

## Proton sharing in bis(4-carbamoyl-pyridinium) squarate

Ahmet Köroglu,<sup>a</sup> Ahmet Bulut,<sup>a</sup> Ibrahim Uçar,<sup>a</sup> Gary S. Nichol,<sup>b</sup> Ross W. Harrington<sup>b</sup> and William Clegg<sup>b\*</sup>

<sup>a</sup>University of Ondokuz Mayıs, Sciences and Arts Faculty, Department of Physics, Kurupelit 55139, Samsun, Turkey, and <sup>b</sup>School of Natural Sciences (Chemistry), Bedson Building, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, England

Correspondence e-mail: w.clegg@ncl.ac.uk

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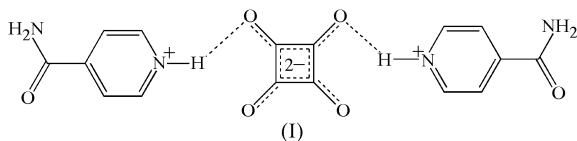
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Reaction in aqueous solution of nickel(II) squarate with isonicotinamide yielded well formed yellow crystals of the title compound,  $2C_6H_6N_2O^+ \cdot C_4O_4^{2-}$ , as a side product. The squarate dianion is bisected by a crystallographic twofold rotation axis, which passes through the centres of two opposite bonds of the ring. Crystal structure analysis reveals that, far from forming discrete ionic species, it is likely that there is a large degree of proton sharing between the anion and cation, with the H atom lying almost symmetrically between the donor and acceptor sites, as evidenced by the long N—H and short H $\cdots$ O distances [1.15 (3) and 1.39 (3) Å, respectively]. Other hydrogen bonding is more conventional, and there are weaker C—H $\cdots$ O interactions contributing additional stability to the structure.

### Comment

Squaric acid and its metal complexes have received considerable attention, not only in consideration of their coordination chemistry but also for their use in crystal engineering (Reetz *et al.*, 1994). Complexes are known for almost all first-row transition metals, with several heavier transition metal and lanthanide complexes also reported. Deprotonation of squaric acid yields either an anion or a dianion, and these anions can behave as either mono- or polydentate ligands



towards first-row transition metal ions, as well as bridging two or more metal atoms (Bernardinelli *et al.*, 1989; Castro *et al.*, 1999). We have also used isonicotinamide as a second ligand. Apart from its biological importance (Ahuja & Prasad, 1976), it is also of interest in chemistry since the ligand has three donor sites, *viz.* (i) the pyridine ring N atom, (ii) the amine N

atom and (iii) the carbonyl O atom. In our ongoing research on squaric acid, we have synthesized some mixed-ligand metal complexes of squaric acid and their structures have been reported (Uçar *et al.*, 2004, 2005; Bulut *et al.*, 2004). Whilst preparing a nickel coordination complex, crystals of diisonicotinamidium squarate, (I), were formed as a side product.

Compound (I) crystallizes in space group  $C2/c$ , with the squarate dianion bisected by the crystallographic twofold rotation axis that passes through the centres of two opposite bonds of the ring (Fig. 1 and Table 1). The most noteworthy aspect of the structure of this compound is the behaviour of the H atoms in hydrogen bonding (Table 2). Hydrogen bonding from the  $NH_2$  group is conventional (in terms of geometry), with both H atoms being donated. However, the N—H $\cdots$ O hydrogen bond linking the squarate dianion to the protonated ring N atom of the isonicotinamidium cation has much more unusual behaviour. The freely refined N—H bond length is 1.15 (3) Å, very long for an N—H covalent bond, which would be expected to be around 0.85 Å in an X-ray crystallographic analysis. Consequently, the H $\cdots$ O distance is 1.39 (3) Å, which is rather short. Given that the overall N $\cdots$ O distance is relatively short at 2.5322 (16) Å, these values indicate a strong hydrogen bond, which nevertheless displays unusual disorder or thermal motion. A difference Fourier map

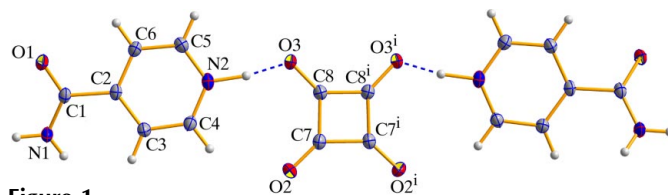


Figure 1

Twice the asymmetric unit of (I), with displacement ellipsoids at the 50% probability level. N—H $\cdots$ O interactions are shown as dashed lines. [Symmetry code (twofold axis): (i)  $-x + 1, y, -z + \frac{1}{2}$ .]

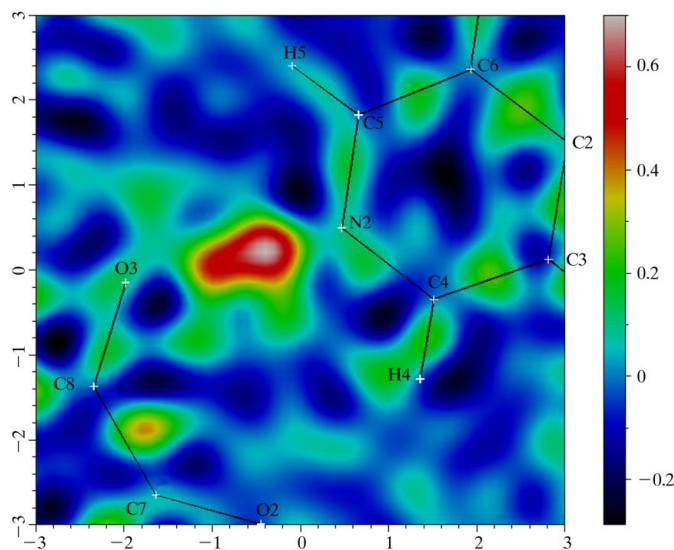
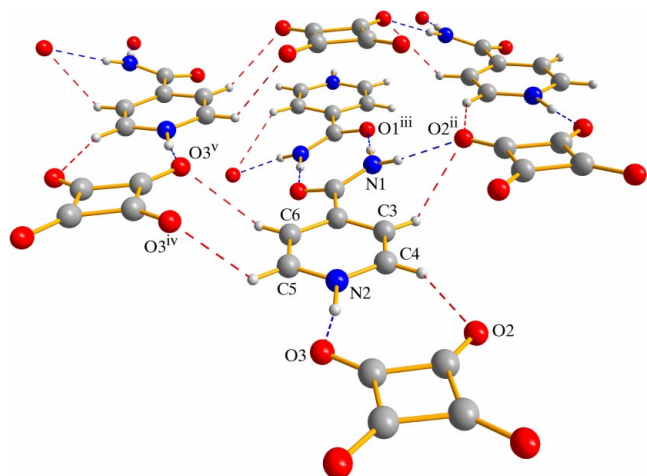


Figure 2

A difference Fourier map of the electron density associated with the N—H $\cdots$ O interaction between the isonicotinamidium cation and the squarate dianion. The diffuse nature of the electron density is clear, with the largest concentration of electron density located closer to the N than to the O atom.



**Figure 3**

A perspective view of the hydrogen bonding in (I). Dashed lines indicate N—H...O and C—H...O interactions. Note the twist of the amide groups forming a hydrogen bond with a squarate dianion out of the plane of the donor parent molecule. [Symmetry codes: (ii)  $x, -y + 1, z + \frac{1}{2}$ ; (iii)  $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 2$ ; (iv)  $-x + 1, -y, -z + 1$ ; (v)  $x, -y, z + \frac{1}{2}$ ]

(Fig. 2; Farrugia, 1999) of the electron density associated with this H atom shows this to be smeared out between the N and O atoms, with the maximum lying closer to the N than the O atom, rather than being bound closely to the N atom to give a discrete ion pair. This has consequences for the assignment of charges to the two species. Although formally the isonicotinamide molecule has been protonated and squaric acid has been doubly deprotonated, the behaviour of the H atom concerned shows that this is not entirely the case and suggests that there is a large degree of covalency in this interaction. The related compound dinicotinamidium squarate (Bulut *et al.*, 2003) has a similar short strong N—H...O hydrogen bond, although the N—H distance is shorter [1.08 (2) Å].

The crystal packing consists of hydrogen-bonded tapes, which are then linked to other tapes by further hydrogen bonding. As shown in Fig. 3, the tapes consist of an  $R_2^2(8)$  graph-set motif (Bernstein *et al.*, 1995) between the amide groups, which connects two isonicotinamidium ions into a dimer, with the hydrogen bond discussed above linking these dimers to the squarate dianion. This interaction combines with a C—H...O interaction to form a second, different,  $R_2^2(8)$  motif. The torsion angle between the amide group and the pyridine ring, O1—C1—C2—C6, is  $-18.8(2)^\circ$ . This twist means that a second hydrogen bond from the amide group to a squarate dianion, which is not in the plane of the donor parent molecule, links the tapes together, such that the overall packing between the tapes is 'stepped' rather than forming flat sheets and generates a three-dimensional network. There is additional, weaker, C—H...O hydrogen bonding securing the tapes together, although it is unlikely that this has a significant structure-directing influence.

## Experimental

Squaric acid (0.57 g, 5 mmol) dissolved in water (25 ml) was neutralized with NaOH (0.40 g, 10 mmol) and the mixture was added

to a hot solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (1.19 g, 5 mmol) in water (50 ml). The mixture was stirred at 333 K for 12 h and then cooled to room temperature. The green crystals that formed were filtered off, washed with water and ethanol, and dried *in vacuo*. A solution of isonicotinamide (0.24 g, 2 mmol) in methanol (50 ml) was added dropwise with stirring to a suspension of NiSq·2H<sub>2</sub>O (0.21 g, 1 mmol) in water (50 ml). The green solution was refluxed for about 2 h and then cooled to room temperature. A few days later, green crystals of the desired Ni complex had formed, along with some well formed yellow block-shaped crystals of (I).

## Crystal data

2C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>O<sup>+</sup>·C<sub>4</sub>H<sub>2</sub>O<sub>4</sub><sup>2-</sup>  
 $M_r = 358.32$   
 Monoclinic, C2/c  
 $a = 11.959(2) \text{ \AA}$   
 $b = 10.691(2) \text{ \AA}$   
 $c = 12.257(3) \text{ \AA}$   
 $\beta = 104.93(3)^\circ$   
 $V = 1514.3(6) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.572 \text{ Mg m}^{-3}$

Mo K $\alpha$  radiation  
 Cell parameters from 4241 reflections  
 $\theta = 2.5\text{--}27.5^\circ$   
 $\mu = 0.12 \text{ mm}^{-1}$   
 $T = 150(2) \text{ K}$   
 Prism, yellow  
 $0.41 \times 0.29 \times 0.12 \text{ mm}$

## Data collection

Nonius KappaCCD diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)  
 $T_{\min} = 0.911, T_{\max} = 0.985$   
 10470 measured reflections  
 1731 independent reflections

1318 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.051$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -15 \rightarrow 15$   
 $k = -13 \rightarrow 13$   
 $l = -15 \rightarrow 15$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.039$   
 $wR(F^2) = 0.105$   
 $S = 1.03$   
 1731 reflections  
 130 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0522P)^2 + 0.9909P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

O1—C1	1.2383 (18)	O3—C8	1.2756 (18)
N1—C1	1.331 (2)	C7—C7 <sup>i</sup>	1.503 (3)
C1—C2	1.518 (2)	C7—C8	1.461 (2)
O2—C7	1.2384 (17)	C8—C8 <sup>i</sup>	1.436 (3)
O1—C1—C2—C3	161.17 (14)	N1—C1—C2—C3	-18.6 (2)
O1—C1—C2—C6	-18.8 (2)	N1—C1—C2—C6	161.46 (14)

Symmetry code: (i)  $-x + 1, y, -z + \frac{1}{2}$

**Table 2**

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N1—H2N...O2 <sup>ii</sup>	0.88 (2)	2.03 (2)	2.8940 (19)	169 (2)
N1—H1N...O1 <sup>iii</sup>	0.91 (2)	2.01 (2)	2.9208 (18)	172 (2)
N2—H3N...O3	1.15 (3)	1.39 (3)	2.5322 (16)	171 (2)
C3—H3...O2 <sup>ii</sup>	0.95	2.57	3.3249 (19)	137
C4—H4...O2	0.95	2.48	3.2909 (19)	143
C5—H5...O3 <sup>iv</sup>	0.95	2.51	3.1921 (19)	129
C6—H6...O3 <sup>v</sup>	0.95	2.54	3.339 (2)	141

Symmetry codes: (ii)  $x, -y + 1, z + \frac{1}{2}$ ; (iii)  $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 2$ ; (iv)  $-x + 1, -y, -z + 1$ ; (v)  $x, -y, z + \frac{1}{2}$

All H atoms were located in a difference Fourier map. H atoms bound to N atoms were freely refined; the N–H distances are in the range 0.88 (2)–1.15 (3) Å. H atoms bound to C atoms were constrained to ride on their parent atom, with C–H distances of 0.95 Å and isotropic displacement parameters 1.2 times the  $U_{eq}$  values of the parent atoms.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *EVALCCD* (Duisenberg *et al.*, 2003); data reduction: *EVALCCD*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg & Putz, 2004); software used to prepare material for publication: *SHELXTL*, *WinGX* (Farrugia, 1999) and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1874). Services for accessing these data are described at the back of the journal.

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