-\text{A}') - E_{\text{BSSE}}(\text{A}-\pi) - E_{\text{BSSE}}(\pi-\text{A}') - E_{\text{BSSE}}(\text{A}-\text{A}') \quad (1)$$

where $E_{\text{BSSE}}(\text{A}-\pi)$, $E_{\text{BSSE}}(\pi-\text{A}')$, and $E_{\text{BSSE}}(\text{A}-\pi-\text{A}')$ terms correspond to the interaction energies of the two binary anion– π assemblies, and the multicomponent anion– π –anion assembly, respectively. The $E_{\text{BSSE}}(\text{A}-\text{A}')$ term is the interaction of the anions in the geometry that they have in the anion– π –anion assembly (in the absence of the π -system). This expression has been successfully used in the study of cooperativity effects in a variety of systems in which two different interactions coexist, including π systems as simultaneous hydride- and hydrogen-bond acceptors and the simultaneous interaction of tetrafluoroethene with anions and hydrogen-bond donors.⁵¹

The “atoms-in-molecules” analysis⁵² has been performed by means of the AIM2000 version 2.0 program⁵³ using the BD86-D/def2-TZVP wave functions.

■ ASSOCIATED CONTENT

■ Supporting Information

Further details are given in Table S1 and Figures S1 and S2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sbrooker@chemistry.otago.ac.nz (S.B.), toni.frontera@uib.es (A.F.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank CONSOLIDER-Ingenio 2010 (project CSD2010-0065) and the MICINN of Spain (project CTQ2011-27512, FEDER funds) for financial support. We thank the Direcció General de Recerca, Desenvolupament Tecnològic i Innovació del Govern Balear (Accions Especials, 2011) for financial support. We thank the CESCA for computational facilities. We are grateful to the University of Otago for supporting this research and to the 2012 International Symposium on Macrocyclic and Supramolecular Chemistry conference, held at the University of Otago, for bringing this collaborative team together in person.

■ REFERENCES

- (1) (a) Schneider, H. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 3924. (b) Schneider, H.-J.; Yatsimirski, A. *Principles and Methods in Supramolecular Chemistry*; Wiley: Chichester, U.K., 2000.
- (2) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim, Germany, 1995.
- (3) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; Wiley: Chichester, U.K., 2000.
- (4) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525–5534.
- (5) Burley, S. K.; Petsko, G. A. *Science* **1985**, *229*, 23–28.
- (6) Kim, K. S.; Tarakeshwar, P.; Lee, J. Y. *Chem. Rev.* **2000**, *100*, 4145–4185.
- (7) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303–1324.
- (8) Kim, K. S.; Lee, J. Y.; Lee, S. J.; Ha, T.-K.; Kim, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 7399–7400.
- (9) Nishio, M.; Hirota, M.; Umezawa, Y. In *The C–H/ π Interaction: Evidence, Nature, Consequences*; Wiley-VCH: New York, 1998.
- (10) Nishio, M. *CrystEngComm* **2004**, *6*, 130–156.
- (11) We note that recent work has concluded that the names π - π and anion- π are inadequate, as the π -system plays no special role in these interactions: (a) Bloom, J. W. G.; Wheeler, S. E. *Angew. Chem., Int. Ed.* **2011**, *50*, 7847–7849. (b) Martinez, C. R.; Iverson, B. L. *Chem. Sci.* **2012**, *3*, 2191–2201.
- (12) Quiñonero, D.; Garau, C.; Rotger, C.; Frontera, A.; Ballester, P.; Costa, A.; Deyà, P. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3389–3392.
- (13) Alkorta, I.; Rozas, I.; Elguero, J. *J. Am. Chem. Soc.* **2002**, *124*, 8593–8598.
- (14) Mascal, M.; Armstrong, A.; Bartberger, M. *J. Am. Chem. Soc.* **2002**, *124*, 6274–6276.
- (15) Mascal, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 2890–2893.
- (16) Frontera, A.; Saczewski, F.; Gdaniec, M.; Dziemidowicz-Borys, E.; Kurland, A.; Deyà, P. M.; Quiñonero, D.; Garau, C. *Chem.—Eur. J.* **2005**, *11*, 6560–6567.
- (17) Gil-Ramirez, G.; Escudero-Adan, E. C.; Benet-Buchholz, J.; Ballester, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 4114–4118.

- (18) Gamez, P.; Mooibroek, T. J.; Teat, S. J.; Reedijk, J. *Acc. Chem. Res.* **2007**, *40*, 435–444.
- (19) Schottel, B. L.; Chifotides, H. T.; Dunbar, K. R. *Chem. Soc. Rev.* **2008**, *37*, 68–83.
- (20) Gural'skiy, I. A.; Solntev, P. V.; Krautscheid, H.; Domasevitch, K. V. *Chem. Commun.* **2006**, 4808–4810.
- (21) Gorteau, V.; Bollot, G.; Mareda, J.; Perez-Velasco, A.; Matile, S. *J. Am. Chem. Soc.* **2006**, *128*, 14788–14789.
- (22) Gorteau, V.; Bollot, G.; Mareda, J.; Matile, S. *Org. Biomol. Chem.* **2007**, *5*, 3000–3012.
- (23) Perez-Velasco, A.; Gorteau, V.; Matile, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 9603–9607.
- (24) Dawson, R. E.; Hennig, A.; Weimann, D. P.; Emeryl, D.; Ravikumar, V.; Montenegro, J.; Takeuchi, T.; Gabutti, S.; Mayor, M.; Mareda, J.; Schalley, C. A.; Matile, S. *Nat. Chem.* **2010**, *2*, 533–538.
- (25) Lehn, J.-M.; Sonveaux, E.; Willard, A. K. *J. Am. Chem. Soc.* **1978**, *100*, 4914–4916.
- (26) Best, M. D.; Tobey, S. L.; Anslyn, E. V. *Coord. Chem. Rev.* **2003**, *240*, 3–15.
- (27) Cho, E. J.; Moon, J. W.; Ko, S. W.; Lee, J. Y.; Kim, S. K.; Yoon, J.; Nam, K. C. *J. Am. Chem. Soc.* **2003**, *125*, 12376–12377.
- (28) Custelcean, R.; Delmau, L. H.; Moyar, B. A.; Sessler, J. L.; Cho, W.-S.; Gross, D.; Bates, G. W.; Brooks, S. L.; Light, M. E.; Gale, P. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 2537–2542.
- (29) Kang, S. O.; Begum, R. A.; Bowman-James, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 7882–7894.
- (30) Wade, C. R.; Broomsgrove, A. E. J.; Aldridge, S.; Gabbai, F. P. *Chem. Rev.* **2010**, *110*, 3958–3984.
- (31) Frontera, A.; Quiñonero, D.; Deyà, P. M. *WIREs: Comput. Mol. Sci.* **2011**, *1*, 440–459.
- (32) Quiñonero, D.; Frontera, A.; Deyà, P. M. *ChemPhysChem* **2008**, *9*, 397.
- (33) Gural'skiy, I. A.; Escudero, D.; Frontera, A.; Solntev, P. V.; Rusanov, E. B.; Chernega, A. N.; Krautscheid, H.; Domasevitch, K. V. *Dalton Trans.* **2009**, 2856.
- (34) Frontera, A.; Gamez, P.; Mascal, M.; Mooibroek, T.; Reedijk, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 9564–9583.
- (35) White, N. G.; Kitchen, J. A.; Brooker, S. *Eur. J. Inorg. Chem.* **2009**, 1172–1180.
- (36) The most recent IUPAC definition of a hydrogen bond states that “in most cases, the distance between H and Y are found to be less than the sum of their van der Waals radii”: Arunan, E.; Desiraju, G. R.; Klein, R. A.; Sadlej, J.; Scheiner, S.; Alkorta, I.; Clary, D. C.; Crabtree, R. H.; Dannenberg, J. J.; Hobza, P.; Kjaergaard, H. G.; Legon, A. C.; Mennucci, B.; Nesbitt, D. J. *Pure Appl. Chem.* **2011**, *83*, 1637–1641. According to this criterion, H...Y distances of less than 2.67 Å for the BF₄⁻ anion and 2.72 Å for the ClO₄⁻ anion are classed as hydrogen bonds.
- (37) Estarellas, C.; Frontera, A.; Quiñonero, D.; Deyà, P. M. *J. Chem. Theor. Comput.* **2008**, *4*, 1981–1989.
- (38) Quiñonero, D.; Frontera, A.; Escudero, D.; Ballester, P.; Costa, A.; Deyà, P. M. *ChemPhysChem* **2007**, *8*, 1182–1187.
- (39) Manna, P.; Seth, S. K.; Das, A.; Hemming, J.; Prendergast, R.; Helliwell, M.; Choudhury, S. R.; Frontera, A.; Mukhopadhyay, S. *Inorg. Chem.* **2012**, *51*, 3557–3571.
- (40) Garau, C.; Quiñonero, D.; Frontera, A.; Ballester, P.; Costa, A.; Deyà, P. M. *New J. Chem.* **2003**, *27*, 211.
- (41) Quiñonero, D.; Frontera, A.; Garau, C.; Ballester, P.; Costa, A.; Deyà, P. M. *ChemPhysChem* **2006**, *7*, 2487.
- (42) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165–169.
- (43) Bernardi, F.; Boys, S. F. *Mol. Phys.* **1973**, *25*, 35–44.
- (44) Frontera, A.; Quiñonero, D.; Garau, C.; Ballester, P.; Costa, A.; Deyà, P. M. *J. Phys. Chem. A* **2005**, *109*, 4632–4637.
- (45) Das, A.; Choudhury, S. R.; Estarellas, C.; Dey, B.; Frontera, A.; Hemming, J.; Helliwell, M.; Gamez, P.; Mukhopadhyay, S. *CrystEngComm* **2011**, *13*, 4519–4527.
- (46) Seth, S. K.; Saha, I.; Estarellas, C.; Frontera, A.; Kar, T.; Mukhopadhyay, S. *Cryst. Growth Des.* **2011**, *11*, 3250–3265.

- (47) Barceló-Oliver, M.; Estarellas, C.; Terrón, A.; García-Raso, A.; Frontera, A. *Chem. Commun.* **2011**, *47*, 4646–4648.
- (48) Choudhury, S. R.; Dey, B.; Das, S.; Robertazzi, A.; Jana, A. D.; Chen, C.-Y.; Lee, H. M.; Gamez, P.; Mukhopadhyay, S. *Dalton Trans.* **2009**, *38*, 7617–7624.
- (49) Hoog, P.; de Robertazzi, A.; Mutikainen, I.; Turpeinen, U.; Gamez, P.; Reedijk, J. *Eur. J. Inorg. Chem.* **2009**, 2684–2690.
- (50) Goetz, R. J.; Robertazzi, A.; Mutikainen, I.; Turpeinen, U.; Gamez, P.; Reedijk, J. *Chem. Commun.* **2008**, 3384–3386.
- (51) Alkorta, I.; Blanco, F.; Deyà, P. M.; Elguero, J.; Estarellas, C.; Frontera, A.; Quiñonero, D. *Theor. Chem. Acc.* **2010**, *126*, 1–14.
- (52) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893–928.
- (53) Biegler-König, F.; Schönbohm, J.; Bayles, D. J. *Comput. Chem.* **2001**, *22*, 545–559.