



# Direct air capture of CO<sub>2</sub> – topological analysis of the experimental electron density (QTAIM) of the highly insoluble carbonate salt of a 2,6-pyridine-bis(iminoguanidine), (PyBIGH<sub>2</sub>)(CO<sub>3</sub>)(H<sub>2</sub>O)<sub>4</sub>

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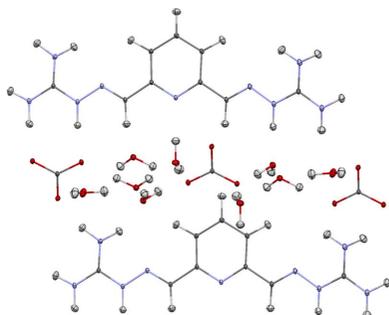
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Chemical bonding and all intermolecular interactions in the highly insoluble carbonate salt of a 2,6-pyridine-bis(iminoguanidine), (PyBIGH<sub>2</sub>)(CO<sub>3</sub>)(H<sub>2</sub>O)<sub>4</sub>, recently employed in the direct air capture of CO<sub>2</sub> via crystallization, have been analyzed within the framework of the quantum theory of atoms in molecules (QTAIM) based on the experimental electron density derived from X-ray diffraction data obtained at 20 K. Accurate hydrogen positions were included based on an analogous neutron diffraction study at 100 K. Topological features of the covalent bonds demonstrate the presence of multiple bonds of various orders within the PyBIGH<sub>2</sub><sup>2+</sup> cation. Strong hydrogen bonds define ribbons comprising carbonate anions and water molecules. These ribbons are linked to stacks of essentially planar dications via hydrogen bonds from the guanidinium moieties and an additional one to the pyridine nitrogen. The linking hydrogen bonds are approximately perpendicular to the anion–water ribbons. The observation of these putative interactions provided motivation to characterize them by topological analysis of the total electron density. Thus, all hydrogen bonds have been characterized by the properties of their (3,−1) bond critical points. Weaker interactions between the PyBIGH<sub>2</sub><sup>2+</sup> cations have similarly been characterized. Integrated atomic charges are also reported. A small amount of cocrystallized hydroxide ion (~2%) was also detected in both the X-ray and neutron data, and included in the multipole model for the electron-density refinement. The small amount of additional H<sup>+</sup> required for charge balance was not detected in either the X-ray or the neutron data. The results are discussed in the context of the unusually low aqueous solubility of (PyBIGH<sub>2</sub>)(CO<sub>3</sub>)(H<sub>2</sub>O)<sub>4</sub> and its ability to sequester atmospheric CO<sub>2</sub>.

## 1. Introduction

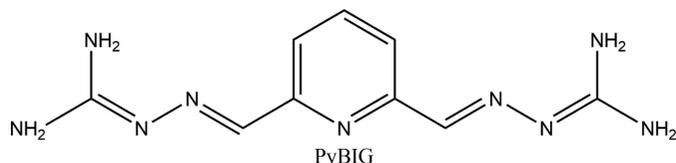
Given the strong connection between climate change and the greenhouse gases in the atmosphere, developing new methods to reduce their concentration in the air and alleviate global warming is of major importance. Besides curbing the use of fossil fuels, one strategy for limiting the increase in the atmospheric CO<sub>2</sub> concentration is based on carbon capture and storage (CCS) (Lackner, 2003; Reiner, 2016). Significant progress has been made in employing CCS at point sources of CO<sub>2</sub> emission, such as coal- or gas-fired power plants. However, this approach does not address the problem of diffuse sources of CO<sub>2</sub>, such as households and transportation, which are responsible for approximately 50% of total greenhouse gas emissions. Most climate change mitigation scenarios aiming to limit global warming to 2°C or less now include implementation of negative emissions technologies (NETs)



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that target net reductions of the atmospheric CO<sub>2</sub> concentration, currently ~408 p.p.m. One promising approach among various NETs under consideration is direct air capture (DAC), a process that removes CO<sub>2</sub> from the air by engineered chemical reactions (Keith, 2009; Lackner *et al.*, 2012; Sanz-Pérez *et al.*, 2016; Keith *et al.*, 2018).

In a recent study, an aqueous solution of a 2,6-pyridine-bis(iminoguanidine), PyBIG [the displayed resonance form is based on the reported crystal structure (Seipp *et al.*, 2017; Brethomé *et al.*, 2018)], was found to efficiently absorb CO<sub>2</sub> from the atmosphere and convert it into the crystalline carbonate salt (PyBIGH<sub>2</sub>)(CO<sub>3</sub>)(H<sub>2</sub>O)<sub>4</sub> (Seipp *et al.*, 2017; Brethomé *et al.*, 2018). The main driver for this reaction is the extremely low aqueous solubility of the carbonate salt ( $K_{sp} = 1.0 \times 10^{-9}$ ), comparable to CaCO<sub>3</sub> ( $3.7\text{--}8.7 \times 10^{-9}$ ), which pushes the overall equilibrium towards the carbonate formation despite the very low concentration of CO<sub>2</sub> in the air. After filtration, crystalline (PyBIGH<sub>2</sub>)(CO<sub>3</sub>)(H<sub>2</sub>O)<sub>4</sub> is mildly heated at 120°C to release the CO<sub>2</sub> (which can be sent to storage) and regenerate the PyBIG sorbent for reuse in another DAC cycle. Thus, this crystallization-based approach offers the prospect for energy-efficient DAC technology, provided the synthesis of PyBIG and the overall CO<sub>2</sub> capture process can be optimized and scaled up cost effectively.



The previously reported X-ray crystal structure of (PyBIGH<sub>2</sub>)(CO<sub>3</sub>)(H<sub>2</sub>O)<sub>4</sub> showed that the hydrated carbonate salt comprises an elaborate hydrogen-bonded network involving the carbonate anion, guanidinium cations, water molecules and the pyridine N atom (Seipp *et al.*, 2017; Brethomé *et al.*, 2018). However, the precise geometrical parameters and energetics of the hydrogen bonds and other intermolecular interactions present in this structure, which presumably play important roles in the unusually low aqueous solubility of (PyBIGH<sub>2</sub>)(CO<sub>3</sub>)(H<sub>2</sub>O)<sub>4</sub>, have yet to be determined. To this end, as reported in this article, we have determined precisely all hydrogen positions from neutron diffraction data, which provides an accurate geometrical description of all the hydrogen bonds present. The interaction energies of these hydrogen bonds have been estimated from a topological analysis of the electron density, as determined from extremely accurate high-resolution X-ray diffraction data. At the same time, we have characterized all of the covalent bonds and the integrated atomic charges within the framework of the quantum theory of atoms in molecules (QTAIM) (Bader, 1994).

## 2. Experimental

### 2.1. Data collection and reduction

**2.1.1. X-ray experiment.** Colorless crystals of (PyBIGH<sub>2</sub>)(CO<sub>3</sub>)(H<sub>2</sub>O)<sub>4</sub> were obtained by slow reaction of an aqueous

solution of PyBIG with atmospheric CO<sub>2</sub>. A single crystal (0.31 × 0.20 × 0.15 mm) was subsequently mounted with oil on top of a thin-walled glass capillary, and cooled to 20 K with an open-flow helium cryostat (Hardie *et al.*, 1998; Kirschbaum *et al.*, 1999). X-ray diffraction measurements were performed with a Rigaku diffractometer equipped with a Mo rotating anode generator operating at 50 kV and 300 mA (ULTRAX-18 Mo K $\alpha$ , curved graphite monochromator) and using a RAPID-II cylindrical image-plate detector. To obtain highly redundant data, runs collecting 30 × 6°  $\omega$  scans were performed at  $\chi = 0^\circ$ ,  $\phi = 0$  and 180°, and at  $\chi = 40^\circ$ ,  $\phi = 0, 90, 180$  and 270°. These runs were augmented by collecting an analogous set with  $\omega$  offset by 3°. Thus, frames were overlapped by a half-frame width to improve scaling and allow for the omission of partial and overlapping reflections. An exposure time of 180 s per image was chosen to maximize the scattering power and avoid saturation of the strongest reflections.

The collected data were indexed and reflection positions predicted using the program *HKL2000* (Otwinowski & Minor, 1997). Data were integrated with the program *VIIPP*, applying an image-plate flood-field correction, and with background and reflection profiles averaged over the whole data set, as described previously (Zhurova *et al.*, 1999, 2008; Zhurov & Pinkerton, 2013). Partial and overlapped reflections were rejected during the integration. The effects of absorption ( $\mu = 0.122 \text{ mm}^{-1}$ ) and thermal diffuse scattering at 20 K were considered to be negligible. Additional outliers were identified and removed manually through equivalence comparison to minimize outlier contamination. This is particularly important for removing errors from multiple scattering, and for identifying previously unidentified partial and overlapping reflections. This resulted in 1.41% of measured data (2730 out of 193 867 reflections) being additionally rejected prior to merging and scaling of the data in the space group  $P\bar{1}$  with the program *SORTAV* (Blessing, 1995, 1987, 1997). Corrections of reflection intensities for  $\lambda/2$  contamination were also made (Kirschbaum *et al.*, 1997; Gianopoulos *et al.*, 2017). Other experimental details are listed in Table 1.

**2.1.2. Neutron experiment.** Data from a single-crystal plate (2.01 × 1.50 × 0.37 mm) prepared as above were obtained using the *TOPAZ* single-crystal neutron time-of-flight (TOF) Laue diffractometer (Jogl *et al.*, 2011; Schultz *et al.*, 2014) at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory. The diffractometer is equipped with 24 detectors, each with an active area of 15 × 15 cm, arranged on a near-spherical detector array tank. The initial moderator-to-sample flight path is 18 m and the sample-to-detector distances vary in the range 39–46 cm. The total path length of 18.4 m and the SNS pulse rate of 60 Hz provides a wavelength bandwidth of 3.6 Å. The crystal was mounted on a MiTeGen loop using cyanoacrylate glue and cooled to 100 K for data collection. A total of 47 crystal orientations optimized with *CrystalPlan* software (Zikovskiy *et al.*, 2011) were used to ensure better than 95% coverage of a hemisphere of reciprocal space. Data were displayed, auto-indexed and integrated using the suite of algorithms in *Mantid* (Arnold *et al.*, 2014). The raw Bragg

**Table 1**  
Experimental details.

CIFs for both experiments are provided in the supporting information.

|   | X-ray   | Neutron   |
|---|---|---|
| Empirical formula   | C <sub>9</sub> H <sub>15</sub> N <sub>9</sub> <sup>2+</sup> ·CO <sub>3</sub> <sup>2-</sup> ·4H <sub>2</sub> O | C <sub>9</sub> H <sub>15</sub> N <sub>9</sub> <sup>2+</sup> ·CO <sub>3</sub> <sup>2-</sup> ·4H <sub>2</sub> O |
| Crystal size (mm)   | 0.31 × 0.20 × 0.15  | 2.01 × 1.50 × 0.37  |
| Crystal shape   | Plate   | Plate   |
| Wavelength (Å)  | 0.71073   | 0.40–3.39 (TOF)   |
| Crystal system  | Triclinic   | Triclinic   |
| Temperature (K)   | 20  | 100   |
| Space group   | <i>P</i> $\bar{1}$  | <i>P</i> $\bar{1}$  |
| <i>a</i> (Å)  | 8.2090(2)   | 8.2420 (2)  |
| <i>b</i> (Å)  | 8.5762 (2)  | 8.6011 (3)  |
| <i>c</i> (Å)  | 13.8676 (4)   | 13.8821 (4)   |
| $\alpha$ (°)  | 72.591 (2)  | 72.792 (3)  |
| $\beta$ (°)   | 78.815 (2)  | 78.998 (3)  |
| $\gamma$ (°)  | 71.0422 (17)  | 70.789 (2)  |
| <i>V</i> (Å <sup>3</sup> ), <i>Z</i>  | 875.97 (4), 2   | 882.92 (5), 2   |
| Density (g cm <sup>-3</sup> )   | 1.447   | 1.436   |
| $\mu$ (mm <sup>-1</sup> )   | 0.122   | 0.1506 + 0.1027 $\lambda$   |
| ( $\sin\theta/\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )  | 1.30  | 2.45  |
| Reflections integrated  | 189348  | 44971   |
| <i>R</i> <sub>int</sub> , average data multiplicity   | 0.027, 9.1  | 0.0963, 5.6   |
| Completeness: $\sin\theta/\lambda < 0.76$ Å <sup>-1</sup> , all data (%)  | 99.0/80.0   | 91.4  |
| Independent reflections   | 25805   | 7955  |
| Used reflections  | 18335 [ <i>I</i> > 3 $\sigma$ ( <i>I</i> )]   | 7955  |
| Spherical refinement  |   |   |
| <i>R</i> <sub>1</sub> [ <i>F</i> , <i>I</i> > 2 $\sigma$ ( <i>I</i> )], <i>wR</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> ), GOF | 0.028, 0.082, 1.055   | 0.034, 0.065, 1.128   |
| $\Delta\rho_{\min/\max}$ for X-rays (e Å <sup>-3</sup> ), for neutrons (fm Å <sup>-3</sup> )                                  | -0.33/0.79  | -1.185/1.104  |
| Multipole refinement  |   |   |
| No. of parameters   | 1232  |   |
| <i>R</i> <sub>1</sub> [ <i>F</i> , <i>I</i> > 3 $\sigma$ ( <i>I</i> )], <i>wR</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> ), GOF | 0.018, 0.020, 1.115   |   |
| $\Delta\rho_{\min/\max}$ (e Å <sup>-3</sup> ), $\sin\theta/\lambda < 1.3$ Å <sup>-1</sup>                                     | -0.186, 0.272   |   |
| Weighting scheme: <i>a</i> , <i>b</i> †   | 0.0038, 0.0038  |   |

†  $w_2 = 1/[\sigma^2(F^2) + (ap)^2 + bp]$ ,  $p = 0.3333F_{\text{obs}}^2 + 0.6667F_{\text{calc}}^2$

intensities were obtained using the three-dimensional ellipsoidal *Q*-space integration method (Schultz *et al.*, 1984). Data reduction including the neutron TOF spectrum, Lorentz, and detector efficiency corrections were carried out with the *ANVRED3* program (Schultz *et al.*, 1984). A Gaussian numerical absorption correction was applied with  $\mu = 0.1506 + 0.1027\lambda$  mm<sup>-1</sup>. The reduced data were saved in *SHELX* HKLF2 format, in which the neutron wavelength for each reflection was recorded separately.

## 2.2. Refinements

The crystal structure of PyBIG carbonate was reported previously (Seipp *et al.*, 2017; Brethomé *et al.*, 2018) and we have preserved the setting of the unit cell and the atom numbering used in that work. Based on our experimental neutron data, the crystal structure was re-refined within the *SHELXTL* program suite (Sheldrick, 2015) using the previously reported structure as the starting model. All atoms

were refined using anisotropic thermal motion. An initial least-squares refinement based on the X-ray data was also carried out (*SHELXTL*). Anisotropic thermal motion was considered for all non-hydrogen atoms, and the hydrogen atoms were refined isotropically. From this starting point, a multipole refinement based on the Hansen–Coppens pseudoatom formalism (Hansen & Coppens, 1978) [equation (1)], as implemented in the *MoPro* program package (Jelsch *et al.*, 2005), using the Volkov and co-workers relativistic data bank (Volkov *et al.*, 2006), was performed,

$$\rho(\mathbf{r}) = P_c\rho_c(r) + P_v\kappa_s^3\rho_v(\kappa_s r) + \sum_{l=0}^4 \kappa_l^3 R_l(\kappa_l r) \sum_{m=0}^l P_{lm\pm} y_{lm\pm}(\mathbf{r}/r), \quad (1)$$

where  $\rho_c$  and  $\rho_v$  are spherical core and valence densities normalized to one electron,  $P_c$  and  $P_v$  are the core and spherical valence populations, respectively,  $R_l$  represents normalized Slater-type radial functions,  $y_{lm}$  are real angular spherical harmonics, and  $P_{lm}$  refers to the multipole population of the *m*th term of the *l*th order. The  $\kappa_s$  and  $\kappa_l$  terms are expansion–contraction coefficients for the spherical and multipolar valence densities, respectively.

All ‘heavy’ atoms were refined to the hexadecapole level, while the hydrogen atoms were refined up to dipoles plus the bond-directed quadrupole, with C–H, N–H and O–H distances constrained to the values obtained from the neutron study. In the initial stages of refinement, chemical constraints for similar atoms were applied; however, these constraints were gradually released, and the final model was refined unconstrained (24 refined multipole populations for each ‘heavy’ atom and 4 refined multipole populations for hydrogen atoms), with the exception of  $\kappa$  parameters (see below). The molecular electroneutrality requirement was applied throughout for the total structure. This allowed for charge transfer among the charged species rather than constraining their formal charge. The expansion–contraction parameters  $\kappa_s$  and  $\kappa_l$  for the non-hydrogen atoms were refined in ten groups according to their chemical equivalence, while  $\kappa_s$  and  $\kappa_l$  for hydrogen atoms were set to 1.2. The final description of the anisotropic thermal motion for the hydrogen atoms was obtained from *SHADE-3.1* (Madsen, 2006).

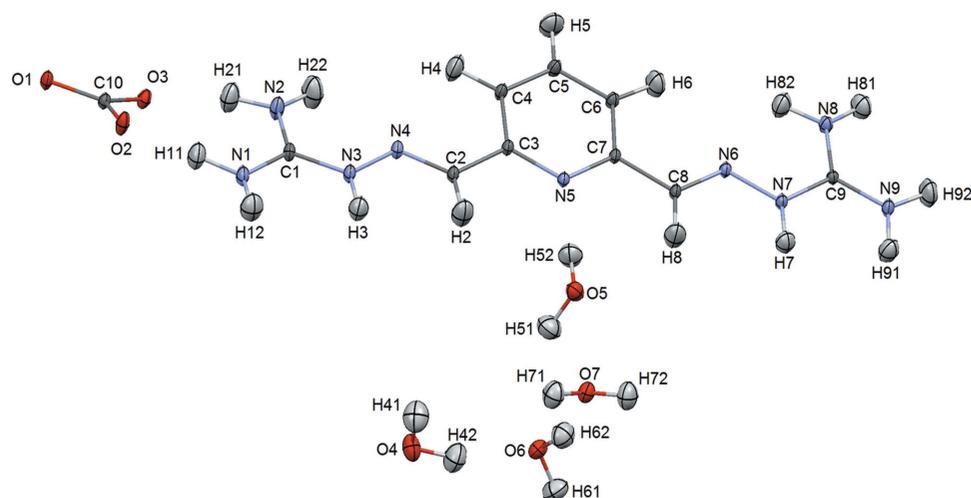
The residual map calculated after the multipole refinement still had one unidentified peak significantly above background. Examination of the neutron residual showed the same small feature along with a negative neighbor (Figs. S8 and S9). These features were identified as a small number of cocrystallized hydroxide ions. The refined occupancies were 0.017 (2) from the X-ray data (IAM model) and 0.022 (2) from neutrons. No evidence was found in the neutron data for the H<sup>+</sup> required for charge balance, hence we assume that it is disordered over the available oxygen and nitrogen sites. The final multipole refinement then included a variable occupancy for the contribution from a spherically modeled oxygen atom.

Topological analysis of the total electron density was carried out with the program packages *MoPro* (Jelsch *et al.*, 2005),

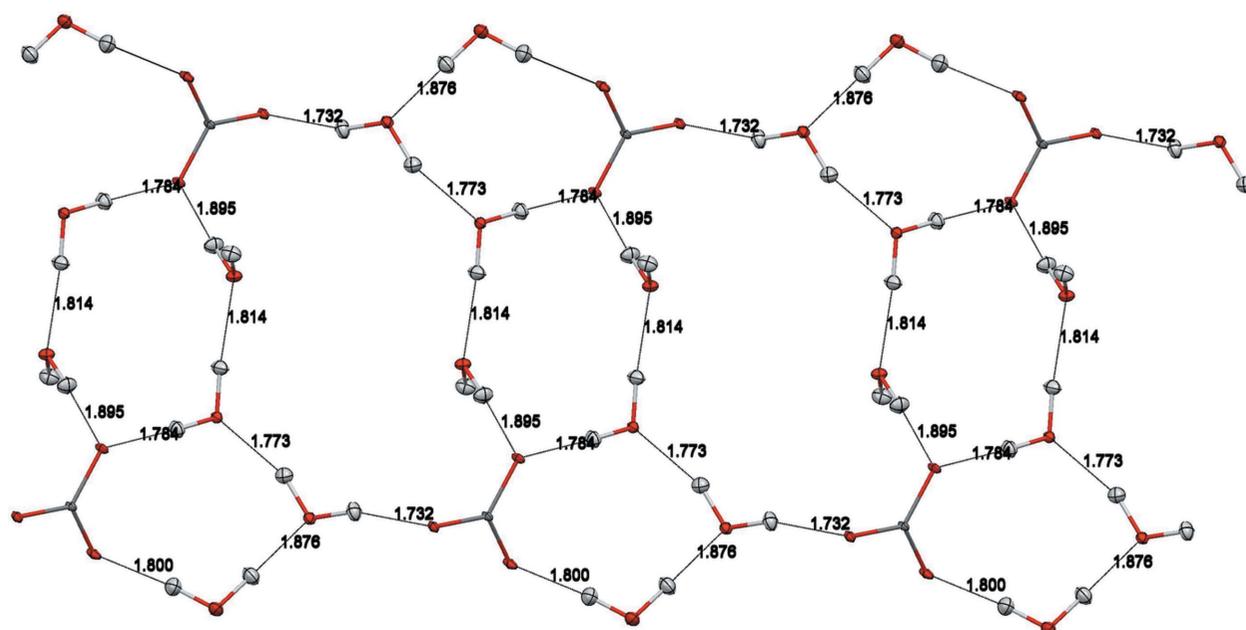
*XDPROP* (Volkov *et al.*, 2006) and *WinXP*RO (Stash & Tsirelson, 2002, 2005).

### 2.3. Evaluation of X-ray data quality

Analysis of statistical measures of data and multipole model quality have been deposited; all suggest excellent data and an excellent model. Averaged ratios (in  $0.05 \text{ \AA}^{-1}$  bins) of observed and calculated structure factors (Fig. S1) as well as the normal probability plot (Fig. S2) indicate good model fitting for the whole  $\sin\theta/\lambda$  range. The residual electron density maps (Fig. S3) are low ( $\rho_{\min/\max} = -0.186/0.272 \text{ e \AA}^{-3}$ , calculated for the complete data set) and featureless as confirmed by a fractal dimension plot (Fig. S4). The total electron density was non-negative everywhere.



**Figure 1**  
The asymmetric unit of PyBIG carbonate tetrahydrate, as determined from 100 K neutron diffraction data, showing the atom numbering. Displacement ellipsoids are at the 50% probability level (Macrae *et al.*, 2008).



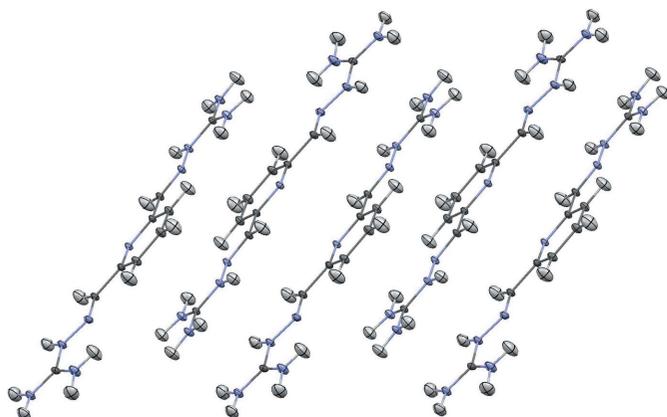
**Figure 2**  
Potential hydrogen bonds in the anion–water ribbons. The figure is based on the neutron structure, with displacement ellipsoids at the 20% probability level and distances in Å (Macrae *et al.*, 2008). Color scheme – oxygen, red; carbon, dark gray; hydrogen, light gray.

## 3. Results and discussion

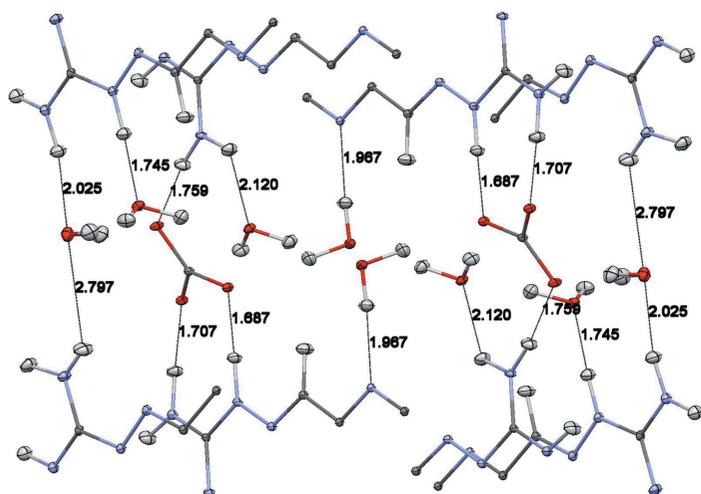
### 3.1. Structure

As reported previously (Seipp *et al.*, 2017; Brethomé *et al.*, 2018), the structure is made up of essentially planar  $\text{PyBIGH}_2^+$  dications, carbonate anions and four water molecules. The asymmetric unit and the atom labeling are shown in Fig. 1. The anions and water molecules form a ribbon (Fig. 2), and based on distance criteria, we may already propose that this structure is strongly hydrogen bonded, as shown in the figure. The cations form stacks (Fig. 3) that are approximately perpendicular to the plane of the anion–water ribbons.

The anion–water ribbon is canted at an angle of  $\sim 23.6^\circ$  above and below the *ac* plane, and extends about  $1.91 \text{ \AA}$  above and below the plane (Fig. S5). The ribbon has a maximal thickness of  $\sim 1.49 \text{ \AA}$  (on the basis of heavy atoms), while the H52 atom is oriented nearly perpendicular ( $81.1^\circ$ ) to the mean plane of the ribbon. While each ribbon extends infinitely along the *a* axis, the width of each ribbon is  $\sim 11.82 \text{ \AA}$ , about  $2 \text{ \AA}$  shorter than the length of the *c* axis. The distance between nearest neighbors on different adjacent ribbons is approximately  $4.2 \text{ \AA}$  and gives rise to a channel between neighboring ribbons. In this context, it is unsurprising that the sites of the partially occupied hydroxide ions fall in this cavity and are suggestive of a stabilizing interaction between neighboring ribbons (Fig.



**Figure 3**  
The stacking of  $\text{PyBIGH}_2^+$  cations. The figure is based on the neutron structure, with displacement ellipsoids drawn at the 20% probability level (Macrae *et al.*, 2008). Color scheme: nitrogen, blue; carbon, dark gray; hydrogen, light gray.



**Figure 4**  
Potential hydrogen bonds between the anion–water ribbon and neighboring cations. All cations have been truncated to enhance the visibility of the hydrogen bonds. The figure is based on the neutron structure, with displacement ellipsoids drawn at the 20% probability level and distances in Å (Macrae *et al.*, 2008). Color scheme: oxygen, red; nitrogen, blue; carbon, dark gray; hydrogen, light gray.

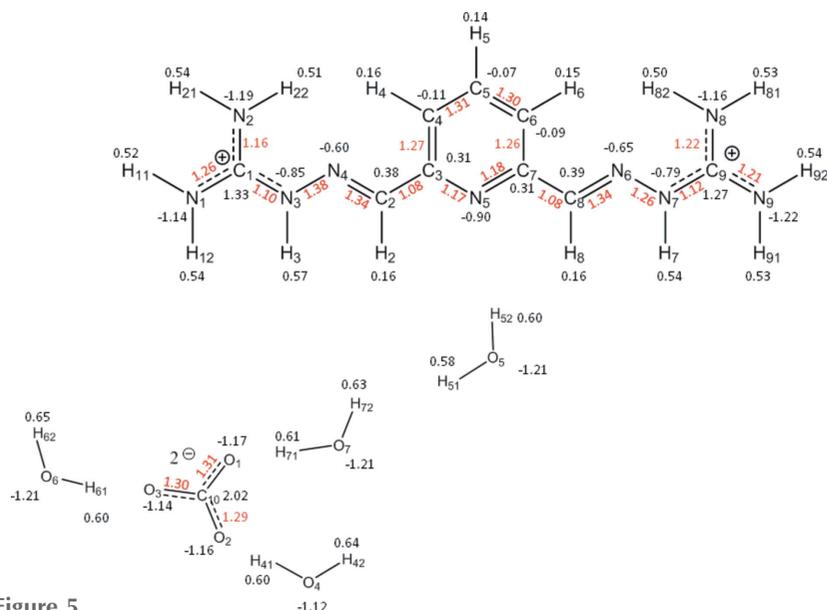
S5). On the basis of the neutron diffraction results, the nearest hydroxide  $\text{HO}\cdots\text{H}$  distance is  $\sim 1.90$  Å, while the nearest  $\text{HO}-\text{H}\cdots\text{OH}$  distance is  $\sim 1.73$  Å. The cations lie roughly above and below the *ac* plane containing the extended network of ribbons. When viewed along the [101] direction it becomes clear that the nearest cations are all hydrogen-bond donors to the water–anion ribbons and form linear arrays along the [101] vector, nearly in the  $(\frac{1}{4}0\frac{1}{4})$  plane. Slightly further from the ribbons are cation arrays (along [101]) wherein the hydrogen-bond-accepting pyridine N5 atom is oriented towards the ribbon (Figs. S6 and S7).

The distances shown in Fig. 4 suggest strong hydrogen bonds between the guanidinium hydrogen atoms and a variety of oxygen atoms, as well as a water hydrogen bonded to the pyridine nitrogen. Note that the cations in Fig. 4 have been truncated to emphasize the possible hydrogen-bond interactions. It is also clear from Fig. 3 that there is potential for additional interactions between the  $\pi$ -systems of neighboring cation sheets as they are only separated by  $\sim 3.2$  Å. The observation of these putative noncovalent interactions provided much of the motivation to characterize them by topological analysis of the total electron density.

## 4. Electron density

### 4.1. Atomic charges

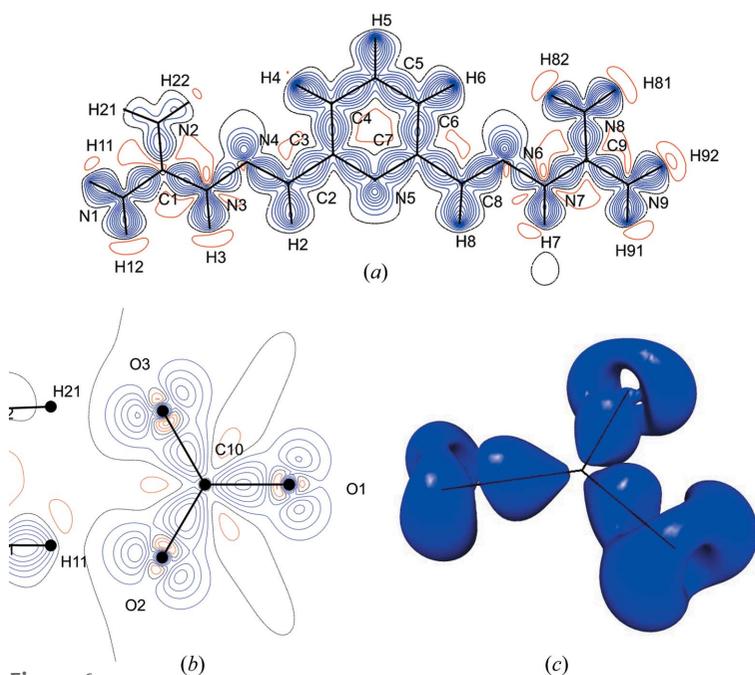
The integrated charges of the atomic basins delimited by the zero-flux surfaces and their volumes are listed in Table 2. For convenience, the charges are also reported in Fig. 5. The accuracy of the integration for each atom was confirmed by a small value of the integrated Laplacian (Lagrangian). The atomic charges sum to zero as required; however, the total charge of the cation and anion differ from the formal value of 2.0, indicating significant charge transfer. Concomitantly, all water molecules are close to neutral, and the disordered OH group contributes a small amount of negative charge. The sum of the atomic volumes is close to the unit-cell volume per asymmetric unit with an error of  $\sim 0.2\%$ . All oxygen atoms have significant negative charges of similar magnitudes, whether in the anion or in the water molecules. The nitrogens are all strongly negative, and may be differentiated according to their type ( $\text{NH}_2 < \text{N}_{\text{pyridine}} < \text{NH} < \text{N}_{\text{imino}}$ ). The carbon atoms have a wide



**Figure 5**  
Integrated atomic charges (black) and topological bond orders (red).

**Table 2**  
 Integrated atomic charges ( $q$ ) and volumes ( $\Omega$ ).

| Atom         | $q$ (e) | $\Omega$ ( $\text{\AA}^3$ ) | Atom          | $q$ (e) | $\Omega$ ( $\text{\AA}^3$ ) |
|--------------|---------|-----------------------------|---------------|---------|-----------------------------|
| PyBIG cation |         |                             | Carbonate     |         |                             |
| N1           | -1.14   | 17.06                       | C10           | 2.02    | 4.43                        |
| H12          | 0.54    | 2.33                        | O1            | -1.17   | 17.90                       |
| H11          | 0.52    | 2.08                        | O2            | -1.16   | 17.97                       |
| C1           | 1.33    | 5.32                        | O3            | -1.14   | 17.08                       |
| N2           | -1.19   | 19.93                       | Total         | -1.45   | 57.38                       |
| H22          | 0.51    | 2.25                        | Water         |         |                             |
| H21          | 0.54    | 2.15                        | O4            | -1.12   | 18.46                       |
| C2           | 0.38    | 10.28                       | H42           | 0.64    | 1.33                        |
| H2           | 0.16    | 7.04                        | H41           | 0.60    | 1.70                        |
| N3           | -0.85   | 12.51                       | Total         | 0.12    | 21.49                       |
| H3           | 0.57    | 1.83                        | Water         |         |                             |
| C3           | 0.31    | 7.98                        | O5            | -1.21   | 20.95                       |
| N4           | -0.60   | 14.72                       | H52           | 0.60    | 1.94                        |
| C4           | -0.11   | 11.65                       | H51           | 0.58    | 2.16                        |
| H4           | 0.16    | 6.12                        | Total         | -0.04   | 25.05                       |
| C5           | -0.07   | 11.61                       | Water         |         |                             |
| H5           | 0.14    | 6.89                        | O6            | -1.21   | 18.00                       |
| N5           | -0.90   | 13.88                       | H62           | 0.65    | 1.57                        |
| C6           | -0.09   | 11.98                       | H61           | 0.60    | 1.75                        |
| H6           | 0.15    | 6.16                        | Total         | 0.04    | 21.32                       |
| N6           | -0.65   | 13.02                       | Water         |         |                             |
| C7           | 0.31    | 8.03                        | O7            | -1.21   | 19.83                       |
| N7           | -0.79   | 12.29                       | H72           | 0.63    | 1.76                        |
| H7           | 0.54    | 1.87                        | H71           | 0.61    | 1.74                        |
| C8           | 0.39    | 10.32                       | Total         | 0.03    | 23.33                       |
| H8           | 0.16    | 7.01                        | Water         |         |                             |
| N8           | -1.16   | 16.23                       | O8            | -0.01   | 14.82                       |
| H82          | 0.50    | 2.94                        | Hydroxyl      |         |                             |
| H81          | 0.53    | 2.23                        | O9            | -0.01   | 14.82                       |
| C9           | 1.27    | 5.09                        | Total/total   |         |                             |
| N9           | -1.22   | 17.51                       |               | 0.01    | 438.94                      |
| H92          | 0.54    | 3.26                        | Cell volume/2 |         |                             |
| H91          | 0.53    | 1.98                        |               |         | 437.99                      |
| Total        | 1.32    | 275.55                      |               |         |                             |


**Figure 6**  
 Deformation density ( $a$ ) in the plane of the dication and ( $b$ ) in the plane of the anion. Blue contours are positive density and red ones are negative. The contour level is  $0.10 \text{ e \AA}^{-3}$ . ( $c$ ) The anion deformation density iso-surface at  $0.15 \text{ e \AA}^{-3}$ .

range of mainly positive charges that strongly correlate with their environment ( $C_{\text{carbonate}} > C_{\text{guanidine}} > C_{\text{imino}} > C_{\text{pyridine}} -$  the latter being slightly negative). As expected, the hydrogen atoms are all strongly positive and again may be grouped by type ( $\text{H}_2\text{O} > \text{NH} > \text{CH}$ ).

The deformation density in the plane of the dication is mapped in Fig. 6( $a$ ) and clearly shows a significant concentration of electron density in all of the covalent bonds, as well as the presence of lone pairs on the imino and pyridine nitrogen atoms. The covalent bonding density is also well represented for the anion and for the water molecules. Again, the expected lone-pair regions on the oxygen atoms are also well defined.

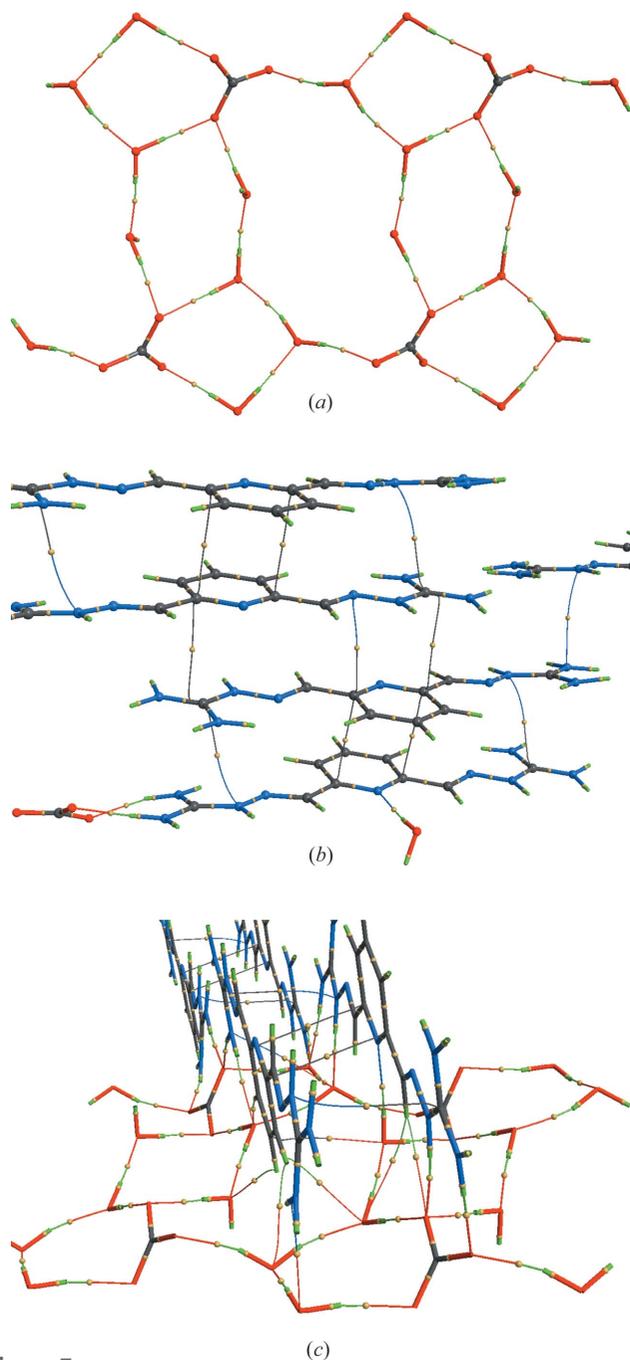
More complete information on the nature of the bonding may be obtained from a topological analysis of the total electron density (Fig. 7 and Table 3). All  $(3, -1)$  critical points for the covalent bonds in the dication, the carbonate anion, and selected water molecules are indicated by yellow spheres in Figs. 7( $a$ ) and 7( $b$ ). Their characteristics are tabulated in Table 3. All covalent bonds have significant electron density at the critical point, with negative values of the Laplacian as required. Of particular interest is the extent of electron delocalization ( $\pi$  bonding) in the essentially planar dication. In general, all bonds in the molecular skeleton are short, with significant ellipticities at the critical points indicating important  $\pi$ -character. Complementary information on the nature of these bonds may be obtained from the topological bond orders as defined by  $n_{\text{topo}} = a + b\lambda_3 + c(\lambda_1 + \lambda_2) + d\rho_{\text{CP}}$ , where  $\rho$  is the electron density at the critical point,  $\lambda_{1,2,3}$  are obtained from the Hessian matrix, and the coefficients ( $a, b, c, d$ ) were taken from the literature (Howard & Lamarche, 2003; Tsirlon *et al.*, 2006, 2007; Bartashevich *et al.*, 2011). The bond

orders for the skeleton of the cation, which range from 1.078 to 1.382 and show close to twofold molecular symmetry in their value, further indicate the delocalized  $\pi$ -character of the C–C and C–N bonds (Table 3 and Fig. 5). The strongest bonds are those involving the imino atoms N4 and N6, whereas the weakest are the substituted guanidinium C–N bonds (C1–N3 and C9–N7) and the substituents of the pyridine ring (C2–C3 and C7–C8). The bond orders of the N–H bonds are significantly lower than those of C–H, corresponding to the higher positive charges on the H(N) atoms compared with H(C).

Although Fig. 6( $b$ ) implies well resolved lone pairs on all the oxygen atoms of the carbonate anion, these are actually cuts through a doughnut-like charge distribution as shown by the iso-surface plot in Fig. 6( $c$ ). As expected, the carbonate anion is strongly covalently bonded, and the charge distribution is highly polarized, the oxygen atoms carrying high negative charges and the carbon atom being strongly positive.

#### 4.2. Closed-shell interactions

The most important noncovalent interactions in this structure are the hydrogen bonds, which range in



**Figure 7**  
Bond paths and critical points (yellow spheres) for (a) all covalent bonds and intermolecular hydrogen bonds in the carbonate–water ribbons, for (b) all covalent bonds in the dication and cation–cation stacking interactions, and (c) selected bond paths and critical points linking the cationic stacks and anionic ribbons. Color scheme: C, black; N, blue; O, red; H, green.

strength from modest to strong. All bond paths have been identified from the topology of the electron density, and their (3,−1) bond critical points characterized (Table 4 and Fig. 7). Every hydrogen atom in the structure bonds to a neighboring oxygen or to the pyridine nitrogen (N5) except H22, which only bonds to the partially occupied OH group. All carbonate oxygen atoms accept three hydrogen bonds and all water

**Table 3**  
Characteristics of covalent bond critical points in PyBIG carbonate tetrahydrate.

$\epsilon = \lambda_1/\lambda_2 - 1$ ;  $n_{\text{topo}} = a + b\lambda_3 + c(\lambda_1 + \lambda_2) + d\rho_{\text{CP}}$  (Howard & Lamarche, 2003; Tsirelson *et al.*, 2006, 2007; Bartashevich *et al.*, 2011); complete tables of bond critical-point properties have been included in the supporting information.

| Atom 1           | Atom 2 | $\rho(r)$ ( $\text{e } \text{\AA}^{-3}$ ) | $\nabla^2\rho(r)$ ( $\text{e } \text{\AA}^{-5}$ ) | $R_{ij}$ ( $\text{\AA}$ ) | $\epsilon$ | $n_{\text{topo}}$ |
|------------------|--------|---|---|---------------------------|------------|-------------------|
| <b>PyBIG</b>     |        |   |   |                           |            |                   |
| C1               | N1     | 2.492                                     | −26.400   | 1.325                     | 0.167      | 1.260             |
| C1               | N2     | 2.455                                     | −30.350   | 1.327                     | 0.219      | 1.157             |
| C1               | N3     | 2.372                                     | −28.050   | 1.352                     | 0.173      | 1.104             |
| C2               | C3     | 1.909                                     | −16.050   | 1.468                     | 0.102      | 1.084             |
| C2               | H2     | 1.832                                     | −19.780   | 1.095                     | 0.046      | 0.894             |
| C2               | N4     | 2.637                                     | −31.840   | 1.286                     | 0.219      | 1.342             |
| C3               | C4     | 2.139                                     | −20.070   | 1.398                     | 0.192      | 1.265             |
| C3               | N5     | 2.349                                     | −22.860   | 1.347                     | 0.113      | 1.169             |
| C4               | C5     | 2.162                                     | −20.020   | 1.391                     | 0.138      | 1.314             |
| C4               | H4     | 1.878                                     | −20.420   | 1.088                     | 0.035      | 0.928             |
| C5               | C6     | 2.168                                     | −20.320   | 1.388                     | 0.163      | 1.304             |
| C5               | H5     | 1.870                                     | −20.250   | 1.086                     | 0.022      | 0.927             |
| C6               | C7     | 2.111                                     | −19.480   | 1.402                     | 0.184      | 1.258             |
| C6               | H6     | 1.892                                     | −20.850   | 1.085                     | 0.028      | 0.921             |
| C7               | C8     | 1.899                                     | −15.870   | 1.470                     | 0.117      | 1.078             |
| C7               | N5     | 2.374                                     | −23.750   | 1.345                     | 0.112      | 1.183             |
| C8               | H8     | 1.836                                     | −19.560   | 1.096                     | 0.055      | 0.912             |
| C8               | N6     | 2.637                                     | −31.870   | 1.284                     | 0.192      | 1.342             |
| C9               | N7     | 2.352                                     | −25.500   | 1.358                     | 0.186      | 1.121             |
| C9               | N8     | 2.486                                     | −28.670   | 1.322                     | 0.209      | 1.215             |
| C9               | N9     | 2.453                                     | −27.400   | 1.326                     | 0.188      | 1.212             |
| N1               | H11    | 2.134                                     | −31.950   | 1.005                     | 0.036      | 0.635             |
| N1               | H12    | 2.129                                     | −32.370   | 1.037                     | 0.042      | 0.689             |
| N2               | H21    | 2.091                                     | −31.280   | 1.029                     | 0.037      | 0.659             |
| N2               | H22    | 2.155                                     | −30.160   | 1.013                     | 0.045      | 0.730             |
| N3               | H3     | 2.031                                     | −31.380   | 1.057                     | 0.043      | 0.626             |
| N3               | N4     | 2.375                                     | −7.047  | 1.362                     | 0.084      | 1.382             |
| N6               | N7     | 2.406                                     | −7.880  | 1.357                     | 0.074      | 1.367             |
| N7               | H7     | 2.039                                     | −30.490   | 1.041                     | 0.047      | 0.622             |
| N8               | H81    | 2.092                                     | −30.960   | 1.030                     | 0.025      | 0.657             |
| N8               | H82    | 2.203                                     | −32.860   | 0.998                     | 0.037      | 0.687             |
| N9               | H91    | 2.124                                     | −31.530   | 1.015                     | 0.043      | 0.663             |
| N9               | H92    | 2.079                                     | −30.100   | 1.045                     | 0.041      | 0.695             |
| <b>Carbonate</b> |        |   |   |                           |            |                   |
| C10              | O1     | 2.506                                     | −30.380   | 1.289                     | 0.111      | 1.309             |
| C10              | O2     | 2.476                                     | −30.030   | 1.289                     | 0.113      | 1.289             |
| C10              | O3     | 2.467                                     | −29.830   | 1.292                     | 0.128      | 1.302             |
| <b>Waters</b>    |        |   |   |                           |            |                   |
| O4               | H41    | 2.274                                     | −36.720   | 0.980                     | 0.046      | 0.595             |
| O4               | H42    | 2.254                                     | −41.790   | 0.971                     | 0.024      | 0.550             |
| O5               | H51    | 2.223                                     | −33.490   | 0.967                     | 0.016      | 0.449             |
| O5               | H52    | 2.248                                     | −37.030   | 0.973                     | 0.009      | 0.528             |
| O6               | H61    | 2.205                                     | −36.630   | 0.981                     | 0.022      | 0.505             |
| O6               | H62    | 2.210                                     | −41.440   | 0.980                     | 0.005      | 0.526             |
| O7               | H71    | 2.243                                     | −38.560   | 0.973                     | 0.005      | 0.516             |
| O7               | H72    | 2.159                                     | −37.750   | 0.984                     | 0.020      | 0.472             |

oxygen atoms accept two. The only nitrogen atom that accepts a hydrogen bond is the pyridine N5 atom.

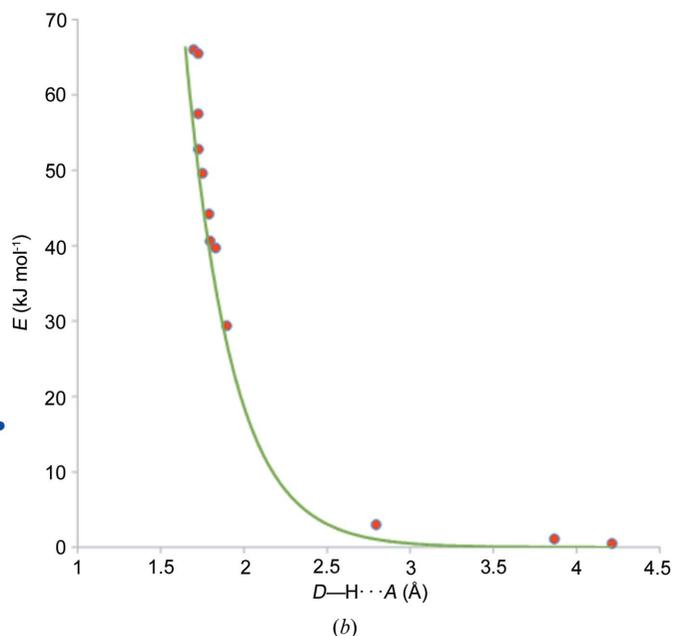
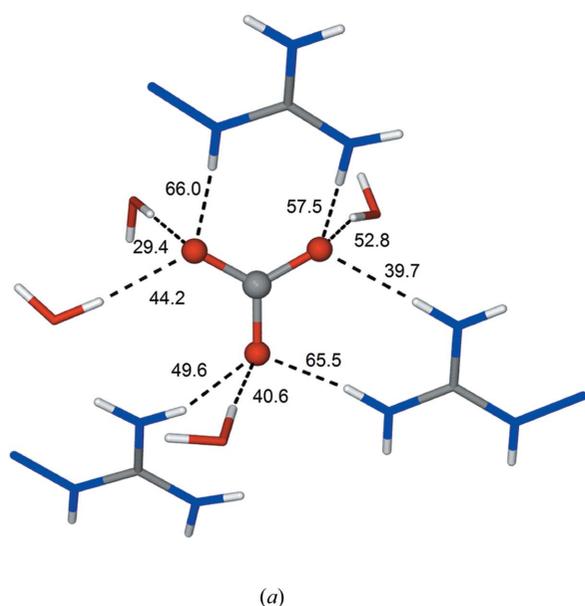
We have estimated the dissociation energy of each hydrogen bond based on the topological analysis and assuming the validity of the relationship by Espinosa *et al.* (1998, 1999). The dissociation energies of the most important hydrogen bonds range from modest ( $\sim 14 \text{ kJ mol}^{-1}$ ) to strong ( $\sim 66 \text{ kJ mol}^{-1}$ ). From the  $|V_{\text{CP}}|/G_{\text{CP}}$  criterion (Espinosa *et al.*, 2002), although these are still closed-shell interactions, the stronger ones are well within the so-called ‘transit’ region,  $(|V_{\text{CP}}|/G_{\text{CP}})_{\text{max}} = 1.40$ .

**Table 4**  
Characteristics of bond critical points for closed shell intermolecular interactions.

Complete tables of bond critical point properties are provided in the supporting information.

| Atom 1 | Atom 2 | Symmetry <sup>†</sup> | $\rho(r)$<br>( $e \text{ \AA}^{-3}$ ) | $\nabla^2 \rho(r)$<br>( $e \text{ \AA}^{-5}$ ) | $R_{ij}$ ( $\text{\AA}$ ) <sup>‡</sup> | $D_e$<br>( $\text{kJ mol}^{-1}$ ) | Acceptor group/<br>donor group |
|--------|--------|-----------------------|---------------------------------------|--|--|-----------------------------------|--------------------------------|
| O1     | H7     | 46401                 | 0.358                                 | 2.093  | 1.698                                  | 66.0                              | Carbonate/imino                |
| O2     | H11    | 55501                 | 0.354                                 | 2.208  | 1.725                                  | 65.5                              | Carbonate/guan                 |
| O3     | H91    | 46401                 | 0.317                                 | 2.527  | 1.725                                  | 57.5                              | Carbonate/guan                 |
| O6     | H3     | 65501                 | 0.299                                 | 2.466  | 1.724                                  | 53.1                              | Water/imino                    |
| O3     | H61    | 66502                 | 0.296                                 | 2.590  | 1.727                                  | 52.8                              | Carbonate/water                |
| O2     | H81    | 45401                 | 0.279                                 | 2.700  | 1.751                                  | 49.6                              | Carbonate/guan                 |
| O1     | H71    | 56502                 | 0.266                                 | 2.170  | 1.790                                  | 44.2                              | Carbonate/water                |
| O7     | H62    | 55501                 | 0.258                                 | 2.544  | 1.766                                  | 44.2                              | Water/water                    |
| O2     | H41    | 56502                 | 0.251                                 | 2.074  | 1.798                                  | 40.6                              | Carbonate/water                |
| O5     | H72    | 65602                 | 0.237                                 | 2.561  | 1.797                                  | 40.0                              | Water/water                    |
| O3     | H21    | 55501                 | 0.244                                 | 2.180  | 1.830                                  | 39.7                              | Carbonate/guan                 |
| O6     | H42    | 55501                 | 0.200                                 | 2.171  | 1.868                                  | 31.3                              | Water/water                    |
| O1     | H51    | 56502                 | 0.187                                 | 2.292  | 1.897                                  | 29.4                              | Carbonate/water                |
| N5     | H52    | 55501                 | 0.201                                 | 1.608  | 1.963                                  | 28.8                              | Pyridine/water                 |
| O4     | H12    | 65501                 | 0.154                                 | 1.475  | 2.003                                  | 20.5                              | Water/guan                     |
| O7     | H82    | 66602                 | 0.108                                 | 1.718  | 2.115                                  | 15.5                              | Water/guan                     |
| O4     | H92    | 55401                 | 0.092                                 | 1.708  | 2.129                                  | 13.6                              | Water/guan                     |
| O7     | H6     | 66602                 | 0.055                                 | 0.527  | 2.561                                  | 4.9                               | Water/pyridine                 |
| O5     | H5     | 54501                 | 0.047                                 | 0.647  | 2.647                                  | 4.9                               | Water/pyridine                 |
| N1     | N3     | 56502                 | 0.051                                 | 0.562  | 3.256                                  | 4.8                               | Guan/imino                     |
| C3     | C9     | 66602                 | 0.057                                 | 0.463  | 3.280                                  | 4.7                               | Pyridine/guan                  |
| C7     | N6     | 66602                 | 0.054                                 | 0.498  | 3.267                                  | 4.7                               | Pyridine/imino                 |
| N3     | C9     | 56602                 | 0.049                                 | 0.458  | 3.398                                  | 4.1                               | Imino/guan                     |
| O5     | C5     | 56602                 | 0.042                                 | 0.454  | 3.216                                  | 3.6                               | Water/pyridine                 |
| O7     | H4     | 64501                 | 0.034                                 | 0.511  | 2.807                                  | 3.4                               | Water/pyridine                 |
| O6     | H4     | 64501                 | 0.028                                 | 0.513  | 2.807                                  | 3.2                               | Water/pyridine                 |
| O1     | H8     | 46401                 | 0.030                                 | 0.453  | 2.796                                  | 3.0                               | Carbonate/imino                |
| O4     | N2     | 64501                 | 0.026                                 | 0.477  | 3.366                                  | 2.9                               | Water/guan                     |
| O4     | N2     | 66502                 | 0.021                                 | 0.277  | 3.550                                  | 1.8                               | Water/guan                     |
| O6     | N8     | 66602                 | 0.019                                 | 0.282  | 3.535                                  | 1.7                               | Water/guan                     |
| O7     | H8     | 65602                 | 0.020                                 | 0.235  | 3.138                                  | 1.5                               | Water/imino                    |
| O1     | C5     | 57502                 | 0.015                                 | 0.166  | 3.867                                  | 1.1                               | Carbonate/pyridine             |
| O1     | N2     | 47502                 | 0.008                                 | 0.087  | 4.214                                  | 0.5                               | Carbonate/guan                 |

<sup>†</sup> ORTEP symmetry codes for Atom 2. <sup>‡</sup> The shorter values for the intermolecular distances compared with those reported for the neutron study are caused by lattice contraction at lower temperature.



**Figure 8**  
Hydrogen bonding involving the carbonate anion. (a) Carbonate ‘binding’ by five guanidinium and four water hydrogen bonds, with estimated dissociation energies in  $\text{kJ mol}^{-1}$ . (b) Observed correlation between hydrogen-bond energies and  $\text{H}\cdots\text{O}$  contact distances; red points are from our experiment and the green line is from the work by Espinosa *et al.* (1998).

of  $-441.9 \text{ kJ mol}^{-1}$  in hydrogen-bonding energy. The strong hydrogen bonding of carbonate and water in these crystals is needed to partially compensate for the large free energy of dehydration of the anion ( $1315 \text{ kJ mol}^{-1}$ ) (Marcus, 1991) involved in the crystallization of  $\text{PyBIGH}_2(\text{CO}_3)(\text{H}_2\text{O})_4$ . Additionally, the lattice energy, consisting of electrostatic as well as other interactions (vide infra), must also contribute to the low aqueous solubility of these crystals.

A complete topological analysis of the electron density reveals a number of additional bond paths, suggesting much weaker interactions. Although not rigorously justified, extrapolating the Espinosa *et al.* (1998, 1999) relationship suggests that dissociation energies for these additional interactions are all  $<5 \text{ kJ mol}^{-1}$  (Table 4). By definition, a bond path must begin and end at a nucleus; however, due to the close face-to-face proximity of the planar cations, many of these interactions may be better described as  $\pi$ - $\pi$  interactions.

#### 4.3. Lattice energy and electrostatic interactions

It is well known that high lattice energies tend to lower the solubility of crystalline compounds:

$$E_{\text{int}} = E_{\text{es}} + E_{\text{ex-rep}} + E_{\text{disp}} + E_{\text{ind}}. \quad (2)$$

Although not the only contributor to the lattice energy [ $E_{\text{int}}$ , equation (2)], electrostatic interactions ( $E_{\text{es}}$ ) tend to dominate this quantity in ionic crystals (Coppens, 1997; Volkov *et al.*, 2006). Determination of the exchange-repulsion and dispersion to the total interaction energy are method dependent and, hence, unreliable. However, the electrostatic term may be obtained from the multipole expansion of the electron density using the methodology proposed by Volkov *et al.* (2004). Thus, we have determined the electrostatic crystal binding energy for  $(\text{PyBIGH}_2)(\text{CO}_3)(\text{H}_2\text{O})_4$  to be  $-583 \text{ kJ mol}^{-1}$ . Although this may seem modest for an ionic compound, we have noted significant charge transfer between the cation and the anion, and the cationic charge is highly delocalized.

## 5. Conclusions

This article reports both a neutron diffraction study and a high-resolution X-ray diffraction study of a highly insoluble carbonate salt formed by crystallization of a guanidine compound with atmospheric  $\text{CO}_2$ . Both diffraction methods confirm the presence of a small amount of cocrystallized hydroxide ion. The accurately determined topological properties of the electron density characterize the delocalized nature of the bonding in the planar cation, as well as two well developed strong hydrogen-bonding schemes, one defining an anion-water ribbon, and the other essentially orthogonal to the anion-water 'plane', linking the anionic ribbons to the cationic stacks. The carbonate anions are strongly hydrogen bonded in these crystals, which likely contributes to the extremely low aqueous solubility of this salt. The water molecules of hydration, hydrogen bonded to the carbonate anions and the guanidinium cations, also play an important role in the stability of these crystals. While the intermolecular

interactions are dominated by strong hydrogen bonds, a number of supplementary weaker interactions have been characterized. Although their bond paths have been identified by their nuclear attractors, many may better be characterized as  $\pi$ - $\pi$  interactions. The electrostatic contribution to the lattice energy is relatively modest due to both charge transfer and charge delocalization.

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## References

- Arnold, O., Bilheux, J. C., Borreguero, J. M., Buts, A., Campbell, S. I., Chapon, L., Doucet, M., Draper, N., Ferraz Leal, R., Gigg, M. A., Lynch, V. E., Markvardsen, A., Mikkelsen, D. J., Mikkelsen, R. L., Miller, R., Palmen, K., Parker, P., Passos, G., Perring, T. G., Peterson, P. F., Ren, S., Reuter, M. A., Savici, A. T., Taylor, J. W., Taylor, R. J., Tolchenov, R., Zhou, W. & Zikovsky, J. (2014). *Nucl. Instrum. Methods Phys. Res. A*, **764**, 156–166.
- Bader, R. F. W. (1994). In *Atoms in Molecules: A Quantum Theory*. Oxford University Press.
- Bartashevich, E. V., Nikulov, D. K., Vener, M. V. & Tsirelson, V. G. (2011). *Comput. Theor. Chem.* **973**, 33–39.
- Blessing, R. H. (1987). *Crystallogr. Rev.* **1**, 3–58.
- Blessing, R. H. (1995). *Acta Cryst. A* **51**, 33–38.
- Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
- Brethomé, F. M., Williams, N. J., Seipp, C. A., Kidder, M. K. & Custelcean, R. (2018). *Nat. Energ.* **3**, 553–559.
- Coppens, P. (1997). In *X-ray Charge Densities and Chemical Bonding*. Oxford University Press.
- Espinosa, E., Alkorta, I., Elguero, J. & Molins, E. (2002). *J. Chem. Phys.* **117**, 5529–5542.
- Espinosa, E., Lecomte, C. & Molins, E. (1999). *Chem. Phys. Lett.* **300**, 745–748.
- Espinosa, E., Molins, E. & Lecomte, C. (1998). *Chem. Phys. Lett.* **285**, 170–173.
- Gianopoulos, C. G., Chua, Z., Zhurov, V. V. & Pinkerton, A. A. (2017). *J. Appl. Cryst.* **50**, 643–646.
- Hansen, N. K. & Coppens, P. (1978). *Acta Cryst. A* **34**, 909–921.
- Hardie, M. J., Kirschbaum, K., Martin, A. & Pinkerton, A. A. (1998). *J. Appl. Cryst.* **31**, 815–817.
- Howard, S. T. & Lamarche, O. (2003). *J. Phys. Org. Chem.* **16**, 133–141.
- Jelsch, C., Guillot, B., Lagoutte, A. & Lecomte, C. (2005). *J. Appl. Cryst.* **38**, 38–54.
- Jogl, G., Wang, X., Mason, S. A., Kovalevsky, A., Mustyakimov, M., Fisher, Z., Hoffman, C., Kratky, C. & Langan, P. (2011). *Acta Cryst. D* **67**, 584–591.
- Keith, D. W. (2009). *Science*, **325**, 1654–1655.
- Keith, D. W., Holmes, G., St. Angelo, D. & Heidel, K. (2018). *Joule*, **2**, 1573–1594.
- Kirschbaum, K., Martin, A., Parrish, D. A. & Pinkerton, A. A. (1999). *J. Phys. Condens. Matter*, **11**, 4483–4490.

- Kirschbaum, K., Martin, A. & Pinkerton, A. A. (1997). *J. Appl. Cryst.* **30**, 514–516.
- Lackner, K. S. (2003). *Science*, **300**, 1677–1678.
- Lackner, K. S., Brennan, S., Matter, J. M., Park, A. H. A., Wright, A. & van der Zwaan, B. (2012). *Proc. Natl Acad. Sci. USA*, **109**, 13156–13162.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Madsen, A. Ø. (2006). *J. Appl. Cryst.* **39**, 757–758.
- Marcus, Y. (1991). *J. Chem. Soc. Faraday Trans.* **87**, 2995–2999.
- Otwinowski, Z. & Minor, W. (1997). In *Methods in Enzymology*, Vol. 276, pp. 307–326. Academic Press.
- Reiner, D. M. (2016). *Nat. Energ.* **1**, 7.
- Sanz-Pérez, E. S., Murdock, C. R., Didas, S. A. & Jones, C. W. (2016). *Chem. Rev.* **116**, 11840–11876.
- Schultz, A. J., Jørgensen, M. R. V., Wang, X., Mikkelsen, R. L., Mikkelsen, D. J., Lynch, V. E., Peterson, P. F., Green, M. L. & Hoffmann, C. M. (2014). *J. Appl. Cryst.* **47**, 915–921.
- Schultz, A. J., Srinivasan, K., Teller, R. G., Williams, J. M. & Lukehart, C. M. (1984). *J. Am. Chem. Soc.* **106**, 999–1003.
- Seipp, C. A., Williams, N. J., Kidder, M. K. & Custelcean, R. (2017). *Angew. Chem. Int. Ed.* **56**, 1042–1045.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Stash, A. & Tsirelson, V. (2002). *J. Appl. Cryst.* **35**, 371–373.
- Stash, A. I. & Tsirelson, V. G. (2005). *Crystallogr. Rep.* **50**, 177–184.
- Tsirelson, V. G., Bartashevich, E. V., Stash, A. I. & Potemkin, V. A. (2007). *Acta Cryst.* **B63**, 142–150.
- Tsirelson, V. G., Stash, A. I., Potemkin, V. A., Rykounov, A. A., Shutalev, A. D., Zhurova, E. A., Zhurov, V. V., Pinkerton, A. A., Gurskaya, G. V. & Zavodnik, V. E. (2006). *Acta Cryst.* **B62**, 676–688.
- Volkov, A., Koritsanszky, T. & Coppens, P. (2004). *Chem. Phys. Lett.* **391**, 170–175.
- Volkov, A., Macchi, P., Farrugia, L., Gattu, C., Mallinson, P., Richter, T. & Koritsanszky, T. (2006). *XD2006*. <http://xd.chem.buffalo.edu/>.
- Zhurova, E. A., Zhurov, V. V. & Tanaka, K. (1999). *Acta Cryst.* **B55**, 917–922.
- Zhurov, V. V. & Pinkerton, A. A. (2013). *Z. Anorg. Allg. Chem.* **639**, 1969–1978.
- Zhurov, V. V., Zhurova, E. A. & Pinkerton, A. A. (2008). *J. Appl. Cryst.* **41**, 340–349.
- Zikovskiy, J., Peterson, P. F., Wang, X. P., Frost, M. & Hoffmann, C. (2011). *J. Appl. Cryst.* **44**, 418–423.