

## Guanidinium pyromellitate

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## Key indicators

Single-crystal X-ray study

T = 293 K

Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$ 

R factor = 0.054

wR factor = 0.148

Data-to-parameter ratio = 9.1

For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound, guanidinium pyromellitate,  $2[\text{C}(\text{NH}_2)_3]^+ \cdot (\text{C}_{10}\text{H}_4\text{O}_8)^{2-}$  or  $2\text{CH}_6\text{N}_3^+ \cdot \text{C}_{10}\text{H}_4\text{O}_8^{2-}$ , comprises a 1,2,4,5-benzenetetracarboxylate anion and two guanidinium cations. The carboxylate anions lie on centers of inversion and involve intramolecular  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bonds. The cations and anions are linked by strong three-dimensional  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds and  $\pi-\pi$ -stacking interactions into a three-dimensional framework containing a one-dimensional channel along the diagonal of the *ca* plane. The  $\text{N}-\text{H} \cdots \text{O}$  hydrogen-bond distances range from 2.899 (6) to 3.068 (5)  $\text{\AA}$ .

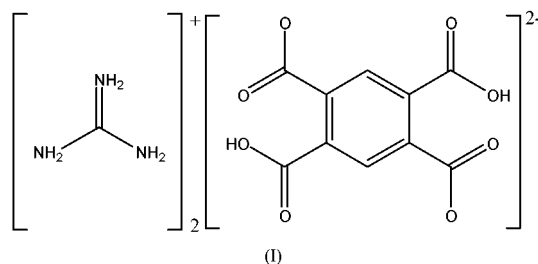
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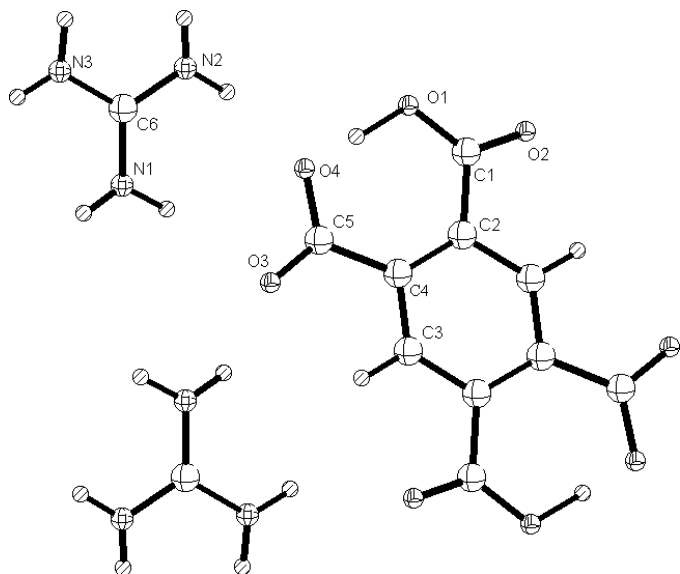
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## Comment

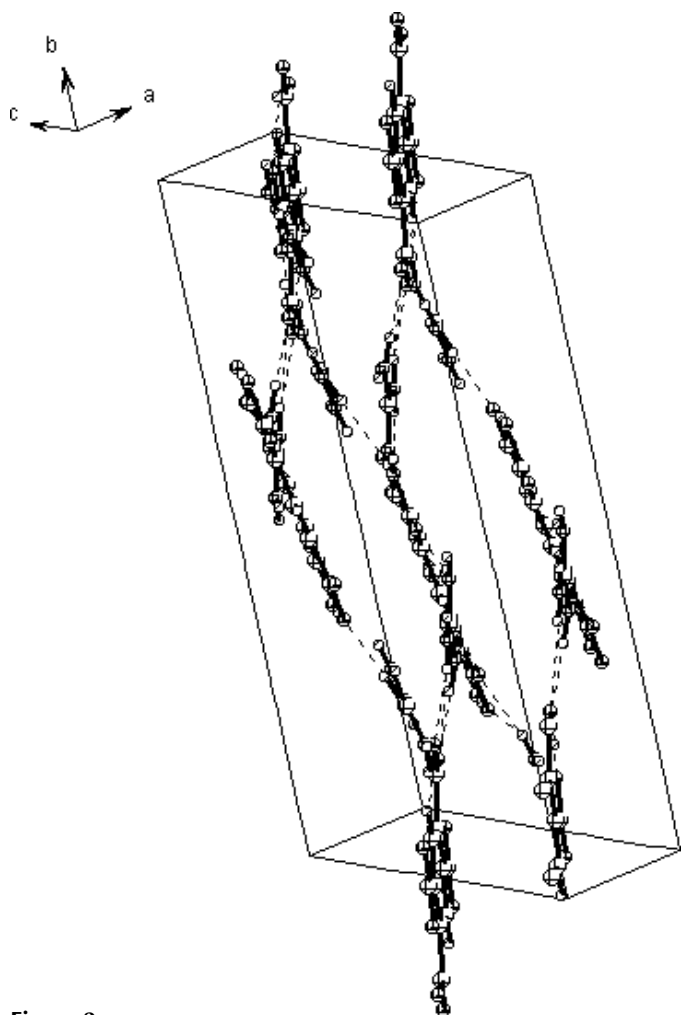
Pyromellitic acid is symmetric and has been extensively employed as a building block in coordination chemistry (Cao *et al.*, 2002; Chu *et al.*, 2001; Cheng *et al.*, 2000; Poleti & Karanovic, 1989; Rochon & Massarweh, 2001). By contrast, its use in supramolecular chemistry has hardly been explored. Only five types of supramolecules of this acid have been reported. They are the adducts with 2,2'-bipyridyl  $[\text{C}_{10}\text{H}_8\text{N}_2\text{H}]^+ \cdot 0.5[\text{C}_6\text{H}_2(\text{COO})_4\text{H}_2]^{2-} \cdot 0.5[\text{C}_6\text{H}_2(\text{COOH})_4]$  (Mrvos-Sermek *et al.*, 1996); with 4,4'-bipyridyl  $2(\text{C}_{10}\text{H}_9\text{N}_2)^+ \cdot (\text{C}_{10}\text{H}_4\text{O}_8)^{2-}$  (Lough *et al.*, 2000); with hexamethylenetetramine  $2(\text{C}_6\text{H}_{13}\text{N}_4)^+ \cdot (\text{C}_{10}\text{H}_4\text{O}_8)^{2-}$  (Lough *et al.*, 2000); with guanidine and hydrogen peroxide  $[\text{C}(\text{NH}_2)_3]_4 \cdot \text{C}_{10}\text{H}_2(\text{COO})_4 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$  (Adams & Ramdas, 1978); and with 3,6,9,16,19,22-hexazatricyclotriaconta-11,13,24,26(1),27,29-hexaene  $(\text{C}_{24}\text{H}_{42}\text{N}_6)^{4+} \cdot (\text{C}_{10}\text{H}_2\text{O}_8)^{4-} \cdot 6\text{H}_2\text{O}$  (Zhu *et al.*, 2002), respectively. We report here the structure of a new adduct, built from the pyromellitate anion and the guanidinium cation, whose supramolecular structure is wholly different from that of  $[\text{C}(\text{NH}_2)_3]_4 \cdot \text{C}_{10}\text{H}_2(\text{COO})_4 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$ .



The title compound, (I), is composed of a 1,2,4,5-benzenetetracarboxylate anion and two guanidinium cations derived from the decomposition of dicyandiamide. The pyromellitate anion lies on a center of inversion. All H atoms are fully ordered. Each cation acts as a donor of hard hydrogen bonds,



**Figure 1**  
The molecular components of the title compound, with the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level.



**Figure 2**  
Packing diagram viewed down the [101] diagonal of the unit cell, showing the hydrogen-bond interactions.

of the type N—H···O, and each anion acts as acceptor of bonds of the type N—H···O and O—H···O. The O—H···O hydrogen bonds are all intramolecular and there are no O—H···N hydrogen bonds. Every anion is linked to six cations by 12 N—H···O hydrogen bonds, while every cation is linked to three anions by six N—H···O hydrogen bonds. The anions and the cations are connected to each other by six different N—H···O hydrogen bonds, whose distances range from 2.899 (6) to 3.068 (5) Å; these form a three-dimensional framework containing a one-dimensional channel along the diagonal of the *ca* plane. The channel size is 16.428 (5) × 3.795 (5) Å, and is composed of four cations and four anions.

In addition to the hydrogen bonds, the supramolecular structure is stabilized by aromatic  $\pi$ - $\pi$ -stacking interactions. Within the network, the aryl ring at (*x*, *y*, *z*) is parallel to the aryl ring at (1 + *x*, *y*, *z*) and the perpendicular distance between the ring planes is 3.731 (9) Å. The  $\pi$ - $\pi$ -stacking interactions generate a one-dimensional network along the *a* axis.

## Experimental

A mixture of pyromellitic dianhydride (0.109 g, 0.5 mmol), dicyandiamide (0.042 g, 0.5 mmol) and H<sub>2</sub>O (10 ml, 567.7 mmol), in a ratio of *ca* 1:1:1135, was sealed in a 35 ml stainless-steel reactor with a Teflon lining and was heated at 433 K for 72 h. After cooling, the mixture was then filtered and single colorless crystals were obtained by slow evaporation of the filtrate at room temperature.

### Crystal data

2CH<sub>6</sub>N<sub>3</sub><sup>+</sup>·C<sub>10</sub>H<sub>4</sub>O<sub>8</sub><sup>2-</sup>  
*M<sub>r</sub>* = 372.31  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 3.7949 (2) Å  
*b* = 20.1494 (9) Å  
*c* = 10.3903 (1) Å  
 $\beta$  = 100.501 (3)°  
*V* = 781.19 (5) Å<sup>3</sup>  
*Z* = 2

*D<sub>x</sub>* = 1.583 Mg m<sup>-3</sup>  
 Mo K $\alpha$  radiation  
 Cell parameters from 172 reflections  
 $\theta$  = 2.0–25.1°  
 $\mu$  = 0.14 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Column, colorless  
 0.36 × 0.30 × 0.18 mm

### Data collection

Siemens SMART CCD diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
*T<sub>min</sub>* = 0.953, *T<sub>max</sub>* = 0.976  
 2373 measured reflections

1372 independent reflections  
 1132 reflections with *I* > 2 $\sigma$ (*I*)  
*R<sub>int</sub>* = 0.029  
 $\theta_{max}$  = 25.1°  
*h* = -4 → 4  
*k* = -23 → 21  
*l* = -4 → 12

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.054  
*wR*(*F*<sup>2</sup>) = 0.148  
*S* = 1.04  
 1372 reflections  
 150 parameters  
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 0.7112P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.19 \text{ e \AA}^{-3}$   
 $\Delta\rho_{min} = -0.26 \text{ e \AA}^{-3}$

**Table 1**  
Selected geometric parameters (Å, °).

O1—C1	1.278 (3)	C2—C4 <sup>i</sup>	1.416 (3)
O2—C1	1.220 (3)	C3—C4	1.396 (3)
O3—C5	1.219 (3)	C4—C5	1.519 (3)
O4—C5	1.279 (3)	C6—N2	1.319 (3)
C1—C2	1.529 (3)	C6—N1	1.324 (4)
C2—C3	1.388 (3)	C6—N3	1.322 (4)
O2—C1—O1	121.3 (2)	C3—C4—C5	113.8 (2)
O2—C1—C2	119.0 (2)	C2 <sup>i</sup> —C4—C5	129.1 (2)
O1—C1—C2	119.6 (2)	O3—C5—O4	120.7 (2)
C3—C2—C4 <sup>i</sup>	117.7 (2)	O3—C5—C4	120.3 (2)
C3—C2—C1	113.8 (2)	O4—C5—C4	119.0 (2)
C4 <sup>i</sup> —C2—C1	128.5 (2)	N2—C6—N1	120.2 (3)
C2—C3—C4	125.2 (2)	N2—C6—N3	119.1 (3)
C3—C4—C2 <sup>i</sup>	117.1 (2)	N1—C6—N3	120.6 (3)

Symmetry code: (i)  $-1 - x, 1 - y, -z$ .

**Table 2**  
Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H6...O4	0.89 (3)	2.02 (3)	2.899 (3)	167.0 (3)
N2—H5...O2 <sup>i</sup>	0.82 (4)	2.18 (4)	2.994 (3)	169.0 (6)
N1—H4...O3	0.90 (3)	2.19 (3)	3.067 (4)	166.0 (3)
N3—H3...O2 <sup>ii</sup>	0.86 (4)	2.15 (4)	2.916 (4)	147.0 (2)
N3—H2...O1 <sup>i</sup>	0.90 (4)	2.02 (4)	2.913 (3)	177.2 (9)
N1—H1...O3 <sup>ii</sup>	0.90 (4)	2.13 (4)	2.970 (3)	153.8 (9)
O4—H8...O1 <sup>iii</sup>	1.19 (4)	1.19 (4)	2.377 (3)	175.6 (4)

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

All H atoms were located in a difference Fourier map and their positions and isotropic displacement parameters were refined.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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