DOI: 10.1002/ejoc.200701209

Crystallographic and Theoretical Evidence of Anion–π and Hydrogen-Bonding Interactions in a Squaramide–Nitrate Salt

Carmen Rotger,*[a] Bartomeu Soberats,[a] David Quiñonero,[a] Antonio Frontera,[a] Pablo Ballester,[b] Jordi Benet-Buchholz,[b] Pere M. Deyà,[a] and Antoni Costa*[a]

Keywords: Amides / Anions / Pi interactions / Molecular recognition

Synthetic anionic receptors are fundamental to the understanding of the mechanism of recognition phenomena, which is the basis of many fundamental biological processes. Recognition studies and X-ray crystallography techniques provide accurate information on the structure of the molecular complexes and the nature of the interactions involved. Here, we present the first example of a squaramide–nitrate salt. X-ray crystallography and theoretical studies show the important roles of anion–π and hydrogen-bonding interactions in the crystal packing of this compound in relation to those found in the free squaramide solid structure.

Introduction

Molecular recognition phenomena are the basis of most biological processes, and especially, anion recognition is a very important process in biochemical systems, as more than 70% of substrates and cofactors are negatively charged[1] The design of receptors for specific anions is fundamental to the understanding of the mechanisms of such processes. Accordingly, the preparation of synthetic anionic receptors may lead to potential medicinal and biological applications and would be paramount for the preparation of new drugs.[2] Along with molecular recognition studies, in the solid state, X-ray crystallography techniques provide accurate information on the structures of molecular complexes and the nature of nonbonding interactions between the binding partners, which include electrostatic, hydrogen-bonding, π–π, cation–π, and anion–π interactions.[3] The analysis of individual nonbonding interactions through the combined use of crystallographic and theoretical studies is a powerful tool to understand the mechanism of such processes and to discover new examples and applications.

Oxoanions have a special relevance in many biological transformations. Synthetic receptors based on squaramide modules can recognize oxoanions in highly competitive media by combining electrostatic and hydrogen-bonding forces.[4] However, the crystal structure of disecondary squaramides is scarcely found in the literature.[5] Less commonly found are examples of the host–guest cocrystalization approach involving a disecondary squaramide unit.[5d]

Herein, we report on the first solid structure of a disquaramide–oxoanion crystalline salt. The crystal structure of the free host was also obtained, and crystallographic analysis of both revealed that many different noncovalent interactions are responsible for the respective crystal packing. In the squaramide–nitrate cocrystal, the observation of the recognition phenomenon of the oxoanion by the squaramide together with an example of anion-π interaction[6] is remarkable.

This study combines crystallographic and computational evidence that anion–π interactions are indeed present in the squaramide–nitrate crystal reported here and that they play an important role in determining the particular structural motif observed relative to the free host.

Results and Discussion

Receptor **1** was synthesized by double condensation of diethyl squarate with 2-(2-pyridyl)ethylamine in ethanol. Crystals of **1** (Figure 1) suitable for X-ray diffraction were obtained from this solvent.

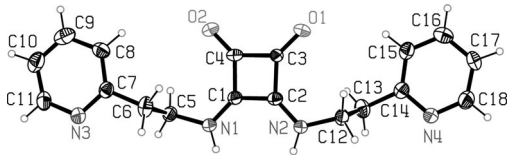

Figure 1. ORTEP drawing (30% probability level) of **1**.

In the solid state, **1** is tiled in a head-to-tail disposition by formation of an array of conventional hydrogen bonds

[a] Departament de Química, Universitat de les Illes Balears, Crta. De Valldemossa km 7.5, 07122 Palma de Mallorca, Spain
Fax: +971-173426
E-mail: carmen.rotger@uib.es
[b] ICREA and Institute of Chemical Research of Catalonia (ICIQ), Avgda Països Catalans, Tarragona, Spain

N–H···O between the squaramide N–H and the carbonyl groups of a neighboring squaramide moiety. This molecule self-organizes in the crystal in a very similar way to that in aromatic derivatives of urea and some disecondary squaramides, which leads to a 1D hydrogen-bonded network.[5d] Additionally, in **1** the two pyridine N atoms stay in a *syn* orientation, which favors two additional C–H···N hydrogen-bonding interactions between the two pyridine N atoms and the 9-H and 16-H from the same neighboring molecule along the column; this adds more stability to the previously mentioned hydrogen-bonded network. The remarkable hydrogen-bond acceptor/donor capability of the squaramide unit can be explained in terms of the gain in aromaticity of the four-membered ring upon the simultaneous formation of hydrogen bonds with the carbonyl and N–H groups.[7] This feature is also manifested in the packing arrangement of the molecules where the compound forms dimeric structures stabilized by two offset π-stacking interactions between the electron-rich squaramide and the electron-deficient pyridine rings, at a centroid distance of 3.93 Å (Figure 2).

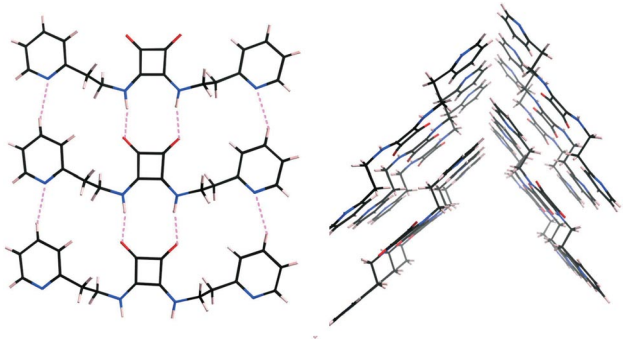

Figure 2. Left: head-to-tail hydrogen-bonded molecules of **1**; right: offset and T-shape π–π interactions are observed in the crystal packing of **1**.

The well-known dipolar character of both the squaramide and pyridine rings is responsible for the head-to-tail packing observed for the hydrogen-bonded columns, and this contributes to the overall stabilization of the 3D structure. The 3D packing is finally reached by the particular disposition of the squaramide columns to assemble in an arrow fashion, which favors a T-shaped edge-to-face interaction between the pyridine rings of neighboring molecules.

Reaction of **1** with zinc(II) nitrate [$Zn(NO_3)_2{\cdot}6H_2O$], in a 1:1 ratio in acetonitrile, leads to the formation of the squaramide–nitrate host–guest cocrystal **2**, which crystallizes from this solvent. X-ray analysis of **2** shows that is formed by one molecule of **1** as the cationic counterpart, and it contains two pyridinium cations and two molecules of nitrate anion to achieve charge neutralization. The complexity of the crystal structure of **2** is readily apparent and interesting features are observed in it. First of all, it is noticeable that the two nitrates are situated in quite different environments (Figure 3). Each nitrate is hydrogen bonded to the host: one to the squaramide moiety and the other to one of the pyridinium rings. The nitrogen atoms from the cationic rings are in an *anti* orientation and one of the two pyridinium rings is twisted 30° with respect to the squaramide plane, which makes differs from the free crystal structure of disquaramide **1**.

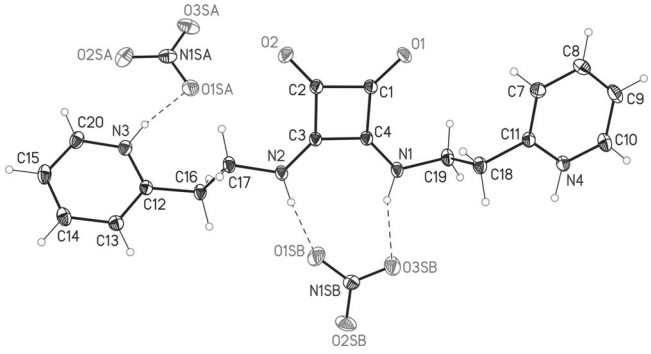

Figure 3. ORTEP drawing of **2** (30% probability level) showing the pyridinium–nitrate and squaramide–nitrate units held together by a strong N^+–H···O and two N–H···O hydrogen bonds.

The simultaneous participation of the two squaramide N–H groups in a nitrate–squaramide motif prevents the formation of the tiled head-to-tail packing observed in **1**. Alternatively, the nitrate is bound to the squaramide moiety by two oxygen atoms through two strong and almost coplanar N–H···O hydrogen bonds, which exhibits recognition of the anion by the host. The third oxygen atom forms a C–H···O hydrogen bonding interaction with C-8–H of the neighboring molecule. Such a hydrogen-bond pattern leads to a repetitive sequence of pyridinium–squaramide–nitrate units (Figure 4).

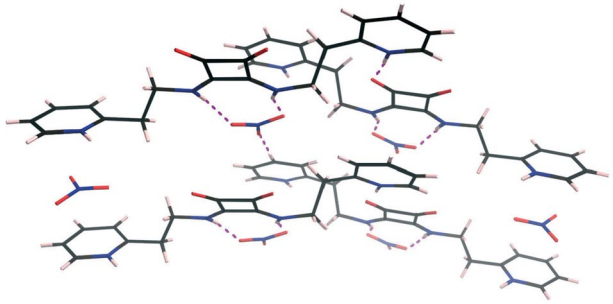

Figure 4. Selected view of the crystal packing of **2** showing the anion–π interactions between the nitrate ions and the two pyridinium rings; the nitrate–squaramide–pyridinium hydrogen bonding motif is also apparent.

The second type of nitrate anion forms conventional N–H···ONO_2 and bifurcated C–H···O_2NO hydrogen bonds with two different pyridinium rings, which links two squaramide molecules. The structural pyridinium–nitrate unit is held together by a strong N–H···O hydrogen bond, and this is a common motive in many crystal structures of pyridinium–nitrate compounds.[8] Theoretical calculations suggest that the interaction energies of the C–H···O bifurcated contacts, classically classified as weak,[9] are increased substantially in systems with protonated nitrogen atoms as in pyridinium moieties.[10] This array of hydrogen bonds is almost coplanar with the pyridinium rings, and an additional

C–H···O contact is also observed between the nitrate and the closest α-methylene squaramide hydrogen of the neighboring molecule located at a distance of 2.63 Å.

Despite the fact that not every organic compound that crystallizes as a salt may classify as an anion receptor, in this example, we found some specificity in the squaramide–nitrate interaction. This weak interaction, in principle, prevails over the formation of an ion pair with one of the two pyridinium rings, which favors nitrate recognition (Figure 3).[11]

In this scenario, the nitrate anion bonded to the organic cation is sandwiched between two electron-poor pyridinium rings, and both anion–π and ion-pair-reinforced hydrogen-bonding interactions are involved.[12] The nitrogen atom is almost axial on the ring centroid, and the nitrate plane is located parallel to the aromatic ring and situated at a ring centroid distance of 3.41 and 3.26 Å, respectively, and with angles of the centroid of 89 and 87°, respectively. The distances are in agreement with those observed for anion–π interactions and comparable to those observed for more electron-poor nitrogenated aromatic rings than pyridine such as triazine and cyanuric acids.[13] The protonation of the pyridine ring enhances its electron-deficient character, which leads to a closer contact distance, for example, in pyridinium···Cl^- anion–π interactions, than those observed between metal coordinated pyridine rings and Cl^- or nitrate.[6,14] The sandwiched location leads to a double anion–π interaction. This arrangement is uncommon but similar to that observed for electron-deficient rings and oxoanions where each anion interacts with two aromatic rings and each ring interacts with two anions.[15] The parallel location of the nitrate ion with respect to the aromatic ring in **2** resembles the first theoretically optimized geometry for a nitrate–π interaction.[16] The energy of the apical and parallel complexes was proven to be similar for systems involving electron-deficient rings. The final geometry observed depends on other favorable nonbonding interactions. In **2**, the hydrogen-bond network with a strong electrostatic component formed by the nitrate–pyridinium moieties favors a planar orientation of the nitrate ion with respect to the aromatic rings.

Anion–π interactions are also observed for the squaramide-bonded nitrate. This is sandwiched between a squaramide and a pyridinium ring. This alternate disposition leaves again the nitrate over the pyridinium plane in an almost parallel orientation at 3.486 Å from the ring centroid. Besides, it is evident that there exists a strong electrostatic component driving the crystal packing of **2**; the particular features observed in **2** point out the role of anion–π interactions together with the squaramide–nitrate interaction.

Computational Studies

The potential role that anion–π interactions may play in the formation of the crystal packing was studied by means of computational analysis of different fragments taken from the X-ray structure. We optimized structures **3**–**7** at the RI-MP2/6-31++G** level of theory and compared the geometries with the experimental ones. The results are summarized in Figure 5.

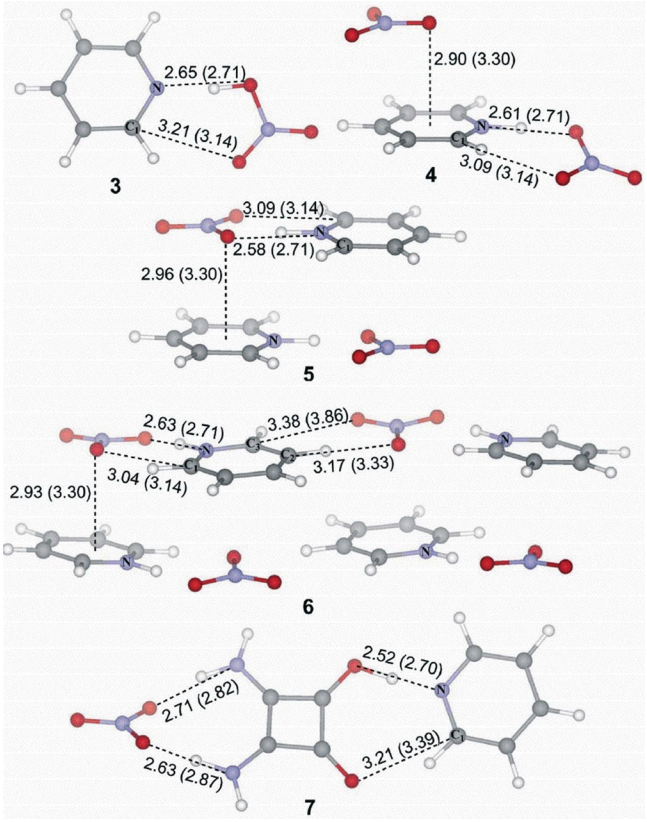

Figure 5. Optimized structures **3**–**7** at the RI-MP2/6-31++G** level of theory and calculated geometries compared with the experimental ones (in brackets). Selected bond lengths [Å] in **3**: N···H 1.62; selected bond lengths [Å] in **4**: N···H 1.08, O···H 1.53.

We first considered structure **3**, which comes from a very strong intermolecular interaction between charged species, that is, the nitrate anion and the pyridinium cation. In the optimized structure of **3**, a proton transfer from the pyridinium ring to the nitrate ion occurred, which gives rise to pyridine and nitric acid and a very large binding energy of –114.6 kcal mol^{-1}. From inspection of the crystal structure, a very interesting π interaction between a pyridinium moiety and a nitrate anion drew our attention. To take into account this contact we studied structure **4**, which comes from the addition of a nitrate anion to **3** (located over the ring). Needless to say, the optimization of pyridinium and a nitrate located above the ring led to **3**. In resulting structure **4**, no proton transfer occurred; instead, two nitrate anions interact with the pyridinium cation: one through a hydrogen bond and the second one by means of an anion–π interaction. The binding energy is –136.3 kcal mol^{-1} and the difference between this and the binding energy of **3** could be considered as the anion–π energy contribution, which is –21.7 kcal mol^{-1}. We expanded our model compounds by taking into consideration structures **5** and **6**, in which two and four anion–π interactions are observed, respectively, together with conventional and nonconven-

tional hydrogen bonds with very large binding energies of –249.0 and –518.8 kcal mol^{-1} for **5** and **6**, respectively. Therefore, **6** is a very robust structural motif in the crystal structure. Another robust structural motif originates from the interaction of a squaramide unit with both pyridinium (by means of the carbonyl groups) and nitrate (by means of the amino groups). The binding energy of resulting compound **7** is –125.8 kcal mol^{-1}, which is a little larger than that for **3**.

The geometry of structures **3**–**7** is similar to the geometry of the X-ray structure, especially when one takes into account that the optimized structures are fully relaxed in the gas phase, whereas the crystal structures are influenced by packing forces. In general, the theoretical distances are shorter than the experimental ones. This is probably due to the environment of the anion and the cation in the solid state, in which they participate in a variety of noncovalent interactions. For instance, O···N and O···C-1 distances are quite comparable. The O···C-3 distance in **6** is much larger in the crystal because there is a methylene in that position interacting with the nitrate. The main difference observed between the experimental and theoretical results is the distance between the center of the pyridinium and the nitrate located above the ring, which is ca. 0.4 Å. A likely explanation of the underestimation of the anion···π distance by the theoretical method is that in the solid state both the anion and cation are involved in more interactions that are not taken into account in the biggest theoretical model **6**.

Conclusions

The important role of anion–π interactions together with hydrogen-bonding interactions is manifested in the crystal packing of the first example of a squaramide–nitrate crystalline salt solid structure. X-ray crystallography and theoretical studies showed that nitrate–squaramide, which contains N^+–H···NO_3, C=O···N*, and C–H···O hydrogen bonds together with anion–π interactions, is a robust structural motif that can be used in very important disciplines such as anion receptor design and crystal engineering.

Experimental Section

General Methods: All commercially available reagents and solvents were used without further purification unless otherwise stated. [D_4]MeOH and [D_6]DMSO were used from freshly opened ampoules. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance at 23 °C. Chemical shifts are reported as parts per million (δ) referenced to the residual hydrogen signal of deuterated solvents. Electrospray mass spectra were recorded with a Micromass Autospec 3000 spectrometer provided with an electrospray module.

Structure Determination: Crystals of **1** and **2** (Table 1) were obtained in ethanol and acetonitrile, respectively. The measured crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation. Measurements were made with a Bruker-Nonius diffractometer equipped with a APPEX 2 4 K CCD area detector, a FR591 rotating anode with Mo-K_α radiation, Montel mirrors as monochromator, and a Kryoflex low-temperature device (T = –173 °C). Full-sphere data collection was used with ω and ϕ scans. Programs used include Data collection Apex2 V. 1.0–22 (Bruker-Nonius 2004), data reduction Saint + Version 6.22 (Bruker-Nonius 2001), and absorption correction SADABS V. 2.10 (2003). Structure solution and refinement were performed with SHELXTL Version 6.10 (Sheldrick, 2000).[17] CCDC-645872 and -645873 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and structure refinement parameters for compounds **1** and **2**.

	1	**2**
Empirical formula	$C_{18}H_{18}N_4O_2$	$C_{18}H_{18}N_6O_8$
Formula weigh	322.26	448.40
Temperature [K]	100	100
Crystal system	orthorhombic	monoclinic
Space group	*Pna*2 (1)	$P2_1/n$
Unit cell dimensions:		
a [Å]	13.116(7)	6.631(6)
b [Å]	6.0797(4)	34.840(3)
c [Å]	19.919(13)	8.5189(8)
α [°]	90.00	90.00
β [°]	90.00	95.418(3)
γ [°]	90.00	90.00
V [Å^3]	1588.5(17)	1959.5(3)
Z	4	4
$D_{calcd.}$ [Mg m^{-3}]	1.348	1.520
Absorption coefficient [mm^{-1}]	0.091	0.122
θ max	37.37	39.57
Reflections collected	23262	23891
Independent reflections	4748 [R_{int} = 0.084]	9191 [R_{int} = 0.055]
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0702	R_1 = 0.068
	wR_2 = 0.1699	wR_2 = 0.1810
R indices (all data)	R_1 = 0.0874	R_1 = 0.078
	wR_2 = 0.1840	wR_2 = 0.1901
Peak/hole [e Å^{-3}]	1.282/–0.337	0.955/–0.416

4-Bis[2-(2-pyridyl)ethylamino]-3-cyclobutene-1,2-dione (1): 2-(2-Pyridiyl)ethylamine (1.44 g, 11.8 mmol) in EtOH (100 mL) was added dropwise to a stirred solution of diethylsquarate (1.00 g, 11.8 mmol) in EtOH (10 mL). The reaction mixture was stirred at room temperature for 12 h. The white precipitate was filtered, and the solid was recrystallized from EtOH to yield **1** (1.46 g, 4.52 mmol) as a white solid. Yield 80%. After 4 d, colorless needle crystals suitable for X-ray diffraction were obtained from EtOH. ^{1}H NMR (300 MHz), [D_6]DMSO): δ = 8.49 (d, J = 2.1 Hz, 2 H), 7.71 (t, J = 7.5, 1.5, Hz, 2 H), 7.40 (bb, 2 H), 7.25 (d, J = 8.10 Hz, 2 H), 7.22 (t, J = 7.2 Hz, 2 H), 3.87 (d, J = 4.8 Hz, 4 H), 2.99 (t J = 6.6 Hz, 4 H) ppm. ^{13}C NMR (75 MHz, [D_4]MeOH): δ = 182.74, 168, 39, 158.40, 148.88, 137.67, 124.26, 122.30, 43.88, 39.05 ppm. HRMS: calcd. for $C_{18}H_{18}N_4O_2Na^+$ 345.1327; found 345.1331.

Preparation of 2: A solution of $Zn(NO_3)_2{\cdot}6H_2O$ (0.014 g, 50 mmol) in acetonitrile (10 mL) was added dropwise to a solution of **1** (0.016 g, 50 mmol) in acetonitrile (10 mL). The resulting reaction mixture was stirred for 10 min at room temperature. The solution was subsequently filtered, and the filtrate was left for slow evaporation of the solvent. After three weeks, translucent plate crystals suitable for X-ray diffraction were obtained.

Computational Methods: The geometries of all complexes studied in this work were fully optimized by using the resolution of the identity MP2 (RI-MP2) level and the 6-31++G** basis set. The

RI-MP2(fu) calculations were done by using the program TURBOMOLE version 5.7.[18] As the TURBOMOLE program does not include an auxiliary basis set for 6-31++G**, we used Ahlrichs VDZ[19] (SVP in TURBOMOLE notation) as the auxiliary basis set. The RI-MP2 method[20] applied to the study of cation–π, anion–π and π–π interactions is considerably faster than the MP2 and the interaction energies and equilibrium distances are almost identical for both methods.[21]

Acknowledgments

This work was supported by Ministerio de Educación y Ciencia (MEC) grant ref. CT Q2005-08989-C02-01 and Govern de les Illes Balears (CAIB) grant ref. PCTIB-2005GC3-08, PROGECIB-15A, and PROGECIB-33A. C. R. thanks the Ministerio de Educación y Ciencia and Govern de les Illes Balears for a "Ramón y Cajal" contract, and D. Q thanks the Ministerio de Educación y Ciencia for a "Juan de la Cierva" contract.

[1] S. Mangani, M. Ferraroni in *Supramolecular Chemistry of Anions* (Eds.: A. Bianchi, K. Bowman-James, E. Garcia-España), Wiley, New York, **1997**, p. 63.
[2] P. D. Beer, A. P. Gale, *Angew. Chem. Int. Ed.* **2001**, *40*, 487–516.
[3] E. A. Meyer, R. K. Castellano, F. Diederich, *Angew. Chem. Int. Ed.* **2003**, *42*, 1210–1250.
[4] a) M. N. Piña, C. Rotger, B. Soberats, P. Ballester, P. M. Deyà, A. Costa, *Chem. Commun.* **2007**, 963–965; b) M. N. Piña, M. C. Rotger, A. Costa, P. Ballester, P. M. Deyà, *Tetrahedron Lett.* **2004**, *45*, 3749–3752; c) R. Prohens, M. C. Rotger, M. N. Piña, P. M. Deyà, J. Morey, P. Ballester, A. Costa, *Tetrahedron Lett.* **2001**, *42*, 4933–4936.
[5] a) A. P. Davis, S. M. Draper, G. Dunne, P. Ashton, *Chem. Commun.* **1999**, 2265–2266; b) A. Frontera, M. Orell, C. Garau, D. Quiñonero, E. Molins, I. Mata, J. Morey, *Org. Lett.* **2005**, *7*, 1437–1440; c) G. Ambrosi, M. Formica, V. Fusi, L. Giorgi, A. Guerri, M. Micheloni, P. Paoli, R. Pontellini, P. Rossi, *Chem. Eur. J.* **2007**, *13*, 702–712; d) Y. Liu, A. H. W. Lam, F. W. Fowler, J. W. Lauher, *Mol. Cryst. Liq. Cryst.* **2002**, *389*, 39–46.
[6] a) B. L. Schottel, H. T. Chifotides, K. R. Dumbar, *Chem. Soc. Rev.* DOI: 10.1039/b614208g; b) P. Hoog, P. Gamez, I. Mutikainen, U. Turpeinen, J. Reedijk, *Angew. Chem. Int. Ed.* **2004**, *43*, 5815–5815; c) D. Quiñonero, C. Garau, C. Rotger, A. Frontera, P. Ballester, A. Costa, P. M. Deyà, *Angew. Chem. Int. Ed.* **2002**, *41*, 3389–3392; d) C. Garau, A. Frontera, D. Quiñonero, P. Ballester, A. Costa, P. M. Deyà, *Recent Res. Devel. Chem. Phys.* **2004**, *5*, 227–255; e) O. B. Berryman, V. S. Bryantsev, D. P. Stay, D. W. Johnson, B. P. Hay, *J. Am. Chem. Soc.* **2007**, *129*, 48–58.
[7] a) D. Quiñonero, C. Garau, A. Frontera, P. Ballester, A. Costa, P. M. Deyà, *Chem. Eur. J.* **2002**, *8*, 433–438; b) D. Quiñonero, R. Prohens, C. Garau, A. Frontera, P. Ballester, A. Costa, P. M. Deyà, *Chem. Phys. Lett.* **2002**, *351*, 115–120.
[8] a) S. R. Zhu, W. D. Chen, H. J. Zhao, M. Shao, M. X. Li, *Acta Crystallogr., Sect. E* **2007**, *63*, o1344–o1346; b) J. S. Gao, Y. Liu, G. F. Hou, Y. H. Yu, P. F. Yan, *Acta Crystallogr., Sect. E* **2006**, *62*, o5645–o5646; c) T. W. Lee, J. P. Lau, S. Lap, *Acta Crystallogr., Sect. E* **2003**, *59*, o792–o793; d) A. S. Batsanov, *Acta Crystallogr., Sect. E* **2004**, *60*, o2426–o2428.
[9] M. Felloni, A. J. Blake, P. Hubberstey, C. Wilson, M. Schröder, *CrystEngComm* **2002**, *4*, 483–495.
[10] H. Casellas, P. Gamez, J. Reedijk, C. Massera, *Polyhedron* **2006**, *25*, 2959–2966.
[11] The crystal structure of the *N*-(2-pyridinium) urea nitrate also shows the urea–nitrate interaction as expected for good oxoanions binding units, together with the pyridinium–nitrate anion–π interaction. However, in this structure, only one nitrate oxygen overlaps the pyridinium ring.V. Velikova, S. Bakardjeva, O. Angelova, *Acta Crystallogr., Sect. C* **1999**, *55*, 1328–1330.
[12] a) M. Mascal, I. Yakoulev, E. B. Nikitin, J. C. Fettinger, *Angew. Chem. Int. Ed.* **2007**, *46*, 8782–8784; b) A. Garcia-Raso, F. M. Albertí, J. J. Fiol, A. Tasada, M. Barceló-Oliver, E. Molins, D. Escudero, A. Frontera, D. Quiñonero, P. M. Deyà, *Inorg. Chem.* **2007**, *46*, 10724–10735; c) A. Garcia-Raso, F. M. Albertí, J. J. Fiol, A. Tasada, M. Barceló-Oliver, E. Molins, D. Escudero, A. Frontera, D. Quiñonero, P. M. Deyà, *Eur. J. Org. Chem.* **2007**, 5821–5825; d) Y. V. Nelyubina, K. A. Lyssenko, D. G. Golovanov, M. Y. Antipin, *CrystEngComm* **2007**, *9*, 991–996; e) P. Gilli, V. Bertolasi, V. Ferreti, G. Gilli, *J. Am. Chem. Soc.* **1994**, *116*, 909–915.
[13] T. Dorn, C. Janiak, K. Abu-Shandi, *CrystEngComm* **2005**, *7*, 633–641.
[14] a) A. Frontera, F. Saczewski, M. Gdaniec, E. Dziemidowicz-Borys, A. Kurland, P. M. Deyà, D. Quiñonero, C. Garau, *Chem. Eur. J.* **2005**, *11*, 6560–6567; b) P. U. Maheswari, B. Modec, A. Pevec, B. Kozlevčar, C. Massera, P. Gamez, J. Reedijk, *Inorg. Chem.* **2006**, *45*, 6637–6645.
[15] a) P. Gamez, G. A. van Albada, I. Mutikainen, U. Turpeinen, J. Reedijk, *Inorg. Chim. Acta* **2005**, *358*, 1975–1980; b) B. L. Schottel, H. T. Chifotides, M. Shatruk, A. Chouai, L. M. Pérez, J. Bacsa, K. R. Dumbar, *J. Am. Chem. Soc.* **2006**, *128*, 5895–5912.
[16] D. Kim, P. Tarakeshwar, K. S. Kim, *J. Phys. Chem. A* **2004**, *108*, 1250–1258.
[17] G. M. Sheldrick, *SHELXTL Crystallographic System Ver. 5.10*, Bruker AXS, Inc., Madison, WI, **1998**.
[18] R. Ahrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165.
[19] A. Schafer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571–2577.
[20] a) M. W. Feyereisen, G. Fitzgerald, A. Komornicki, *Chem. Phys. Lett.* **1993**, *208*, 359–363; b) O. Vahtras, J. Almlof, M. W. Feyereisen, *Chem. Phys. Lett.* **1993**, *213*, 514–518.
[21] a) A. Frontera, D. Quiñonero, C. Garau, P. Ballester, A. Costa, P. M. Deyà, *J. Phys. Chem. A* **2005**, *109*, 4632–4637; b) D. Quiñonero, C. Garau, A. Frontera, P. Ballester, A. Costa, P. M. Deyà, *J. Phys. Chem. A* **2006**, *110*, 5144–5148.

Received: December 20, 2007
Published Online: February 22, 2008

