4-(3-Azaniumylpropyl)morpholin-4-ium chloride hydrogen oxalate: an unusual example of a dication with different counter-anions

Telisha Traut-Johnstone,[a,b] Frederik H. Kriel,[a] Raymond Hewer[a] and D. Bradley G. Williams[b,c]*

[a]Centre for Metals-based Drug Discovery, Advanced Materials Division, Mintek, Private Bag X3015, Randburg, 2125, South Africa, [b]Research Centre for Synthesis and Catalysis, Department of Chemistry, University of Johannesburg, PO Box 524, Auckland Park 2006, South Africa, and [c]The Ferrier Research Institute, Victoria University of Wellington, 69 Gracefield Rd, Lower Hutt, 5040, New Zealand
Correspondence e-mail: bradley.williams@vuw.ac.nz

The mixed organic–inorganic title salt, $C_7H_{18}N_2O^{2+}\cdot C_2HO_4^-\cdot Cl^-$, forms an assembly of ionic components which are stabilized through a series of hydrogen bonds and charge-assisted intermolecular interactions. The title assembly crystallizes in the monoclinic $C2/c$ space group with $Z = 8$. The asymmetric unit consists of a 4-(3-azaniumylpropyl)morpholin-4-ium dication, a hydrogen oxalate counter-anion and an inorganic chloride counter-anion. The organic cations and anions are connected through a network of N—H$\cdots$O, O—H$\cdots$O and C—H$\cdots$O hydrogen bonds, forming several intermolecular rings that can be described by the graph-set notations $R_3^3(13)$, $R_2^1(5)$, $R_1^2(5)$, $R_2^1(6)$, $R_2^3(6)$, $R_2^2(8)$ and $R_3^3(9)$. The 4-(3-azaniumylpropyl)morpholin-4-ium dications are interconnected through N—H$\cdots$O hydrogen bonds, forming $C(9)$ chains that run diagonally along the ab face. Furthermore, the hydrogen oxalate anions are interconnected via O—H$\cdots$O hydrogen bonds, forming head-to-tail $C(5)$ chains along the crystallographic b axis. The two types of chains are linked through additional N—H$\cdots$O and O—H$\cdots$O hydrogen bonds, and the hydrogen oxalate chains are sandwiched by the 4-(3-azaniumylpropyl)morpholin-4-ium chains, forming organic layers that are separated by the chloride anions. Finally, the layered three-dimensional structure is stabilized via intermolecular N—H$\cdots$Cl and C—H$\cdots$Cl interactions.

1. Introduction

As part of our continued interest in the multicomponent synthesis of compounds with the pyrrolidinedione skeleton, some of which have reportedly demonstrated promising antimicrobial properties (Gein et al., 2007), we report here the structure of 4-(3-azaniumylpropyl)morpholin-4-ium chloride hydrogen oxalate, (I), an organic–inorganic mixed salt formed as a by-product during the synthesis of the hydrochloride salt of the pyrrolidinone carbaldehyde parent compound, 4-(benzofuran-2-carbonyl)-5-(4-tert-butylphenyl)-3-hydroxy-1-[3-(morpholin-4-yl)propyl]-1H-pyrrol-2(5H)-one, (II). Mixed salts have many practical and potential applications in the fields of magnetism and electric conductors, energy storage, solar energy conversion, as well as catalysis and the biomedical field (Hill & Prossner-McCartha, 1995; Mizuno & Misomo, 1998; Gouzerh & Proust, 1998; Proust et al., 1993; Zhuang et al., 2010; Huang et al., 2009; Zhou & Yu, 2012; You et al., 2006). The crystal packing of such salts is often characterized by extensive hydrogen bonding and charge-assisted intermolecular interactions (Brammer et al., 2002; Huang et al., 2009).
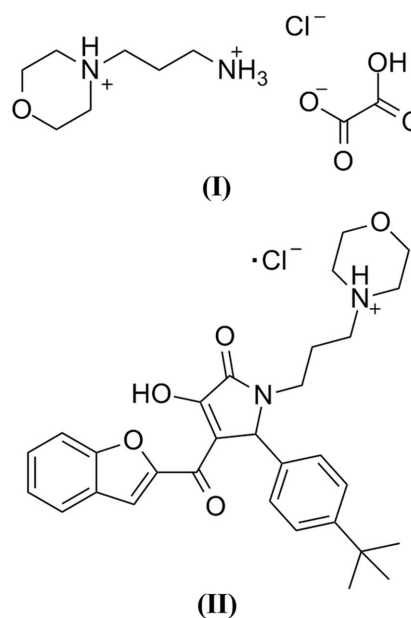
2. Experimental

2.1. Synthesis and crystallization

Methyl (2Z)-4-(1-benzofuran-2-yl)-2-hydroxy-4-oxobut-2-enoate (0.200 g, 0.816 mmol) was dissolved in 1,4-dioxane (5 ml). One molar equivalent of 4-(3-aminopropyl)morpholine (0.816 mmol, 0.119 ml) was added to the 1,4-dioxane mixture, resulting in the formation of a yellow precipitate upon addition. One molar equivalent of 4-tert-butylbenzaldehyde (0.816 mmol, 0.137 ml) was added to the mixture which was stirred at room temperature for 5 min. 4-(Benzofuran-2-carbonyl)-5-(4-tert-butylphenyl)-3-hydroxy-1-[3-(morpholin-4-yl)propyl]-1H-pyrrol-2(5H)-one was isolated as a yellow powder (yield: 0.579 mmol, 0.291 g, 71%) and dried in vacuo. Subsequently, the dried powder (0.050 g, 0.093 mmol) was dissolved in dry methanol (2.5 ml). One drop of 15% HCl

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_7H_{18}N_2O^{2+}\cdot C_2HO_4^-\cdot Cl^-$
M_r	270.71
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	100
a, b, c (Å)	18.949 (5), 5.685 (5), 24.783 (5)
β (°)	109.575 (5)
V (Å³)	2515 (2)
Z	8
Radiation type	Mo $K\alpha$
μ (mm⁻¹)	0.32
Crystal size (mm)	$0.32 \times 0.24 \times 0.14$
Data collection	
Diffractometer	Bruker APEXII CCD diffractometer
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	46562, 3150, 2954
R_{int}	0.033
$(\sin\theta/\lambda)_{max}$ (Å⁻¹)	0.668
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.080, 1.03
No. of reflections	3150
No. of parameters	154
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å⁻³)	1.26, −0.23

Computer programs: *APEX2* (Bruker, 2012), *SAINT* (Bruker, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), *SHELXTL* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2006), *DIAMOND* (Brandenburg, 2006), *ORTEP-3 for Windows* (Farrugia, 2012), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

was added to this solution which was agitated to cause mixing. 4-(Benzofuran-2-carbonyl)-5-(4-*tert*-butylphenyl)-3-hydroxy-1-[3-(morpholin-4-yl)propyl]-1*H*-pyrrol-2(5*H*)-one hydrochloride salt, (II), precipitated out of the solution and was isolated as an off-white powder (yield: 0.0716 mmol, 0.039 g, 77%), while colourless crystals of the title salt, (I), crystallized out of the methanolic solution as a by-product (<5% yield).

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were placed in idealized positions and were allowed to ride on their parent atoms, with C—H = 0.97 Å, N—H = 0.89 Å and O—H = 0.82 Å, and with $U_{iso}(H) = 1.5U_{eq}(C,O)$ for primary ammonium and hydroxy groups, and $1.2U_{eq}(C)$ otherwise.

3. Results and discussion

The asymmetric unit of salt (I) consists of one 4-(3-azaniumylpropyl)morpholin-4-ium dication, doubly protonated at atoms N1 and N2, counter-balanced by two different anions, *viz.* a hydrogen oxalate anion and a chloride anion (Fig. 1). The morpholine ring assumes a low-energy chair conformation, with the azaniumylpropyl side chain in an antiperiplanar (*anti* or *trans*) conformation [the C5—C6—C7—N2 torsion angle is 173.05 (8)°]. All other bond lengths and angles in the 4-(3-azaniumylpropyl)morpholin-4-ium dication fall within expected ranges. Typical variations in the C—O bond lengths can be observed for the hydrogen oxalate anion; whereas the
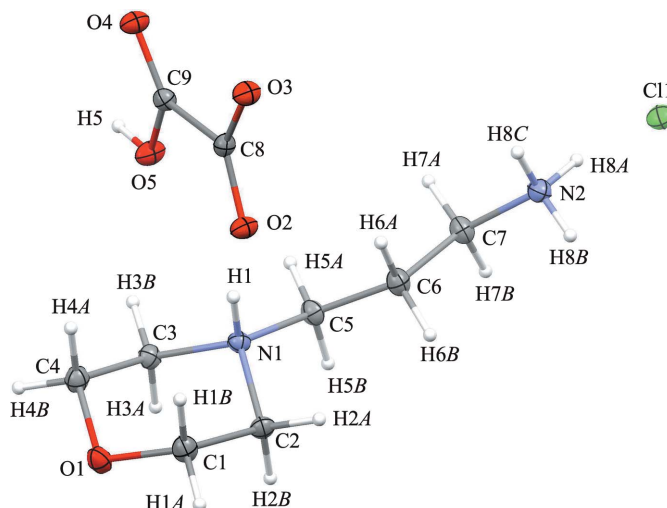
Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

short bond distances of the charged carboxylate end [C8—O2 = 1.2474 (12) Å and C8—O3 = 1.2570 (14) Å] indicate a delocalization of charge across both C—O bonds. The longer bond length observed for C9—O5 [1.3114 (14) Å] and the shorter length observed for C9—O4 [1.2150 (13) Å] are consistent with a carboxylic acid group containing distinct C=O and C—OH bonds.

Fig. 2 shows the crystal packing along the crystallographic *b* axis in the form of layers. Hydrogen oxalate anions are sandwiched by the 3-(morpholin-4-yl)propan-1-aminium cations, which are in turn separated by the chloride anions, as viewed in the *ac* plane. The sandwiched hydrogen oxalate anions interact through a number of different hydrogen bonds, as shown in Fig. 3. The individual sandwich layers are connected through Coulombic interactions involving the chloride anions.
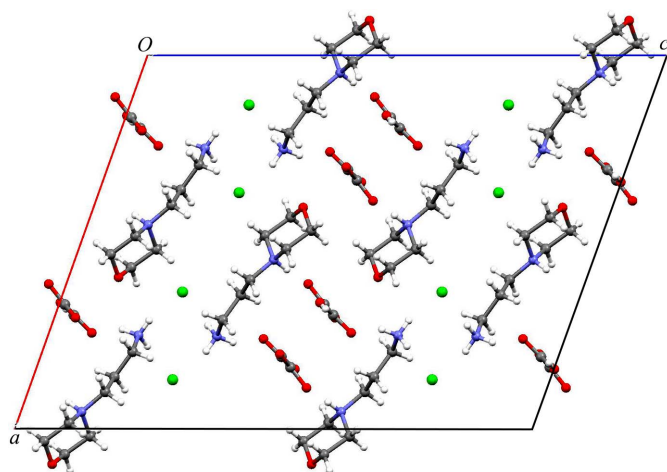
The extensive network of intermolecular interactions displayed in the structure of salt (I) can be described by a combination of graph-set motifs (Bernstein *et al.*, 1995). Atom H8*C* is a triple donor to O1ⁱⁱⁱ, O3ⁱᵛ and O4ⁱᵛ, with the
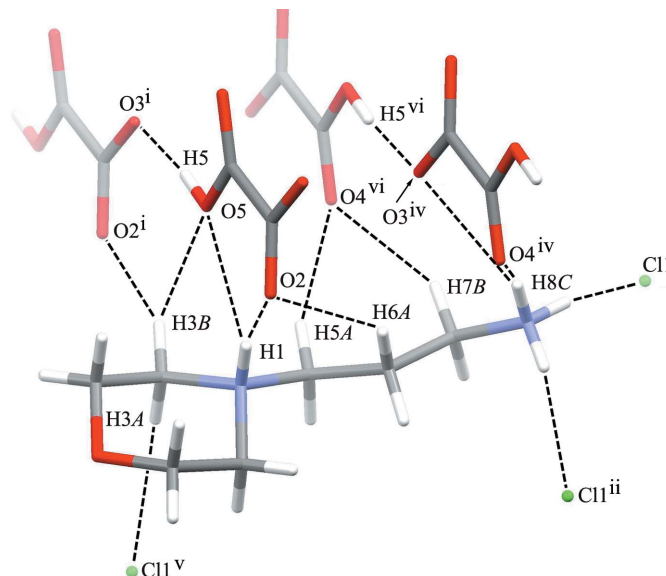
Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O2	0.91	1.87	2.7400 (16)	160
N1—H1⋯O5	0.91	2.44	3.0568 (12)	125
N2—H8*A*⋯Cl1	0.89	2.32	3.1846 (11)	162
N2—H8*B*⋯Cl1ⁱ	0.89	2.27	3.1445 (13)	166
N2—H8*C*⋯O4ⁱⁱ	0.89	2.11	2.9093 (16)	149
N2—H8*C*⋯O3ⁱⁱ	0.89	2.52	3.1901 (13)	133
N2—H8*C*⋯O1ⁱⁱⁱ	0.89	2.55	3.0583 (13)	117
O5—H5⋯O3ⁱᵛ	0.82	1.73	2.548 (2)	172
C3—H3*A*⋯Cl1ᵛ	0.97	2.71	3.6067 (12)	154
C3—H3*B*⋯O2ⁱᵛ	0.97	2.33	3.233 (2)	154
C3—H3*B*⋯O5	0.97	2.58	3.1050 (14)	114
C5—H5*A*⋯O4ᵛⁱ	0.97	2.41	3.3323 (16)	158
C6—H6*A*⋯O2	0.97	2.60	3.3733 (15)	137
C7—H7*B*⋯O4ᵛⁱ	0.97	2.47	3.359 (2)	153

Symmetry codes: (i) $-x-\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x-\frac{1}{2}, -y-\frac{1}{2}, -z+1$; (iii) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (iv) $x, y+1, z$; (v) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (vi) $-x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$.

Figure 2
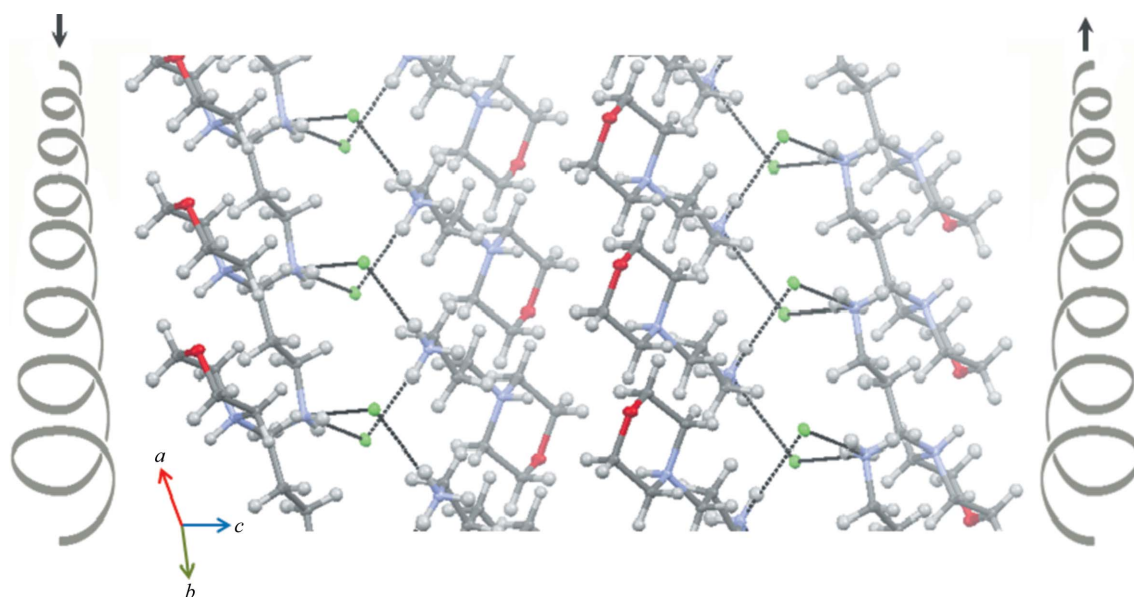Packing diagram of (I), viewed down the crystallographic *b* axis.

Figure 3
N—H···O, O—H···O and C—H···O hydrogen bonding, and N—H···Cl and C—H···Cl intermolecular interactions (dashed lines) between the 4-(3-azaniumylpropyl)morpholin-4-ium dication, hydrogen oxalate anions and chloride anions of (I). The symmetry codes are as in Table 2.

H8C···O4^{iv} distance shorter than the corresponding H8C···O3^{iv} distance (see Table 2 for hydrogen-bond geometry and symmetry codes; Fig. 3). This results in a cyclic $R_1^2(5)$ motif. Atoms H8A and H8B link the cations in a head-to-head manner through Cl1, resulting in chains that spiral down the crystallographic *b* axis (Fig. 4). Furthermore, an additional head-to-tail pairing can be observed for the cations through a weak N2—H8C···O1^{iii} hydrogen bond. The H8C···O1^{iii} interaction connects the 4-(3-azaniumylpropyl)morpholin-4-ium dications in a head-to-tail manner, forming $C(9)$ chains that run diagonally along the *ab* face (Fig. 5a). Furthermore, the hydrogen oxalate anions are interconnected *via* O—H···O hydrogen bonds, forming head-to-tail $C(5)$ chains along the crystallographic *b* axis (Fig. 5b). Additional inter-molecular C—H···Cl interactions formed between H3A and

the chloride counter-ion result in chains that spiral down the crystallographic *b* axis (Fig. 4). Furthermore, atom O2 is involved in interactions with H6A and N1—H1, resulting in a ring denoted $R_2^1(6)$ in graph-set notation, while the presence of two additional hydrogen bonds (O5—H5···O3^i and C3—H3B···O2^i) results in the formation of a third ring, denoted $R_3^3(12)$ (Fig. 3). Due to the fact that atom O5 is a double donor to H3B and H1, several smaller rings can be identified that are contained within ring $R_3^3(13)$. These include $R_3^3(9)$ formed by N—H1···O5, O5—H5···O3^i and O2^i···C3—H3B; $R_2^2(8)$

Figure 4
N—H···Cl and C—H···Cl intermolecular interactions (dashed lines) between the chloride anions and 4-(3-azaniumylpropyl)morpholin-4-ium dications arranged in a head-to-head fashion, spiralling down the crystallographic *b* axis.

(a)

(b)
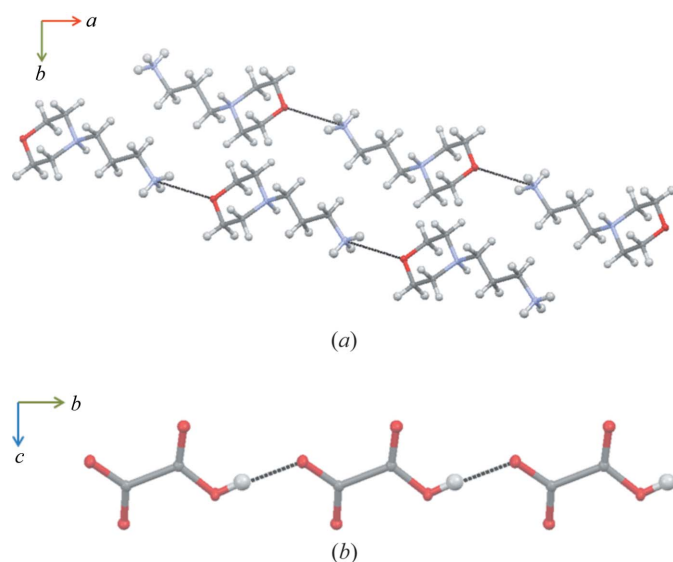
Figure 5
(a) C(9) chains formed diagonally along the crystallographic ab plane through intermolecular N—H···O interactions (dashed lines) between the 4-(3-azaniumylpropyl)morpholin-4-ium dications and (b) C(5) chains formed along the crystallographic b axis through intermolecular O—H···O interactions (dashed lines) between the hydrogen oxalate anions. In both chains, the molecules are arranged in a head-to-tail fashion.

formed by N—H1···O2 and O5···C3—H3B; and $R_2^1(5)$ formed by N—H1···O5 and O5···C3—H3B, as well as $R_1^2(5)$ formed by (N)H1···O2 and O5···(N)H1 and lastly $R_2^3(6)$ formed by H3B···O5, O5—H5···O3^i and O2^i···H3B. The C—H···O, O—H···O and N—H···O hydrogen-bond distances vary between 1.73 and 2.60 Å, while the N—H···Cl and C—H···Cl interaction distances vary between 2.27 and 2.71 Å (Table 2). All interactions in the structure are shorter than the sum of the van der Waals radii of the interacting atoms, where r(O) + r(H) = 2.72 Å and r(Cl) + r(H) = 3.00 Å (Mantina et al., 2009). In addition, the hydrogen-bond angles range between 133 and 172°, with the exception of N1—H1···O5 (125°), N2—H8C···O1^{iii} (117°) and the nonclassical C3—H3B···O5 (114°). Most of the interactions observed in the structure therefore correspond well to what is considered strong hydrogen bonding, thereby contributing to the stability of the structure.

Residual electron density is found on a twofold axis near atoms H6B (2.33 Å), H2A (2.38 Å) and Cl1 (2.89 Å). Probing of the electron density showed it to be well positioned to be a water molecule with possible C—H···O(water) hydrogen bonding to H6B and H2A, as well as showing a possible O—H···Cl short interaction. Refining of the residual electron density as an O atom, however, indicated that the occupancy would be very low as well as having huge uncertainty in the H-atom placement due to lack of electron density. Taking into account the low occupancy of any atom placed in this position, it is plausible that the residual electron density is an artefact in the data.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Brammer, L., Swearingen, J. K., Bruton, E. A. & Sherwood, P. (2002). *Proc. Natl Acad. Sci.* **99**, 4956–4961.
Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2012). *APEX2, SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Gein, V. L., Yushkov, V. V., Kasimova, N. N., Panina, M. A., Rakshina, N. S., Strelkova, L. V. & Voronina, E. V. (2007). *Pharm. Chem. J.* **41**, 367–371.
Gouzerh, P. & Proust, A. (1998). *Chem. Rev.* **98**, 77–111.
Hill, C. L. & Prossner-McCartha, C. M. (1995). *Coord. Chem. Rev.* **143**, 407–455.
Huang, Q., Chen, W.-Q., Chen, X., Liu, X.-B., Zhou, J.-R., Zuo, H.-R., Yu, L.-L. & Ni, C.-L. (2009). *Transition Met. Chem.* **34**, 765–771.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Mantina, M., Chamberlin, A. C., Valero, R., Cramer, C. J. & Truhlar, D. G. (2009). *J. Phys. Chem. A*, **113**, 5806–5812.
Mizuno, N. & Misomo, M. (1998). *Chem. Rev.* **98**, 199–218.
Proust, A., Gouzerh, P. & Robert, F. (1993). *Inorg. Chem.* **32**, 5291–5298.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
You, C., Miyazaki, T., Ishida, E., Ashizuka, M. & Ohtsuki, C. (2006). *Key Eng. Mater.* **309–311**, 1153–1156.
Zhou, W. & Yu, H. (2012). *Appl. Mater. Interfaces*, **4**, 2154–2159.
Zhuang, X.-M., Yin, W.-T., Xie, X.-D., Huang, Q., Zuo, H.-R., Yu, L.-L., Yang, L.-M. & Ni, C.-L. (2010). *Synth. React. Inorg. Met. Org. Chem.* **40**, 51–55.

supporting information

4-(3-Azaniumylpropyl)morpholin-4-ium chloride hydrogen oxalate: an unusual example of a dication with different counter-anions

Telisha Traut-Johnstone, Frederik H. Kriel, Raymond Hewer and D. Bradley G. Williams

Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINT* (Bruker, 2012); data reduction: *SAINT* (Bruker, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2006), *DIAMOND* (Brandenburg, 2006) and *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

4-(3-Azaniumylpropyl)morpholin-4-ium chloride hydrogen oxalate

Crystal data

$C_7H_{18}N_2O^{2+} \cdot C_2HO_4^- \cdot Cl^-$	$F(000) = 1152$
$M_r = 270.71$	$D_x = 1.430$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 9809 reflections
$a = 18.949$ (5) Å	$\theta = 2.4$–28.3°
$b = 5.685$ (5) Å	$\mu = 0.32$ mm^{-1}
$c = 24.783$ (5) Å	$T = 100$ K
$\beta = 109.575$ (5)°	Block, colourless
$V = 2515$ (2) Å^3	$0.32 \times 0.24 \times 0.14$ mm
$Z = 8$	

Data collection

Bruker APEX-II CCD diffractometer	2954 reflections with $I > 2\sigma(I)$
Radiation source: sealed tube	$R_{int} = 0.033$
Graphite monochromator	$\theta_{max} = 28.4°$, $\theta_{min} = 1.7°$
φ and ω scans	$h = -25 \rightarrow 25$
46562 measured reflections	$k = -7 \rightarrow 7$
3150 independent reflections	$l = -33 \rightarrow 33$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.028$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.080$	
$S = 1.03$	Hydrogen site location: inferred from neighbouring sites
3150 reflections	
154 parameters	H-atom parameters constrained
0 restraints	

$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 2.538P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 1.26$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Special details

Experimental. Crystals of [C7H18N2O]2+·C2HO4-·Cl-, (I), were grown by slow evaporation from a saturated methanolic solution of 4-(benzofuran-2-carbonyl)-5- (4-(*tert*-butyl)phenyl)-3-hydroxy-1-(3-morpholinopropyl)-1*H*-pyrrol-2(5*H*)-one (II), acidified with hydrochloric acid.

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 of F^2 against ALL reflections. The weighted R-factor wR and goodness 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 threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *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.

Crystal evaluation and data collection were performed on a Bruker APEXII CCD diffractometer with Mo $K\alpha$ ($\lambda = 0.71069$ Å) radiation and a diffractometer-to-crystal distance of 4.00 cm, at the Department of Chemistry, Auckland Park campus of the University of Johannesburg, South Africa. The initial cell matrix was obtained from two series of scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5° in a 6° range with the exposure time of 10 s per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite (*APEX2* and *SAINT*; Bruker, 2012). The final cell constants were calculated from a set of 3150 strong reflections from the actual data collection.

The data were collected by using the full-sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.75 Å. Data were harvested by collecting frames at intervals of 0.5° scans in ω and φ, with exposure times of 20 s per frame. These highly redundant data sets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements (*SADABS*; Bruker, 2012).

The systematic absences in the diffraction data were uniquely consistent for the space group $C2/c$ that yielded chemically reasonable and computationally stable refinement results. A successful solution by direct methods (*SHELXS97*; Sheldrick, 2008) provided all non-H atoms from the *E*-map. All non-H atoms were refined with anisotropic displacement parameters.

The final least-squares refinement of parameters against data resulted in residuals R (based on F^2 for $I \geq 2\sigma$) and wR (based on F^2 for all data) values unique to the crystal.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.06713 (6)	−0.09471 (18)	0.61326 (5)	0.0148 (2)
H1A	0.1097	−0.1902	0.6347	0.018*
H1B	0.0384	−0.1826	0.5795	0.018*
C2	0.01853 (6)	−0.04815 (18)	0.65010 (4)	0.01290 (19)
H2A	0.0008	−0.1958	0.6604	0.015*
H2B	0.0476	0.0319	0.6850	0.015*
C3	−0.01715 (6)	0.32481 (17)	0.60042 (4)	0.01205 (19)
H3A	0.0121	0.4099	0.6345	0.014*
H3B	−0.0583	0.4243	0.5785	0.014*
C4	0.03162 (6)	0.26306 (18)	0.56479 (5)	0.0143 (2)
H4A	0.0017	0.1812	0.5304	0.017*
H4B	0.0504	0.4065	0.5533	0.017*
C5	−0.10022 (6)	0.15209 (18)	0.64870 (4)	0.01321 (19)
H5A	−0.1368	0.2676	0.6277	0.016*

H5B	−0.0728	0.2174	0.6860	0.016*
C6	−0.14042 (6)	−0.07162 (19)	0.65617 (5)	0.0148 (2)
H6A	−0.1570	−0.1585	0.6204	0.018*
H6B	−0.1061	−0.1707	0.6851	0.018*
C7	−0.20762 (6)	−0.01054 (18)	0.67407 (5)	0.0142 (2)
H7A	−0.1907	0.0587	0.7120	0.017*
H7B	−0.2390	0.1033	0.6476	0.017*
N1	−0.04685 (5)	0.10181 (15)	0.61690 (4)	0.01050 (17)
H1	−0.0725	0.0236	0.5842	0.013*
N2	−0.25144 (5)	−0.22804 (16)	0.67412 (4)	0.01376 (18)
H8A	−0.2908	−0.1926	0.6845	0.021*
H8B	−0.2226	−0.3313	0.6987	0.021*
H8C	−0.2672	−0.2902	0.6391	0.021*
O1	0.09326 (4)	0.11814 (13)	0.59603 (3)	0.01537 (16)
C8	−0.16604 (6)	−0.21555 (17)	0.48876 (4)	0.01075 (18)
C9	−0.19432 (6)	0.03209 (17)	0.46434 (4)	0.01088 (19)
O2	−0.11121 (4)	−0.22588 (13)	0.53391 (3)	0.01368 (15)
O3	−0.20129 (4)	−0.38517 (13)	0.45938 (3)	0.01467 (16)
O4	−0.24188 (4)	0.05627 (13)	0.41753 (3)	0.01467 (16)
O5	−0.16082 (4)	0.20390 (13)	0.49869 (3)	0.01502 (16)
H5	−0.1775	0.3303	0.4840	0.023*
Cl1	−0.367263 (14)	−0.01834 (4)	0.729512 (10)	0.01563 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0145 (5)	0.0119 (4)	0.0192 (5)	0.0021 (4)	0.0073 (4)	0.0019 (4)
C2	0.0116 (4)	0.0125 (4)	0.0138 (5)	0.0029 (3)	0.0032 (4)	0.0025 (4)
C3	0.0128 (4)	0.0093 (4)	0.0140 (4)	−0.0003 (3)	0.0044 (4)	0.0005 (3)
C4	0.0151 (5)	0.0131 (4)	0.0156 (5)	0.0013 (4)	0.0061 (4)	0.0021 (4)
C5	0.0124 (4)	0.0140 (4)	0.0150 (5)	0.0011 (4)	0.0068 (4)	−0.0008 (4)
C6	0.0141 (5)	0.0142 (5)	0.0178 (5)	−0.0002 (4)	0.0076 (4)	0.0003 (4)
C7	0.0137 (5)	0.0139 (5)	0.0166 (5)	−0.0012 (4)	0.0070 (4)	−0.0006 (4)
N1	0.0099 (4)	0.0101 (4)	0.0110 (4)	0.0004 (3)	0.0029 (3)	0.0000 (3)
N2	0.0121 (4)	0.0160 (4)	0.0129 (4)	−0.0013 (3)	0.0039 (3)	−0.0006 (3)
O1	0.0125 (3)	0.0139 (3)	0.0210 (4)	0.0012 (3)	0.0071 (3)	0.0027 (3)
C8	0.0117 (4)	0.0098 (4)	0.0115 (4)	0.0011 (3)	0.0049 (3)	0.0007 (3)
C9	0.0106 (4)	0.0099 (4)	0.0125 (4)	0.0006 (3)	0.0044 (3)	−0.0001 (3)
O2	0.0144 (3)	0.0116 (3)	0.0122 (3)	0.0010 (3)	0.0007 (3)	0.0003 (3)
O3	0.0162 (4)	0.0101 (3)	0.0149 (3)	−0.0007 (3)	0.0013 (3)	−0.0006 (3)
O4	0.0151 (4)	0.0128 (3)	0.0132 (3)	0.0018 (3)	0.0009 (3)	0.0000 (3)
O5	0.0178 (4)	0.0079 (3)	0.0152 (4)	0.0007 (3)	0.0000 (3)	−0.0003 (3)
Cl1	0.01616 (14)	0.01693 (13)	0.01260 (13)	0.00007 (8)	0.00323 (10)	−0.00131 (8)

Geometric parameters (Å, º)

C1—O1	1.4260 (15)	C5—H5B	0.9700
C1—C2	1.5215 (15)	C6—C7	1.5224 (15)

C1—H1A	0.9700	C6—H6A	0.9700
C1—H1B	0.9700	C6—H6B	0.9700
C2—N1	1.5018 (13)	C7—N2	1.4897 (16)
C2—H2A	0.9700	C7—H7A	0.9700
C2—H2B	0.9700	C7—H7B	0.9700
C3—N1	1.4983 (16)	N1—H1	0.9100
C3—C4	1.5177 (14)	N2—H8A	0.8900
C3—H3A	0.9700	N2—H8B	0.8900
C3—H3B	0.9700	N2—H8C	0.8900
C4—O1	1.4270 (13)	C8—O2	1.2474 (12)
C4—H4A	0.9700	C8—O3	1.2570 (14)
C4—H4B	0.9700	C8—C9	1.5550 (18)
C5—N1	1.5030 (13)	C9—O4	1.2150 (13)
C5—C6	1.5253 (17)	C9—O5	1.3114 (14)
C5—H5A	0.9700	O5—H5	0.8200
O1—C1—C2	111.88 (9)	C7—C6—H6A	109.6
O1—C1—H1A	109.2	C5—C6—H6A	109.6
C2—C1—H1A	109.2	C7—C6—H6B	109.6
O1—C1—H1B	109.2	C5—C6—H6B	109.6
C2—C1—H1B	109.2	H6A—C6—H6B	108.1
H1A—C1—H1B	107.9	N2—C7—C6	109.38 (9)
N1—C2—C1	108.91 (8)	N2—C7—H7A	109.8
N1—C2—H2A	109.9	C6—C7—H7A	109.8
C1—C2—H2A	109.9	N2—C7—H7B	109.8
N1—C2—H2B	109.9	C6—C7—H7B	109.8
C1—C2—H2B	109.9	H7A—C7—H7B	108.2
H2A—C2—H2B	108.3	C3—N1—C2	108.26 (8)
N1—C3—C4	108.69 (9)	C3—N1—C5	111.23 (8)
N1—C3—H3A	110.0	C2—N1—C5	113.41 (8)
C4—C3—H3A	110.0	C3—N1—H1	107.9
N1—C3—H3B	110.0	C2—N1—H1	107.9
C4—C3—H3B	110.0	C5—N1—H1	107.9
H3A—C3—H3B	108.3	C7—N2—H8A	109.5
O1—C4—C3	111.42 (9)	C7—N2—H8B	109.5
O1—C4—H4A	109.3	H8A—N2—H8B	109.5
C3—C4—H4A	109.3	C7—N2—H8C	109.5
O1—C4—H4B	109.3	H8A—N2—H8C	109.5
C3—C4—H4B	109.3	H8B—N2—H8C	109.5
H4A—C4—H4B	108.0	C1—O1—C4	110.43 (9)
N1—C5—C6	110.86 (9)	O2—C8—O3	127.20 (10)
N1—C5—H5A	109.5	O2—C8—C9	117.81 (9)
C6—C5—H5A	109.5	O3—C8—C9	114.97 (10)
N1—C5—H5B	109.5	O4—C9—O5	125.34 (10)
C6—C5—H5B	109.5	O4—C9—C8	121.51 (9)
H5A—C5—H5B	108.1	O5—C9—C8	113.14 (9)
C7—C6—C5	110.22 (9)	C9—O5—H5	109.5

O1—C1—C2—N1	58.32 (11)	C6—C5—N1—C3	170.13 (8)
N1—C3—C4—O1	−60.11 (11)	C6—C5—N1—C2	−67.56 (11)
N1—C5—C6—C7	−165.38 (8)	C2—C1—O1—C4	−58.45 (11)
C5—C6—C7—N2	173.05 (8)	C3—C4—O1—C1	59.29 (11)
C4—C3—N1—C2	58.92 (10)	O2—C8—C9—O4	171.81 (10)
C4—C3—N1—C5	−175.84 (8)	O3—C8—C9—O4	−7.03 (14)
C1—C2—N1—C3	−58.00 (10)	O2—C8—C9—O5	−7.05 (13)
C1—C2—N1—C5	178.06 (8)	O3—C8—C9—O5	174.11 (9)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2	0.91	1.87	2.7400 (16)	160
N1—H1···O5	0.91	2.44	3.0568 (12)	125
N2—H8A···Cl1	0.89	2.32	3.1846 (11)	162
N2—H8B···Cl1[i]	0.89	2.27	3.1445 (13)	166
N2—H8C···O4[ii]	0.89	2.11	2.9093 (16)	149
N2—H8C···O3[ii]	0.89	2.52	3.1901 (13)	133
N2—H8C···O1[iii]	0.89	2.55	3.0583 (13)	117
O5—H5···O3[iv]	0.82	1.73	2.548 (2)	172
C3—H3A···Cl1[v]	0.97	2.71	3.6067 (12)	154
C3—H3B···O2[iv]	0.97	2.33	3.233 (2)	154
C3—H3B···O5	0.97	2.58	3.1050 (14)	114
C5—H5A···O4[vi]	0.97	2.41	3.3323 (16)	158
C6—H6A···O2	0.97	2.60	3.3733 (15)	137
C7—H7B···O4[vi]	0.97	2.47	3.359 (2)	153

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