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Aminoguanidinium Squarate

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Abstract

The structure determination of the aminoguanidinium salt of 3,4-dihydroxy-3-cyclobutene-1,2-dione, $2CH_7N_4^{+}\cdot C_4O_4^{2-}$, was undertaken as part of a project investigating optical properties of new classes of organic compounds involving salts of optically active amino acids, optically active amines and guanidine derivatives with squaric acids as well as its sulfur derivatives.

Comment

The series of investigations has been started with the structure of the *L*-arginium hydrogensquarate (Angelova, Velikova, Kolev & Radomirska, 1996) and has been followed by the structure of (*R*)-(-)-1-phenylglycinium hydrogensquarate monohydrate (Angelova, Petrova, Radomirska & Kolev, 1996). These compounds crystallize noncentrosymmetric and are suitable for Second Harmonic Generation (SHG) applications. Encapsulations of an optically nonlinear octupolar guadinium cation in a host polianionic squarate lattice follows a new trend in the engineering of new materials for nonlinear applications like a guanidinium *L*-hydrogentartrate (Zyss, Pecaut, Levy & Masse, 1993), guanidinium hydrogensquarate (Kolev, Preut, Bleckmann & Radomirska, 1997*a*), guanidinium squarate (Kolev, Preut, Bleckmann & Radomirska, 1997*b*). The two aminoguanine molecules adopt the two protons from the squaric acids. The squarate dianion $C_4O_4^{2}$ is a interesting cyclic compound with aromaticity with its symmetry likely to be $D_{4\ h}$. Hence this dianion exists like a quadropole while the aminoguanidinium exists like a asymetrized octupolar cations. The packing shows strong interlocking between the anions and cationic sublattices by a multidirectional hydrogen-bonding network which exhibits interesting nonlinear-optically efficient properties.

Experimental

The compound was prepared by adding an aqueous solution of aminoguanidinium carbonate to a water solution of squaric acid with continuous stirring by room temperature for 30 minutes in 1:1 molecular ratio. The product was isolated and purified by multifold recrystallization from doubly destilled water. Colourless crystals were grown by slow evaporation from an aqueous solution at room temperature.

Refinement

The structure was solved by direct methods (Sheldrick, 1990) and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods (Sheldrick, 1993).

CIF access

Computing details

Data collection: *SDP* (Frenz, 1978); cell refinement: *SDP* (Frenz, 1978); data reduction: *SDP* (Frenz, 1978); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL93* (Sheldrick, 1993), *PARST95* (Nardelli, 1995).

(c458)

Crystal data

$2C_1H_7N_4^{1+}\cdot C_4O_4^{2-}$	$V = 578.8\ (2)\ Å^3$
$M_r = 262.25$	$Z = 2$
Monoclinic, $P2_1/n$	Ag $K\alpha$
$a = 4.0930\ (10)$ Å	$\mu = 0.08\ mm^{-1}$
$b = 11.438\ (2)$ Å	$T = 293\ (2)$ K
$c = 12.365\ (2)$ Å	0.3 × 0.3 × 0.2 mm
$\beta = 90.73\ (3)^o$	

Data collection

Enraf-Nonius CAD-4 diffractometer	$R_{int} = 0.029$
Absorption correction: none	2 standard reflections
4206 measured reflections	every 250 reflections
1081 independent reflections	intensity decay: none
785 reflections with $I > 2\sigma(I)$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	110 parameters
$wR(F^2) = 0.092$	All H-atom parameters refined
$S = 1.03$	$\Delta\rho_{max} = 0.13\ e\ Å^{-3}$
1081 reflections	$\Delta\rho_{min} = -0.17\ e\ Å^{-3}$

Table 1
Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H42···O2	0.88 (2)	2.01 (2)	2.857 (2)	161 (2)
N5—H52···N3	0.86 (2)	2.32 (2)	2.690 (2)	106 (2)
N6—H6···O1	0.81 (2)	1.98 (2)	2.778 (2)	167 (2)
N3—H31···O1^{i}	0.91 (3)	2.38 (3)	3.214 (2)	152 (2)
N4—H41···O1^{ii}	0.91 (2)	1.92 (2)	2.809 (2)	166 (2)
N5—H51···O2^{iii}	0.90 (2)	1.97 (2)	2.823 (2)	159 (2)

N5—H52···N3^{iv}	0.86 (2)	2.45 (2)	3.097 (2)	133 (2)

Symmetry codes: (i) x+1, y, z; (ii) −x+1/2, y−1/2, −z+3/2; (iii) x+1/2, −y−1/2, z+1/2; (iv) −x+2, −y, −z+2.

Acknowledgements

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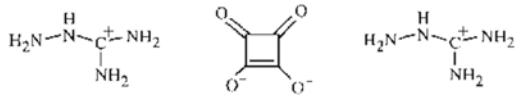
CIF access

Scheme 1



supplementary materials

(c458)

Crystal data

$2C_1H_7N_4^{1+}\cdot C_4O_4^{2-}$	$F_{000} = 276$
$M_r = 262.25$	$D_x = 1.505$ Mg m^{-3} D_m = not determined Mg m^{-3} D_m measured by ?
Monoclinic, $P2_1/n$	Ag $K\alpha$ radiation $\lambda = 0.56086$ Å
$a = 4.0930$ (10) Å	Cell parameters from 24 reflections
$b = 11.438$ (2) Å	$\theta = 9.7$–11.1º
$c = 12.365$ (2) Å	$\mu = 0.08$ mm^{-1}
$\beta = 90.73$ (3)º	$T = 293$ (2) K
$V = 578.8$ (2) Å^3	Prismatic, colourless
$Z = 2$	0.3 × 0.3 × 0.2 mm

Data collection

Enraf-Nonius CAD-4 diffractometer	$R_{int} = 0.029$
Radiation source: fine-focus sealed tube	$\theta_{max} = 20.0$º
Monochromator: graphite	$\theta_{min} = 3.1$º
$T = 293(2)$ K	$h = -4\rightarrow4$
ω–2θ scans	$k = -13\rightarrow13$
Absorption correction: none	$l = -15\rightarrow15$
4206 measured reflections	2 standard reflections
1081 independent reflections	every 250 reflections
785 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.034$	All H-atom parameters refined
$wR(F^2) = 0.092$	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0545P)^2 + 0.055P]$ where $P = (F_o^2 + 2F_c^2)/3$?
$S = 1.03$	$\Delta\rho_{max} = 0.13$ e Å^{-3}
1081 reflections	$\Delta\rho_{min} = -0.17$ e Å^{-3}
110 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement on F^2 for ALL reflections except for 0 with very negative F^2 or flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The observed criterion of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating _R_factor_obs *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.2574 (3)	0.09586 (10)	0.63895 (9)	0.0527 (4)
O2	0.1257 (4)	−0.17486 (10)	0.57935 (9)	0.0587 (4)
N3	0.8484 (5)	0.08084 (15)	0.85873 (13)	0.0512 (4)
N4	0.3888 (4)	−0.17544 (14)	0.79449 (13)	0.0529 (4)
N5	0.6980 (4)	−0.12856 (15)	0.94375 (12)	0.0521 (4)
N6	0.6438 (4)	0.00170 (13)	0.80341 (12)	0.0490 (4)
C7	0.5777 (4)	−0.10116 (14)	0.84766 (13)	0.0413 (4)
C8	0.0564 (4)	−0.07909 (14)	0.53573 (13)	0.0445 (4)
C9	0.1156 (4)	0.04296 (14)	0.56227 (12)	0.0430 (4)
H51	0.660 (5)	−0.1996 (19)	0.9712 (16)	0.057 (5)*
H52	0.821 (5)	−0.0782 (17)	0.9750 (17)	0.057 (6)*
H6	0.549 (5)	0.0226 (17)	0.7487 (16)	0.051 (5)*
H41	0.332 (5)	−0.244 (2)	0.8264 (17)	0.067 (6)*
H42	0.310 (5)	−0.1573 (18)	0.7301 (19)	0.063 (6)*
H31	1.005 (7)	0.104 (2)	0.811 (2)	0.090 (8)*
H32	0.733 (6)	0.143 (2)	0.8705 (18)	0.077 (8)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0742 (9)	0.0428 (7)	0.0405 (7)	0.0072 (6)	−0.0207 (6)	−0.0064 (5)
O2	0.0935 (11)	0.0399 (7)	0.0420 (7)	0.0105 (6)	−0.0209 (6)	−0.0026 (5)
N3	0.0599 (10)	0.0447 (9)	0.0489 (9)	−0.0069 (8)	−0.0063 (8)	0.0065 (7)
N4	0.0746 (11)	0.0425 (8)	0.0414 (8)	−0.0057 (8)	−0.0145 (7)	0.0038 (7)
N5	0.0724 (11)	0.0419 (9)	0.0415 (8)	−0.0114 (7)	−0.0139 (7)	0.0081 (7)
N6	0.0603 (10)	0.0442 (8)	0.0422 (8)	−0.0045 (7)	−0.0139 (7)	0.0100 (6)
C7	0.0467 (10)	0.0407 (9)	0.0364 (8)	0.0045 (7)	−0.0010 (7)	0.0021 (7)
C8	0.0593 (11)	0.0413 (9)	0.0326 (8)	0.0095 (7)	−0.0065 (7)	−0.0039 (6)
C9	0.0543 (10)	0.0418 (9)	0.0326 (8)	0.0081 (7)	−0.0057 (7)	−0.0040 (7)

Geometric parameters (Å, °)

O1—C9	1.260 (2)	N5—C7	1.318 (2)
O2—C8	1.252 (2)	N5—H51	0.90 (2)
N3—N6	1.405 (2)	N5—H52	0.86 (2)
N3—H31	0.91 (3)	N6—C7	1.327 (2)
N3—H32	0.86 (3)	N6—H6	0.81 (2)
N4—C7	1.319 (2)	C8—C9^{i}	1.454 (2)
N4—H41	0.91 (2)	C8—C9	1.454 (2)
N4—H42	0.88 (2)	C9—C8^{i}	1.454 (2)
N6—N3—H31	106.9 (16)	N3—N6—H6	119.4 (14)
N6—N3—H32	106.7 (16)	N5—C7—N4	120.4 (2)
H31—N3—H32	105.3 (22)	N5—C7—N6	120.4 (2)
C7—N4—H41	119.4 (13)	N4—C7—N6	119.15 (15)
C7—N4—H42	120.3 (14)	O2—C8—C9^{i}	135.4 (2)
H41—N4—H42	120.2 (19)	O2—C8—C9	134.98 (15)
C7—N5—H51	119.6 (13)	C9^{i}—C8—C9	89.58 (13)
C7—N5—H52	117.3 (13)	O1—C9—C8^{i}	134.8 (2)
H51—N5—H52	122.9 (18)	O1—C9—C8	134.82 (15)
C7—N6—N3	119.61 (14)	C8^{i}—C9—C8	90.42 (13)
C7—N6—H6	120.5 (14)		
N3—N6—C7—N5	1.2 (3)	C9^{i}—C8—C9—O1	179.9 (3)
N3—N6—C7—N4	−179.1 (2)	O2—C8—C9—C8^{i}	179.9 (3)
O2—C8—C9—O1	−0.2 (4)	C9^{i}—C8—C9—C8^{i}	0.0

Symmetry codes: (i) −*x*, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H42···O2	0.88 (2)	2.01 (2)	2.857 (2)	161 (2)
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N5—H51···O2^{iv}	0.90 (2)	1.97 (2)	2.823 (2)	159 (2)
N5—H52···N3^{v}	0.86 (2)	2.45 (2)	3.097 (2)	133 (2)

Symmetry codes: (ii) *x*+1, *y*, *z*; (iii) −*x*+1/2, *y*−1/2, −*z*+3/2; (iv) *x*+1/2, −*y*−1/2, *z*+1/2; (v) −*x*+2, −*y*, −*z*+2.