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Experimental observation and theoretical investigation on a novel Cd(II) complex with π-hole interaction involving nitro groups

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Some of us have recently demonstrated combining theory and a statistical survey of the Cambridge Structural Database (CSD) that the interaction between the π-holes of nitro groups and electron-rich atoms is somewhat directional (*Chem. Commun.*, 2015, 51, 1491-1493). In this communication, we present a joint experimental and theoretical study on a novel cadmium(II) complex, [Cd(C$_7$H$_3$N$_2$O$_6$)$_2$(C$_{12}$H$_8$N$_2$)$_2$]·H$_2$O·DMF (1) [where C$_7$H$_4$N$_2$O$_6$=3,5-dinitrobenzoic acid and C$_{12}$H$_8$N$_2$= 1,10-phenanthroline] to unravel the important role of this π-hole interaction.

σ-Hole and π-hole are attractive intermolecular interactions which have witnessed a resurgent interest in recent times.[1] A σ-hole is termed as a region of positive electrostatic potential on the extension of a covalent bond.[2-6] A counterpart of a σ-hole is a π-hole. According to a definition laid down by Murray *et al.*,[7] it is a region of positive electrostatic potential that is perpendicular to a portion of a molecular framework. On going from the lighter to the heavier atoms in a given group of the periodic table, σ/π-holes become more positive and the existence of electron withdrawing groups in the rest of the molecule bear a strong effect on the σ/π-hole magnitude.[5,8-9] Positive σ/π-holes are found to interact in a highly directional manner with concentrations of negative charge. Competition and interplay between σ-hole and π-hole interactions have been subject to several theoretical investigations.[1,10-12] More recently, a remarkable experimental evidence for the occurrence of both σ-hole and π-hole interactions at work in Fmoc-Leu-Ψ[CH$_2$-NCS] is reported.[13]

Some of us have recently communicated that the interaction of the π-hole found on a nitro group with electron rich entities (ElR, e.g. H$_2$O, Cl⁻) is energetically favourable (varying in strength between –0.5 and –27.9 kcalmol⁻¹).[14] Moreover, we have demonstrated that this 'NO$_2$$^\pi$···ElR' interaction is directional by analysing the data compiled within the Cambridge Structural Database (CSD) using nitromethane and nitrobenzenes. As a matter of fact, the potential of intermolecular N···O interactions of nitro groups in crystal engineering was revealed by

Gagnon *et al.* in the X-ray structures of hexakis(4-nitrophenyl)benzene.[15] Moreover, different types of interactions containing nitro groups in nitroarenes have been previously reported.[16–18] In the present study, a cadmium(II) 3,5-dinitrobenzoate coordination complex containing 1,10-phenanthroline as an ancillary ligand, [Cd(C$_7$H$_3$N$_2$O$_6$)$_2$(C$_{12}$H$_8$N$_2$)$_2$]·H$_2$O·DMF (1), has been synthesized[†] and structurally characterized (Fig. 1). We have selected the 3,5-dinitrobenzoate ligand that incorporates two nitro groups with the purpose to demonstrate the importance of π-hole interactions in the solid state and their crucial role in the crystal packing. Interestingly, compound 1 exhibits an intricate combination of π–hole interactions involving both nitro groups of the 3,5-dinitrobenzonate ligand in its solid state architecture, thus confirming the initial expectations.
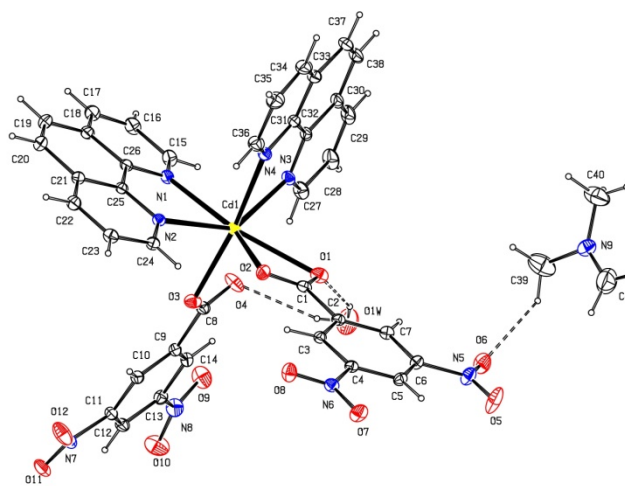

Fig.1 The molecular structure of **1**, showing the atom labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. Dashed lines indicate hydrogen bonds.

Table 1. Bond distances (Å) and angles (°) in **1** and related complexes.

	1	[(phen)$_2$Cd(O$_2$C-C$_6$H$_4$NO$_2$)$_2$]	[(phen′)$_2$Cd(O$_2$C-C$_6$H$_3$N$_2$O$_4$)$_2$]
Cd-O (κ_O)	2.286(2)	2.265(4)	2.216(3), 2.298(3)
Cd-O (κ_O,κ_O)	2.404(2), 2.584(2)	2.353(5), 2.611(4)	-
Cd-N	2.415(2)-2.460(2)	2.410(3)-2.466(5)	2.325(3)-2.429(3)
Cd-O-C (κ_O)	107.0(2)	108.8(4)	116.2(2), 130.2(3)
Cd-O-C (κ_O,κ_O)	87.4(2), 96.0(2)	86.5(3), 98.6(3)	-
N-Cd-N (bite angle)	68.1(1), 68.4(1)	67.8(1), 68.4(1)	68.5(1), 70.8(1)

The X-ray crystallographic study§ reveals that in **1** the cadmium(II) ion is hepta-coordinated with four nitrogen atoms from two 1,10-phenanthroline ligands and three oxygen atoms from two 3,5-dinitrobenzoatemolecules. The coordination of the dinitrobenzoate ligands is best described as κ_O, κ_O-bidentate for dinitrobenzoate **I** (C1, O1, O2) and κ_O-monodentate for dinitrobenzoate **II** (C8, O3, O4). The geometry of the metal coordination sphere can be considered to be a distorted pentagonal bipyramid, with one phenanthroline nitrogen and the monodentate benzoate in the apical positions. A mixed coordination of two carboxylate ligands is quite common for similar Cd(II) complexes. About half of the twenty eight (28) bis(bipyridyl)-or bis(phenanthroline) cadmium(II) bis(carboxylate) complexes reported in the Cambridge Structural database,[19] present a mixed monodentate/bidentate coordination of the carboxylate ligands. Most of the others display bis-monodentate coordination, while bis-bidentate carboxylate coordination is observed rather rarely. Bond distances and angles in **1** are similar to those observed for other bis(benzoate) bis(phenanthroline) cadmium(II) complexes, in particular to that of [(phen)$_2$Cd(O$_2$C-C$_6$H$_4$NO$_2$)][20] carrying a single nitro-substituent in the meta position and to [(phen′)$_2$Cd(O$_2$C-C$_6$H$_3$N$_2$O$_4$)$_2$] with two imidazo[4,5-f]phenanthroline ligands and two monodentate bis(3,5-dinitrobenzoate) ligands.[21]

The co-crystallized water molecule forms moderate to weak hydrogen bonds with coordinated atom O1 of dinitrobenzoate **I** and
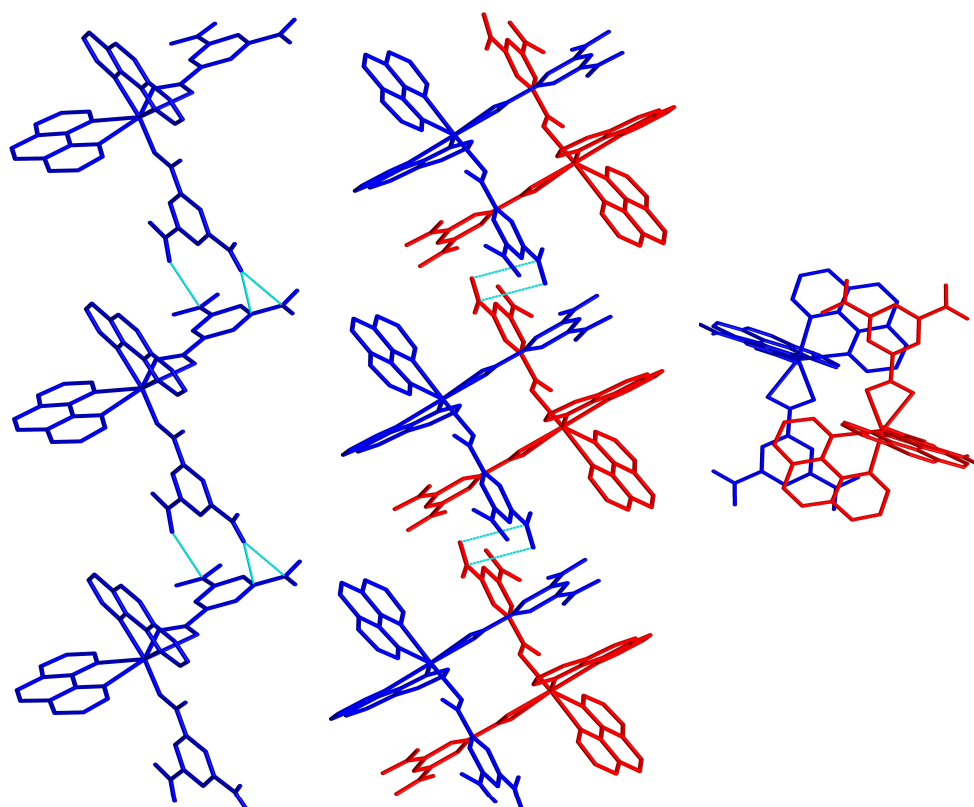

Fig.2 Packing diagrams of **1**. Water and DMF molecules are not shown. Left: one-dimensional ladder formed by perpendicular NO$_2$-NO$_2$ interactions. Middle: Combination of two such ladders by anti-parallel NO$_2$-NO$_2$ interactions. Right: Supporting π-π stacking of benzoate and phenanthroline ligands
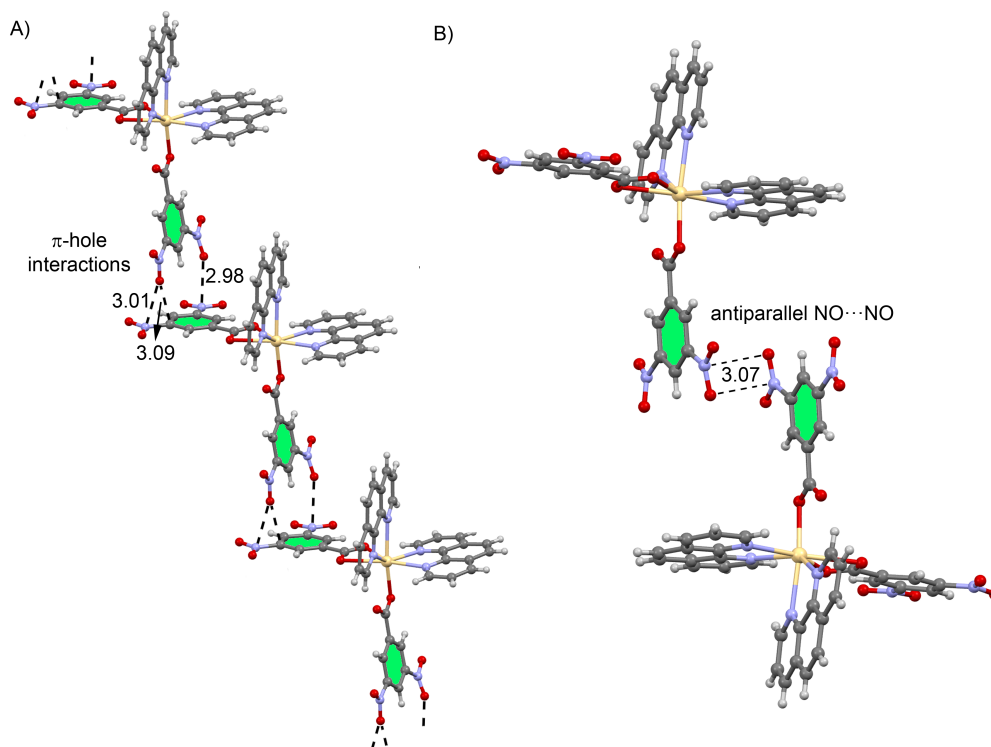
Fig. 3 Infinite ladder in the solid state of compound **1** (A) and a self-assembled dimer (B) formed by an antiparallel NO···NO interactions. Distances in Å

with uncoordinated atom O4 of dinitrobenzoate **II** (Table S2). Co-crystallized DMF is involved in C-H··O interaction with a oxygen atom O6 of a nitro group (Table S2). There are also some other C-H··O interactions present in **1** (Table S2). More notable are the non-bonding interactions between nitro-groups of neighbouring molecules. **1** displays two common motifs of NO_2-NO_2 interactions: perpendicular NO_2-NO_2 interactions, with a close to linear N-O···N angle and anti-parallel interactions of two NO bonds. Perpendicular NO_2-NO_2 interactions have been analyzed recently and shown to be comparable in energy to hydrogen bonds and π-π stacking interactions.[22] In **1** two such short intermolecular O-N distances ($d_{O10-N5*}$ = 3.01 Å, $d_{O11-N6*}$ = 2.98 Å) with a close to perpendicular orientation of the NO_2 groups are observed (N8-O10-N5* = 160°, N7-O11-N6* = 157°). The two related

cadmium nitrobenzoate complexes shown in Table 1 likewise show such short, perpendicular NO_2-NO_2 interactions with d_{N-O} ca. 3.0 Å. In addition, in **1** the N7-O11 bonds of two neighbouring molecules stack near perfectly with an O11-N7-O11* angle of 89° and an N7-O11* distance of 3.07 Å. Such anti-parallel NO_2-NO_2 interactions are absent in the complexes mentioned in Table 1, but are otherwise very common for nitro compounds. (The Cambridge Structural database lists around 700 structures showing antiparallel NO_2-NO_2 interactions below 3.1 Å.) Perpendicular NO_2-NO_2 interactions with neighbouring molecules give rise to one-dimensional ladder (Figure 2). Two of such ladders combine to provide anti-parallel NO_2-NO_2 interactions. The combination of the two ladders is further supported by π-π stacking interactions between dinitrobenzoate rings in one chain and phenanthroline ligands in
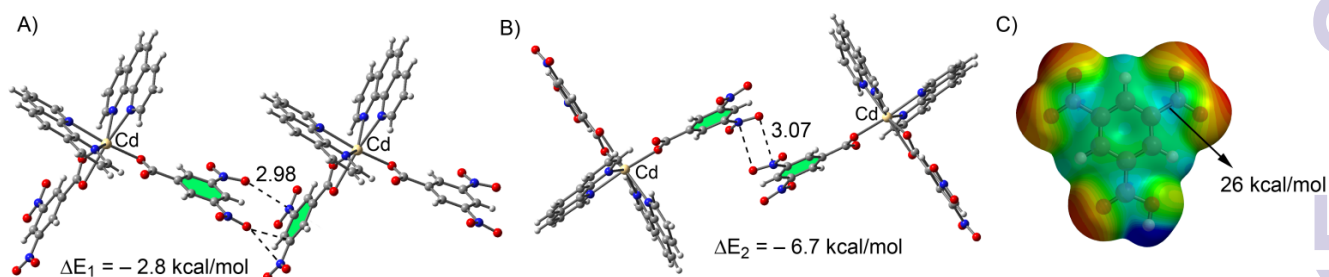

Fig.4 Theoretical models (A and B) used to evaluate the π–hole interaction in compound **1** at the BP86-D3/def2-TZVP level of theory. The MEP surface of 3,5-dinitrobenzoic acid is also shown. Distances in Å.

another (d = 3.4 – 3.6 Å).

The theoretical study (see ESI† for computational details) is focused to analyse the interesting noncovalent interactions observed in the solid state architecture with special interest to π–hole interactions involving the nitro groups (acting as both donor and acceptor groups) (see Figure 3). As aforesaid, these interactions are responsible for the formation of interesting supramolecular assemblies (infinite 1D ladder and self-assembled dimers). We have used two theoretical models to evaluate the π–hole interactions in compound **1** based on the X-ray fragments shown in Figure 3. In one model (Figure 4A), we evaluate the double π–hole interaction that is weak (ΔE_1 = –2.8 kcal/mol) in agreement with previous theoretical calculations in nitrobenzene.[14] In the second theoretical model, we evaluate the antiparallel NO···NO interaction. The binding energy is larger than in the first model (ΔE_2 = – 6.7 kcal/mol) and is comparable to similar interactions like antiparallel CO···CO[23] and CF···CF interactions.[24] We have also included in Figure 4 the molecular electrostatic potential (MEP) surface of 3,5-dinitrobenzoic acid as a model of the ligand in order to show the existence of the π-holes over the C–NO$_2$ bonds. It can be clearly observed two regions of electropositive potential almost over the nitrogen atoms of the nitro groups that explain the formation of the infinite ladder observed in the solid state of **1** (Figure 3A) since a good complementarity between both π-holes and the negative oxygen atoms is achieved.

We have further analyzed the π-hole interactions using the Bader's theory of "atoms in molecules" that provides an unambiguous definition of chemical bonding.[25] We have used two theoretical models where, using the X-ray geometry, we have protonated the ligand and eliminated the Cd ions and the rest of ligands. The AIM analyses of the model complexes of both π-hole interaction modes observed in compound **1** are shown in Figure 5. In the double π-hole complexation mode (Figure 5A), one interaction is characterized by the presence of a critical point that connects the oxygen atom to the nitrogen atom confirming the π-hole noncovalent bonding. The other interaction is characterized by the presence of a bond critical point that connects the oxygen atom to the carbon atom of the ring. Finally, a secondary C–H/π interaction is observed that is expected to be electrostatically repulsive since the π-system is electron deficient thus reducing the total interaction energy. The computed binding energy of this complex is ΔE_3 = –4.0 kcal/mol that is higher in absolute value than ΔE_1 indicating that the ligand complexation to Cd weakens the π-hole interaction. The antiparallel NO···NO interaction (Figure 5B) is characterized by the presence of two bond critical points that connect the oxygen atoms to the nitrogen atoms. The interaction is further characterized by the presence of a ring critical point as a consequence of the formation of the supramolecular N$_2$O$_2$ ring. The interaction energy computed for this model is ΔE_4 = –5.8 kcal/mol, which is similar to ΔE_2 indicating that the complexation of the ligand to the Cd does not influence the binding strength of the antiparallel NO···NO interaction likely because of a compensating effect. That is, since the N becomes more positive (stronger acceptor) and the O less negative (weaker donor) upon complexation, the resulting interaction energy remains almost unchanged. Finally, to corroborate that the C–H/π interaction is contrary to the binding, we have used another computational model where the CH group has been replaced by a nitrogen atom (pyridine instead of benzene, see Figure 5C). The nitrogen atom incorporated in this model does not participate in the binding because the distance to the ring plane is large (~ 4 Å). The distribution of critical points confirms this issue, since only two bond critical points are observed in the complex. The interaction energy of this complex is ΔE_5 = –5.1 kcal/mol, i.e. 1.1 kcal/mol more favorable than ΔE_3 thus confirming that the C–H/π interaction is repulsive and compensated by the double π-hole interaction.

In this present work, we synthesized and X-ray characterized compound **1** especially designed to analyze π-hole interactions in the solid state involving the nitro groups. Interestingly, several supramolecular arrangements involving this interaction are observed in the crystal packing. Thus, the present compound represents a novel example of supramolecular system bearing a network of π-hole interactions. From the DFT study, we have demonstrated by analyzing the molecular electrostatic potential surface the presence of two π-holes. In addition, we have computed the contributions of the different binding forces using several models that confirm the favorable interaction energies of NO$_2^\pi$···O interactions. Crystal engineering comprises deep comprehension of weak intermolecular forces that govern crystal packing, thus potentially allowing a rational design of
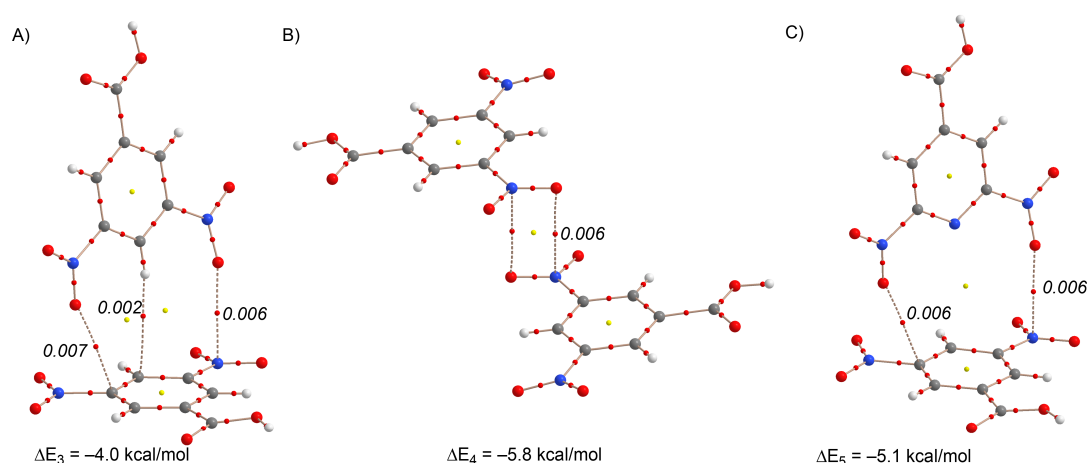

Fig.5 Distribution of critical points in three models of compound **1**. Bond and ring critical points are represented by red and yellow spheres, respectively. The bond paths connecting bond critical points are also indicated. The values in italics correspond the values of the charge density ρ(r) at the bond critical points in a.u.

solids with tailored physical and chemical properties. The results described above are certainly of importance in this regard.

Notes and references

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†To a solution of 3,5-dinitrobenzoic acid (0.424 g, 2.0 mmol) in methanol (15 mL) cadmium(II) nitrate tetrahydrate (0.308 g, 1.0 mmol) dissolved in water (15 mL) was added and stirred for 10 min. To this reaction mixture an aqueous solution (10 mL) of 1,10-phenanthroline (0.396 g, 2.0 mmol) was added with constant stirring. After stirring this reaction mixture for about 15 min precipitation appeared. The precipitate was dissolved by adding 10 mL of DMF to it. The reaction mixture was then allowed to stir for another 45 min, then filtered and kept for crystallization. Diffraction quality colorless crystals of **1** were obtained after about one month. Due to low yield **1** could solely be characterized by X-ray diffraction.

§The intensity data for **1** were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) by the ω-scan method. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Integration and scaling of intensity data were accomplished using the program SAINT. The structures were solved by direct methods using SHELXS[26] and refinement was carried out by full-matrix least-squares technique using SHELXL.[26] Anisotropic displacement parameters were calculated for all non-hydrogen atoms. The water H atoms (H1W and H2W) were located in difference Fourier maps and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(O)$. The distances of O-H were constrained with 0.85 Å. All other H atoms were located in a difference electron density map but were positioned geometrically and included as riding atoms, with C-H = 0.93 – 0.96 Å and with $1.5U_{eq}(C)$ for methyl H and $1.2U_{eq}(C)$ for other H atoms. The Crystal data, data collection and structure refinement details are summarized in Table S1, ESI†. Hydrogen bonding parameters are listed in Table S2, ESI†. CCDC 1051813 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

Electronic Supplementary Information (ESI) available: [Computational details, crystal data, structure refinement and hydrogen bonding parameters are included here. CCDC reference number 1051813]. See DOI: 10.1039/c000000x/

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