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# Supramolecular Lone Pair– $\pi/\pi$ – $\pi/\pi$ –Anion Assembly in a Mg(II)–Malonate–2-Aminopyridine–Nitrate Ternary System

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The solid-state structure of an alkaline-earth metal complex reveals the formation of a remarkable supramolecular framework based on concurrent lone pair– $\pi$ ,  $\pi$ – $\pi$ , and  $\pi$ –anion interactions whose stability has been investigated by density functional theory.

## 1. Introduction

Noncovalent interactions with  $\pi$  aromatic clouds such as C–H– $\pi$ , cation– $\pi$ , and  $\pi$ – $\pi$  stacking have been studied extensively, both experimentally and theoretically.<sup>1–4</sup> In recent years, crystallographic as well as theoretical evidence for “anion– $\pi$  interactions”, which were primarily thought to be improbable due to the electron-donating character of anions and the expected repulsive interactions with aromatic  $\pi$ -systems, has been increasingly reported.<sup>5–25</sup> Anion– $\pi$  interactions are starting to be recognized by the scientific community as an important type of supramolecular interactions, as are cation– $\pi$  and  $\pi$ – $\pi$  contacts.<sup>15,24–26</sup> Likewise, experimental proofs for carbonyl– $\pi$  interactions, and more generally for lone pair (lp)– $\pi$  interactions, are scarce in the literature.<sup>3,27–29</sup> Searches of the Cambridge Structural Database (CSD) revealed the occurrence of carbonyl– $\pi$  interactions in some crystal structures of proteins,<sup>16,30,31</sup> as well as in some other organic crystals and between aromatic analytes and polyacrylate derivatives supported on silica.<sup>32,33</sup> Recently, Egli and Sarkhel<sup>3</sup> have pointed out the different possible orientations of a carbonyl group over the interacting  $\pi$ -face of aromatic rings. The carbonyl (a) may be stacked onto the plane of the ring, (b) may form an angle  $0^\circ < \alpha < 90^\circ$  with the ring plane, or (c) may be perpendicular to the ring plane.<sup>3</sup> In relation to anion– $\pi$  interactions, energetically carbonyl– $\pi$  interactions are intuitively favorable in the case of electron-deficient aromatic rings and destabilizing for electron-rich rings.<sup>27</sup> Even though similar interactions between a (carboxylate) carbonyl group and an aromatic ring have been noticed before,<sup>34–36</sup> this supramolecular feature has not been thoroughly exploited so far as a routine tool in the design and construction of supramolecular structures.<sup>37–39</sup>

In the present study, a coordination compound of Mg(II), a hard metal ion, has been synthesized. The metal center is hexacoordinated by hard oxygen donors from two primary malonate ligands and two water molecules. Complex **1**,  $(\text{C}_5\text{H}_7\text{N}_2)_4[\text{Mg}(\text{mal})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$  [where mal =  $\text{C}_3\text{H}_2\text{O}_4$  =

malonate dianion and  $\text{C}_5\text{H}_7\text{N}_2$  = protonated 2-aminopyridine], exhibiting protonated 2-aminopyridine moieties as counterions, is obtained from purely aqueous media simply by mixing the reactants in stoichiometric ratio. The X-ray structural analysis of **1** reveals a remarkable supramolecular extended architecture generated by lone pair– $\pi$ ,  $\pi$ – $\pi$ , and  $\pi$ –anion interactions.

## 2. Experimental Section

IR spectra were recorded on a Perkin-Elmer RXI Fourier transform infrared (FT-IR) spectrophotometer with the sample prepared as a KBr pellet in the range 4000–600  $\text{cm}^{-1}$ . Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240C elemental analyzer.

All reactions were carried out in aerobic conditions and in water as the solvent. Malonic acid (Aldrich), magnesium(II) nitrate hexahydrate (Lancaster), and 2-aminopyridine (Aldrich) were used as received. Freshly boiled, doubly distilled and then deionized water was used throughout the investigation.

**2.1. Synthesis of Compound 1.** Magnesium(II) nitrate hexahydrate (0.256 g, 1.0 mM) dissolved in 25 mL of water was allowed to react with malonic acid (0.208 g, 2.0 mM) in water (25 mL) at 60 °C, resulting in a clear colorless solution. A warm aqueous solution (20 mL) of 2-aminopyridine (0.376 g, 4.0 mM) was added dropwise to the above colorless solution with continuous stirring. The reaction mixture thus obtained was further heated at 60 °C for an hour with continuous stirring. The resulting solution was then cooled down to room temperature (the pH of this solution was 3.7) and kept unperturbed for the slow evaporation of the solvent. After a few weeks, flat, colorless single crystals suitable for X-ray analysis were obtained. The crystals were collected by filtration, washed with cold water, and dried in air (yield 35%). Anal. Calcd for  $\text{C}_{26}\text{H}_{36}\text{N}_{10}\text{O}_{16}\text{Mg}$ : C, 40.61; H, 4.72; N, 18.21%. Found: C, 39.89; H, 4.21; N, 17.65%. Main IR absorption bands observed for **1** (KBr pellet,  $\text{cm}^{-1}$ ) were 3326 (br), 3155 (w), 2908 (br), 1681 (s), 1635 (m), 1575 (s), 1482 (s), 1435 (vs), 1360 (m), 770 (s), 734 (s). We further noted that the same complex **1** could be prepared when the pH of the resulting solution was increased to 5.5 (from pH 3.7 as described above) by adding NaOH and then leaving the solution for crystallization.

**2.2. X-ray Crystal Structure Determination of 1.** A crystal with dimensions  $0.10 \times 0.19 \times 0.41 \text{ mm}^3$  for **1** was used for

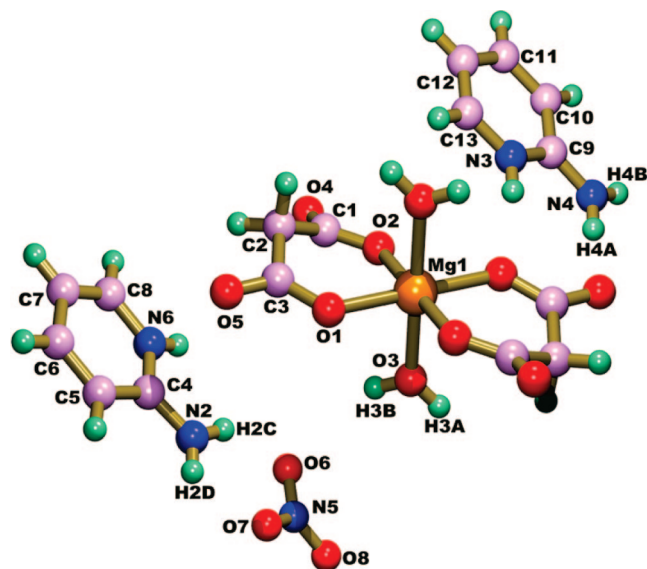
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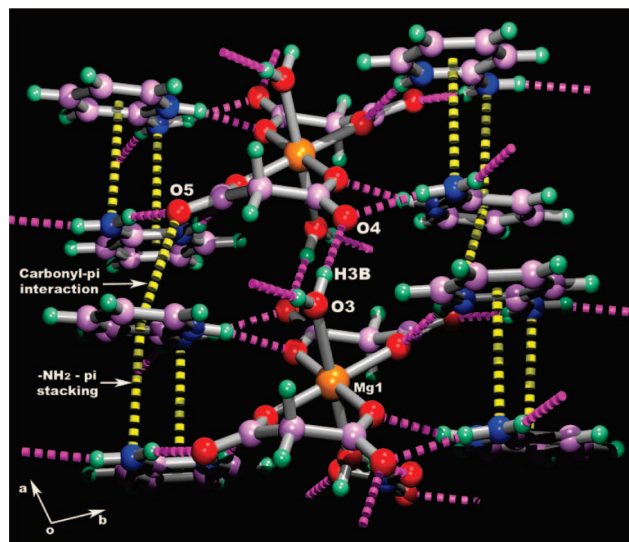
<sup>||</sup> National Changhua University of Education.



**Figure 1.** Representation of the molecular structure of **1**. Unlabeled atoms are generated by the inversion operation ( $-x, 1 - y, 1 - z$ ).

data collection on a Bruker Smart Apex II diffractometer equipped with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.710\,73\text{ \AA}$ ) at 150(2) K. A total of 10 708 reflections were measured to give 4358 unique reflections ( $R_{\text{int}} = 0.020$ ) for **1**. A total of 3544 data points [ $I > 2\sigma(I)$ ] were used for solution and refinement by full-matrix least-squares on  $F^2$  with SHELX-97.<sup>40</sup> The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. The final  $R$  and  $R_w$  values are 0.0339 and 0.0975, respectively. Information concerning crystallographic data collection and refinement for **1** are listed in Table S1 (Supporting Information), while Tables S2 and S3 (Supporting Information) collect information about selected bond lengths and angles and hydrogen-bonding interactions, respectively.

**2.3. Computational Details.** Calculations were carried out with the Gaussian03 suite of programs,<sup>41</sup> employing Becke's half-and-half (BHandH) density functional theory (DFT) functional.<sup>42</sup> Previous studies on model systems featuring lone pair- $\pi$  and anion- $\pi$  interactions have shown that while Hartree-Fock and DFT calculations provide a fair description, Møller-Plesset methods<sup>43</sup> (in particular MP2) ensure the best performance.<sup>16,19,44</sup> This is perhaps not surprising, as Hartree-Fock and most popular DFT functionals are not suitable for systems governed by dispersive forces.<sup>45-49</sup> However, high-level ab initio methods such as MP2<sup>43</sup> and CCSD,<sup>50</sup> which correctly describe these forces, require a computational cost that is only affordable for relatively small molecules.<sup>16,49,51,52</sup> For supramolecular complexes such as the one investigated in the present study, a valuable alternative is represented by the hybrid BHandH functional, which has recently been shown to describe surprisingly well geometries and energies of a variety of systems for which dispersive forces are crucial.<sup>53-59</sup> Single-point calculations at the BHandH/6-31+G(d) level were performed on model **1** (whose structure was extracted from the X-ray data of **1**, Figure 3A) to estimate the formation energy calculated via supermolecule approach with no correction for basis-set superposition error (BSSE). The main issue about this approach is that DFT (as with all quantum mechanics-based methods) may wrongly reproduce electronic structures that are away from the minimum. Despite the qualitative character of such an approach, many studies have been successfully proposed that are fully or partially



**Figure 2.** Formation of a 1D tape in **1** through association of discrete  $[\text{Mg}(\text{mal})_2(\text{H}_2\text{O})_2]^{2-}$  monomeric units. The occurrence of hydrogen-bonding interactions ( $\text{O3-H3B}\cdots\text{O4}$ ) along the  $a$  axis generates a  $R_2^2(12)$  cyclic motif. Each monomeric unit is connected to four 2-aminopyridine molecules. The nitrate anions are omitted for clarity.

based on experimental structures (NMR and X-ray), where molecular properties such as electron density were calculated.<sup>60-65</sup>

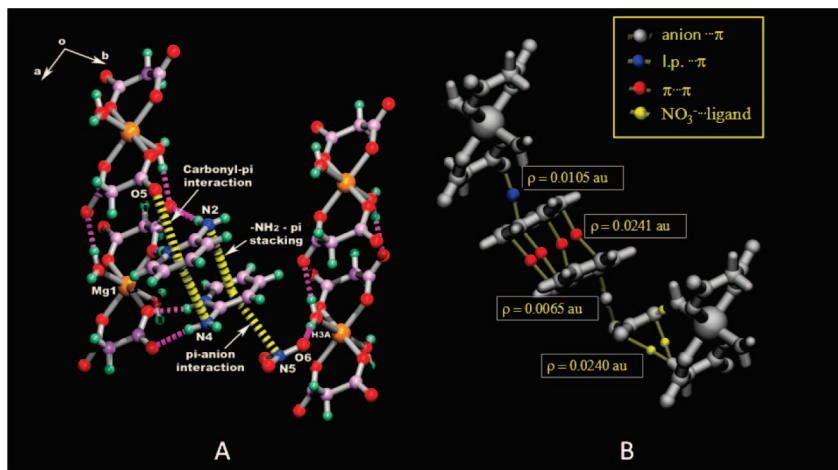
Following early studies by Alkorta et al.,<sup>19,44</sup> the Atoms-In-Molecules (AIM) theory<sup>66,67</sup> was also performed to estimate the intermolecular interactions. In particular, AIM is based upon critical points where the density gradient, namely,  $\nabla\rho$ , vanishes. Two bonded atoms are connected with a bond path (yellow lines in Figure 3B) through the bond critical point (colored spheres in Figure 3B). Importantly, several studies have shown that the electron density at bond critical points correlates with the strength of chemical bonds and interactions.<sup>53,67-70</sup>

### 3. Results and Discussion

Compound **1** crystallizes in the triclinic space group  $P\bar{1}$  with the asymmetric unit consisting of half the molecular anion  $[\text{Mg}(\text{C}_3\text{H}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$ , two crystallographically independent  $\text{C}_5\text{H}_7\text{N}_2^+$  cations, and a nitrate anion. The full anion is generated by the symmetry operation of an inversion center. A perspective view of the asymmetric unit is shown in Figure 1. Crystallographic data collection and refinement, selected bond lengths and angles, and supramolecular interactions are listed respectively in Tables S1-S3 (Supporting Information).

The magnesium(II) ion, located on an inversion center, is in an octahedral coordination environment whose equatorial plane is formed by oxygen atoms O1 and O2 from one malonate unit and their symmetry related counterparts O1\*\* and O2\*\* (where \*\* =  $-x, 1 - y, 1 - z$ ) from a second malonate unit (Figure 1). Two water molecules (O3 and O3\*\*) occupy the trans axial positions, thus generating a  $\text{MgO}_4\text{O}_2$  chromophore. The Mg-O bond distances in the equatorial plane vary between 2.0064(8) and 2.0343(8) Å, and the angle subtended at the Mg atom by the malonate ligand is 88.34(3)°. The value of the apical Mg(1)-O(3) bond length is 2.1080(8) Å. These bond lengths and angles are comparable to those found in the literature for related magnesium compounds.<sup>71-76</sup> However, the equatorial and axial bonds in **1** are found to be shorter and larger, respectively, compared to the recently reported structure of the catenapoly[[diaquamagnesium(II)]- $\mu$ -oxalato],  $[\text{Mg}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2]_n$  complex.<sup>77</sup> Malonate ligands usually adopt an envelope conformation





**Figure 3.** (A) Two-dimensional assembly of monomeric units of **1** via carbonyl (lp)- $\pi/\pi-\pi/\pi$ -anion interactions. Other 2-aminopyridine and nitrate molecules are omitted for clarity. (B) Schematic view of Atoms-in-Molecules topology of model 1. Yellow lines represent the bond paths. Colored spheres are the bond critical points as follows: gray, anion- $\pi$ ; blue, lp- $\pi$ ; red,  $\pi$ - $\pi$ ; yellow, secondary interactions between  $\text{NO}_3^-$  and the ligand. Further details on the AIM theory and topology are reported in the text.

in which only the methylene group is significantly displaced from the chelate ring plane,<sup>78</sup> and the present example is also in line with this generalization.

The monomeric anionic units are interlinked to each other via strong self-complementary  $\text{O3-H3B}\cdots\text{O4}$  [2.7168(12) Å] hydrogen bonds, which give rise to a  $\text{R}_2^2(12)$  motif, ultimately generating an infinite 1D tape along the crystallographic *a* axis. Each monomeric anionic unit also recognizes four aminopyridinium cations ( $\text{C}_5\text{H}_7\text{N}_2^+$ ) through hydrogen-bonded carboxylate ends, leading to  $\text{R}_2^2(8)$  hydrogen-bonding assemblies involving the hydrogen bonds  $\text{N2-H2C}\cdots\text{O4}$ ,  $\text{N6-H6A}\cdots\text{O2}$  and  $\text{N3-H3}\cdots\text{O1}$ ,  $\text{N4-H4A}\cdots\text{O5}$  (Figure 2). Two dangling nitrate ions are also attached to each monomeric unit by  $\text{O3-H3A}\cdots\text{O6}$  hydrogen bonds. The noncoordinating O5 atom is orientated toward the  $\pi$ -face of a 2-aminopyridine moiety. The distance between O5 and the centroid of the aminopyridine ring is 3.1211(11) Å [angle  $\alpha = \text{C3-O5}\cdots\text{Cg}(1) = 4.0230(12)$  Å, where Cg(1) is the centroid of the ring defined by the atoms N(6)/C(4)/C(5)/C(6)/C(7)/C(8)]. In this case, the carbonyl group approaches the  $\pi$ -face of the aminopyridine ring with an angle 129.80(8)°, suggesting a significant lp- $\pi$  interaction.<sup>3</sup> The shortest separation distances reflecting this interaction are  $\text{O5}\cdots\text{N6} = 3.0204(14)$  Å and  $\text{O5}\cdots\text{C4} = 2.9776(15)$  Å, which is below the sum of the corresponding van der Waals radii (sum of van der Waals radii of O and N is 3.07 Å, and that of O and C is 3.22 Å).<sup>79</sup> The 2-aminopyridine ring is further stacked over a second aminopyridine molecule [ $\text{R}(1) = \text{N}(6)/\text{C}(4)/\text{C}(5)/\text{C}(6)/\text{C}(7)/\text{C}(8)$ ;  $\text{R}(2) = \text{N}(3)/\text{C}(9)/\text{C}(10)/\text{C}(11)/\text{C}(12)/\text{C}(13)$ , symmetry code  $1-x, 1-y, 1-z$ ]. The centroid-to-centroid distance is 4.1005(7) Å, and the dihedral angle amounts to 6.33°. The amino nitrogen atoms N2 and N4 lie only 3.36 and 3.32 Å above the  $\pi$  face of the parallel stacked 2-aminopyridine ring, revealing an unusual stacking of the -NH<sub>2</sub> group over the aromatic- $\pi$  cloud. This coupled carbonyl (lp)- $\pi/\pi-\pi$  interaction within the monomeric units adds stability to the formation of a 1D tape. Interestingly, one nitrate anion from an adjacent monomeric unit along the *a* and *b* axes is in contact with this carbonyl (lp)- $\pi/\pi-\pi$  assembly (Figure 3A) from the open opposite face of the 2-aminopyridine ring through  $\pi$ -anion interaction [ $\text{O7}\cdots\text{Cg} = 3.4669(13)$  Å,  $\text{N5}\cdots\text{Cg} = 3.6480(12)$  Å]. The shortest separation distance reflecting this interaction is  $\text{N5}\cdots\text{C10} = 3.1476(17)$  Å, which is below the sum of the corresponding van der Waals radii (sum of van der Waals radii

of N and C is 3.25 Å). Such multilayered carbonyl (lp)- $\pi/\pi-\pi/\pi$ -anion interaction in a nickel complex, that is,  $(\text{C}_5\text{H}_7\text{N}_2)_4[\text{Ni}(\text{mal})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ , has been recently observed by us where this sandwich association plays a similar role in the formation of a 2D assembly.<sup>60</sup> The present Mg(II) complex therefore represents an unusual example where a carbonyl (lp)- $\pi/\pi-\pi/\pi$ -anion supramolecular assembly leads to formation of a 2D network that propagates along the *b* axis. Compared to the Ni(II) complex recently reported<sup>60</sup> [where the distance between the carbonyl oxygen atom (O2) and the centroid of the aminopyridine ring is 3.1607(15) Å, and the shortest separation distances are  $\text{O2}\cdots\text{N3} = 3.0488(19)$  and  $\text{O2}\cdots\text{C9} = 3.004(2)$ ], in **1**, the carbonyl- $\pi$  contact is shortened to 3.1211(11) Å, with the shortest separation distances being  $\text{O5}\cdots\text{C4} = 2.9776(15)$  and  $\text{O5}\cdots\text{N6} = 3.0204(14)$ . Moreover, in **1**, the aminopyridine moieties come even closer, as is evidenced by the Cg $\cdots$ Cg distance, which is 4.10 Å, while this distance between the two aminopyridine moieties is 4.174 Å for the related Ni(II) compound.<sup>60</sup> The nitrate- $\pi$  contact becomes shorter in **1** as well (the smaller separation distance  $\text{N5}\cdots\text{C10}$  is 3.148 Å) compared to the Ni(II) complex (where the shortest separation distance  $\text{N5}\cdots\text{C5}$  is 3.237 Å). The overall 3D association is mainly guided by the  $\text{N4-H4B}\cdots\text{O8}$  hydrogen bond.

This outstanding lone pair- $\pi/\pi-\pi/\pi$ -anion assembly has been theoretically investigated. Single-point calculations performed on model 1 at the BHandH/6-31+G(d) level (Figure 3) suggest that the complex is stable, that is, the formation energy is -160 kcal mol<sup>-1</sup>. Figure 3B displays the intermolecular interactions that stabilize model 1, quantified by AIM theory. As observed experimentally, our theoretical approach reveals a remarkable network of lone pair- $\pi/\pi-\pi/\pi$ -anion interactions. In particular, the lone pair- $\pi$  interaction between a malonato ligand and one of the 2-aminopyridine rings shows an electron density of 0.0105 au, equivalent to that observed in the nickel complex investigated recently.<sup>60</sup> On the other hand, the  $\pi$ -stacking interactions between the 2-aminopyridine rings are somewhat weaker than those in the Ni compound, as the overall electron density amounts to 0.0241 au (while the corresponding value is 0.106 au for the nickel complex<sup>60</sup>). This significant difference may represent the main cause of the lower stability of model 1 compared to the related nickel compound. The AIM analysis also reveals the role played by the  $\text{NO}_3^-$  anion, which interacts

via fairly strong H-bonds with the ligand, resulting in an overall electron density of 0.0240 au (Figure 3B). The *weak* anion- $\pi$  interaction (Figure 3B) is an additional interesting feature of this assembly ( $\rho = 0.0065$  au). Calculations carried out on the complex without  $\text{NO}_3^-$  lead to a nearly unchanged formation energy (from -160 to -170 kcal mol $^{-1}$ ), suggesting that the assembly may be stable even in the absence of this anionic group. Considering that the  $\text{NO}_3^-$  group is experimentally observed as part of the supramolecular assembly, it may be speculated that the  $\text{NO}_3^-$  group is most likely involved in the dynamic process of crystal formation, rather than playing a thermodynamic role.

In summary, single-point calculations and AIM analysis carried out on model 1 (derived from the single-crystal X-ray structure) indicate that this complex is thermodynamically stable. Moreover, electron density analysis is consistent with the experimental observation that the unique lone pair- $\pi/\pi$ - $\pi/\pi$ -anion interaction contributes to the overall stability of the supramolecular assembly.

#### 4. Concluding Remarks

Anion- $\pi$  and lone pair- $\pi$  interactions are being recognized as important supramolecular bonding contacts by the scientific community. Thus, research investigations are increasingly dedicated to the study of these noncovalent contacts. In the present paper, the first alkaline-earth metal complex is described where strong carbonyl (lone pair)- $\pi$  interactions contribute to the formation of a 1D assembly and where a multilayered carbonyl (lp)- $\pi/\pi$ - $\pi/\pi$ -anion interaction dictates the generation of a 2D assembly, as shown by DFT calculations. This illustrative example clearly indicates that associative interactions between electron-rich molecules with  $\pi$ -acidic rings are certainly important bonding contacts that should be used by the supramolecular chemist to build multidimensional molecular structures. Other non-transition-metal carboxylate complexes with various heterocyclic bases are under investigation to increase the present state of knowledge of these supramolecular interactions in the solid state.

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**Supporting Information Available:** Tables summarizing the crystallographic data collection and refinement (Table S1), selected bond lengths and angles (Table S2), and supramolecular interactions (Table S3). Full crystallographic data in CIF format for **1** have been deposited with the Cambridge Crystallographic Data Centre (CCDC 702637). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K.; fax +44(0)-1223-336033;

e-mail deposit@ccdc.cam.ac.uk. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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