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SHORT COMMUNICATION

2-(Phenylethyl)ammonium hydrogensquarate hemihydrate: crystal structure, solid-state IR-spectroscopic and theoretical characterization

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Abstract The title compound, 2-(phenylethyl)ammonium hydrogensquarate hemihydrate, was synthesized and structurally and spectroscopically characterized by a single crystal X-ray diffraction and solid-state polarized IR spectroscopy of oriented colloids in a nematic host. The crystal structure consists of two crystallographically independent 2-(phenylethyl)ammonium cations, joined in a 2D hydrogen-bonded network with hydrogensquarate anions and solvent water molecules. Surprisingly, the crystallographically non-equivalent cations exhibit differing pseudo *T* and *G trans* configurations.

Keywords 2-(Phenylethyl)ammonium hydrogensquarate hemihydrate · Crystal structure · Solid-state linear polarized IR spectroscopy · Amino acid derivatives · Biogenic amines

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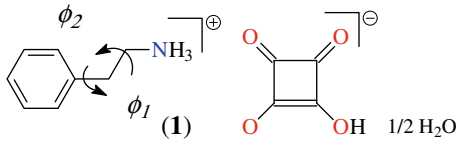
Introduction

As a part of our systematic structural and spectroscopic studies of amino acid derivatives (Kolev et al. 2007, 2009a, b, c, d, e; Koleva et al. 2009a), we now report the characterization of 2-(phenylethyl)ammonium hydrogensquarate hemihydrate (Scheme 1). 2-(phenylethyl)amine as a catecholamine-related biogenic amine is an endogenous ligand for mammalian trace amine-associated receptors and may act as a neuromodulator that regulates neuronal activity in basal ganglia (Holmes et al. 2005). The full understanding of the competitive receptor binding manner of small molecules requires knowledge of the conformational preference of these molecules depending mainly on the protonation processes. Experimental studies on the correlation of the structure and spectroscopic properties of 2-(phenylethyl)ammonium derivatives are relatively rare. Only the crystal structures of several 2-(phenylethyl)ammonium salts have been previously reported (Fig. 3; Hlel and Smiri 1999; Huh et al. 2006; Rademeyer et al. 2006; Abdi et al. 2004, 2005; Ishida et al. 1983; Ebina et al. 1994; Willett 1990; Mitzi 1999; Mitzi et al. 2002; Tsoucaris 1961; Groh et al. 1997). Corresponding hydrogensquarates of the organic salts have been also systematic studied by Yesilel et al. 2006, 2007, 2008. Hence, in this paper, we focus on the correlation of the structure and IR-spectroscopic properties of the 2-phenylethylammonium cation in the solid state using a single crystal X-ray diffraction and solid-state IR-polarized (IR-LD) spectroscopy of oriented colloids as a suspension in a nematic liquid crystal (Kolev et al. 2007, 2009a, b, c, d, e; Koleva et al. 2009a). The preferenced conformers of tryptammonium molecule in the solid state is discussed by comparing our present data with the previously reported structures.



Scheme 1 Chemical diagram of 2-(phenylethyl)ammonium hydrogensquarate hemihydrate (**1**)

Experimental

Methods

The X-ray diffraction intensities were measured in the ω scan mode on an Oxford Diffraction Xcalibur^{TM}2 diffractometer with a Sapphire2 CCD using Mo K_α radiation. The data were corrected for Lorentz and polarization effects. An absorption correction was carried out in a semi-empirical manner based on multiply scanned reflections (Blessing 1995). The crystal structure was solved by direct methods using SHELXS-97 and refined by full-matrix least squares refinement against F^2 using SHELXL-97 (Sheldrick 2008). The crystallographically independent β-phenylethylammonium cations were each found to be disordered over two sites with occupancies of, respectively, 53:47 and 50:50. Anisotropic displacement parameters were introduced for non-hydrogen atoms with the exception of those affected by disorder. Standard similar distance restraints were applied to the disordered cations and the phenyl groups were fitted as regular hexagons. Hydrogen atoms attached to carbon atoms were placed at geometrically calculated positions and refined with the appropriate riding model. The initial torsion angles of the ammonium groups were determined via a difference Fourier synthesis and refined while retaining the tetrahedral geometry. The positions of the hydroxyl hydrogen atoms were confirmed from the difference map and subsequently constrained to calculated positions and refined by allowing them to ride on their parent oxygen atoms. The water hydrogen atoms were located in a difference Fourier synthesis and refined with a U_{eq} value of 1.2 times that of the parent oxygen atom and holding the O–H distance at 0.84(2) Å. Relevant crystallographic structure data and refinement details are presented in Table 1.

Conventional and polarized IR-spectra were measured on a Thermo Nicolet OMNIC FTIR spectrometer (4,000–400 cm^{-1}, 2 cm^{-1} resolution, 200 scans) equipped with a Specac wire-grid polarizer. Non-polarized solid-state IR spectra were recorded using the KBr disk technique. The oriented samples were obtained as a colloid suspension in a nematic liquid crystal ZLI 1695. The theoretical approach, experimental technique for preparing the samples, procedures for polarized IR-spectra interpretation and the validation of this new linear-dichroic infrared (IR-LD) orientation solid-state method for accuracy and precision have been previously presented. The influence of the liquid crystal medium on peak positions and integral absorbances of the guest molecule bands, the rheological model, the nature and balance of the forces in the nematic liquid crystal suspension system, and morphology of the suspended particles have also been discussed (Ivanova et al. 2004, 2006, 2007, 2008; Tchapkanov 2008; Tchapkanov and Zareva 2008). The positive ESI mass spectra were recorded on a Fisons VG autospect.

The UV spectroscopic data were obtained on Evolution 300 spectrometer in a 1-cm quartz cell in ethanol solution (Uvasol, Merck).

Table 1 Crystal and refinement data for the title compound (**1**)

Empirical formula	$(C_8H_{12}N)(C_4HO_4)\cdot 0.5\ H_2O$
M_r	488.48
T (K)	110 (2)
λ (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.921 (2)
b (Å)	9.032 (2)
c (Å)	25.327 (7)
β (°)	98.84 (2)
Volume (Å^3)	2,468.6 (10)
Z	8
ρ_{calc} (mg m^{-3})	1.314
μ (mm^{-1})	0.101
F (000)	1,032
Crystal size (mm)	0.29 × 0.13 × 0.15
θ Range for data collection	$2.78 \leq \theta \leq 25.00$
Reflections collected/unique	33,581/4,332 ($R_{int} = 0.076$)
Observed reflections [$I > 2\sigma$ (I)]	2,009
Goodness-of-fit on F^2	0.883
R_1 [$I > 2\sigma$ (I)]	0.066
wR_2 (all data)	0.180
Residuals (e Å^{-3})	0.57/−0.41

Synthesis

The title compound (**1**) was synthesized by mixing 2-(phenylethyl)amine (0.122 g, 1.00 mmol) with squaric acid (0.111 g, 0.97 mmol) dissolved in 10 ml water. The resulting mixture was continuously stirred for 4 h at 30°C. Colorless crystals were obtained after ca. 1 week when the solvent was allowed to evaporate slowly. The product was filtered off and air-dried. The most intensive signal in the positive ESI mass spectrum is that of the peak at m/z 123.66, corresponding to the singly charged cation

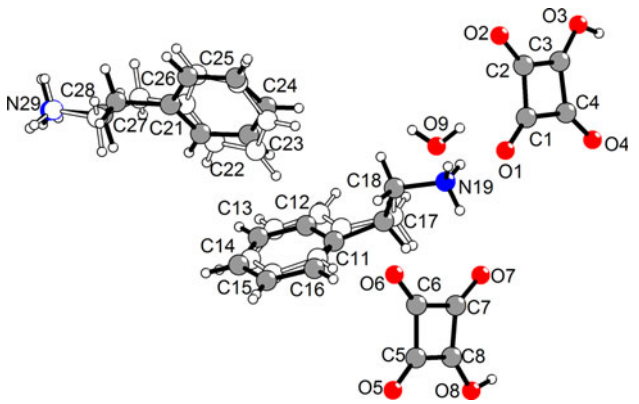


Fig. 1 Representation of the asymmetric unit of the title compound (**1**) showing the atom labeling scheme and illustrating the disorder of the cations

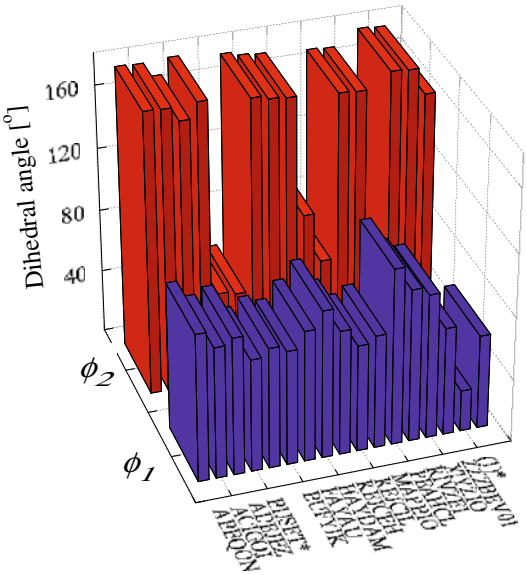


Fig. 3 3D graph of ϕ_i (i = 1, 2, Scheme 1) in different conformers of crystallographically determined 2-(phenylethyl)ammonium salts: (**1**) = 2-(phenylethyl)ammonium hydrogensquarate hemihydrate; (Hlel and Smiri 1999; Huh et al. 2006; Rademeyer et al. 2006; Abdi et al. 2004, 2005; Ishida et al. 1983; Ebina et al. 1994; Willett 1990; Mitzi 1999; Mitzi et al. 2002; Tsoucaris 1961; Groh et al. 1997); crystal structures with two crystallographically non-equivalent molecules in the unit cell (the name definition of the CCDC code is used for comparing compounds)

$[C_8H_{12}N]^+$ with a molecular weight of 123.19. The negative ESI mass spectrum shows a peak at *m/z* 113.55 corresponding to singly charged $[C_4HO_4]^-$ with a molecular weight of 113.06.

Results and discussion

The title compound (**1**) crystallizes monoclinic in the space group $P2_1/c$ with all atoms occupying general positions. Figure 1 depicts the asymmetric unit. The crystal structure comprises two crystallographically independent 2-(phenylethyl)ammonium cations and hydrogensquarate anions and a co-crystallized water molecule. Molecular geometry parameters lie within the expected ranges. The 2-(phenylethyl)ammonium cations are both disordered over two sites. The hydrogensquarate anions form common hydrogen-bonded α-chains (Koleva et al. 2009b) running along the crystallographic *a* axis direction with O3-H2···O5 ($x + 1$, $y - 1$, z) and O8-H8···O2 (x, $y + 1$, z) distances of 2.470(3) and 2.474(3) Å, respectively. Two α-chains are stacked via $\pi\cdots\pi$ interactions in the *c* axis direction and are connected by hydrogen bonding interactions of the co-crystallized water molecules with O9-H9A···O2 ($-x + 1$, $-y$, $-z$) and O9-H9B···O2 (x, $y - 1$, z) distances of 2.837(3) and 2.817(3) Å, respectively. The ammonium groups form hydrogen bonds to the hydrogensquarate anions as well to the water molecules with N–H···O distances in the range

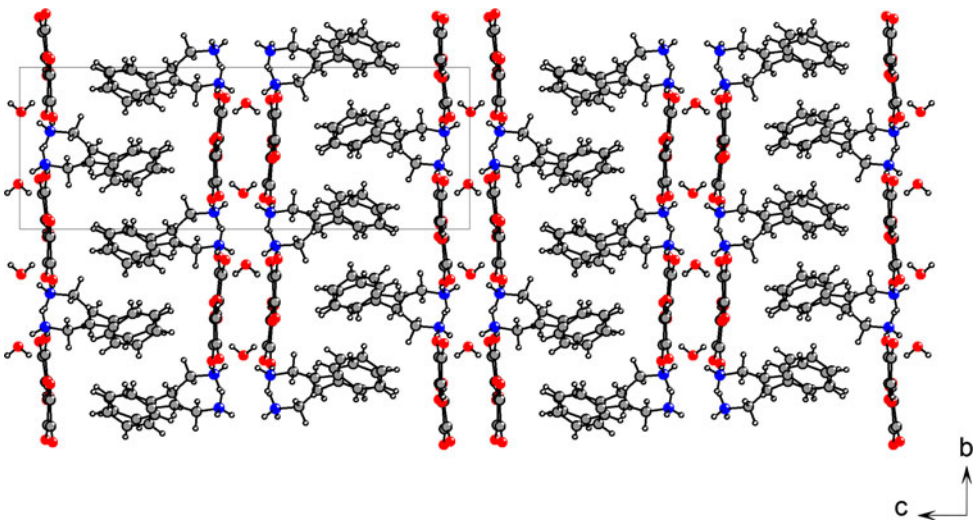


Fig. 2 Projection of the crystal structure of **1** along the *a* axis direction. The disorder of the cations is not shown for clarity

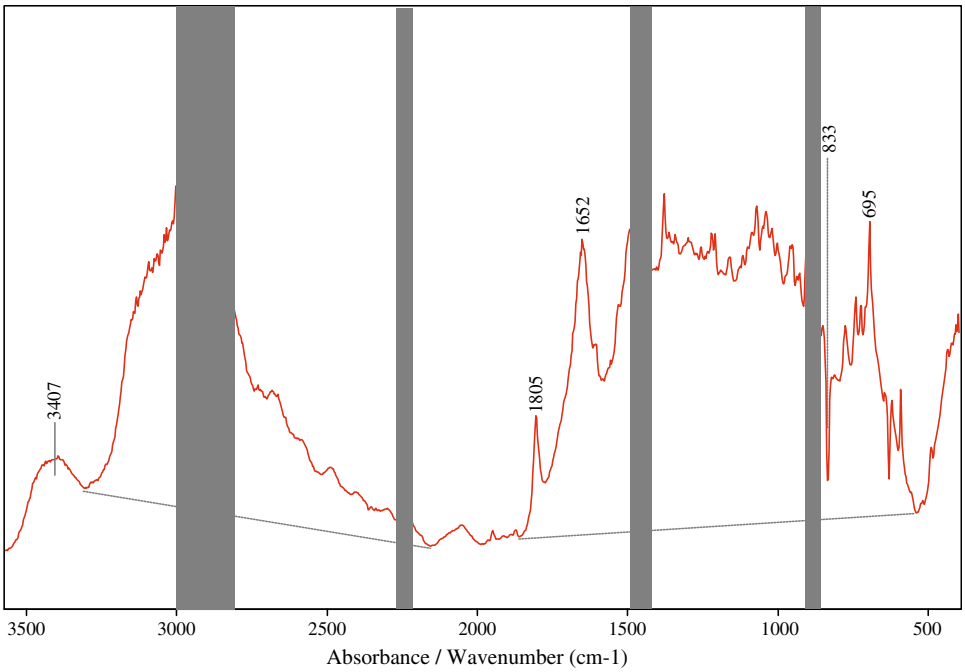


Fig. 4 Non-polarized IR-(1) and difference IR-LD (2) spectra of 2-(phenylethyl)ammonium hydrogensquarate hemihydrate

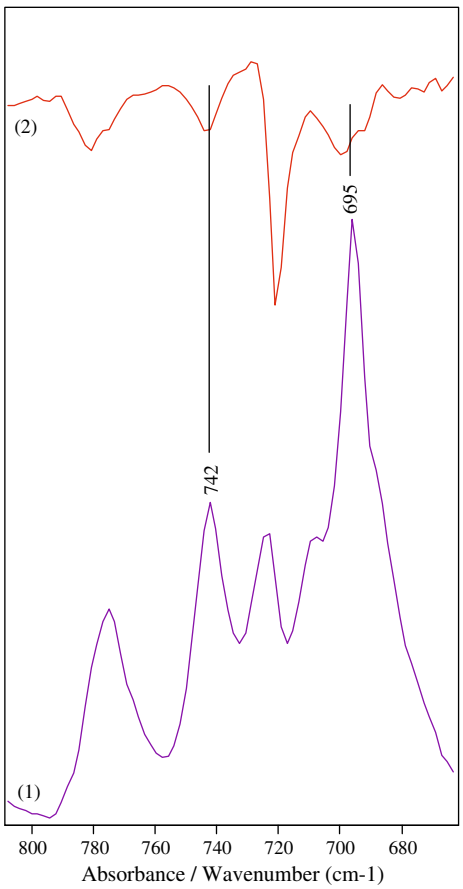


Fig. 5 Non-polarized IR-(1) and reduced IR-LD spectrum (2) of (**1**) after the elimination of the band at 695 cm^{-1}

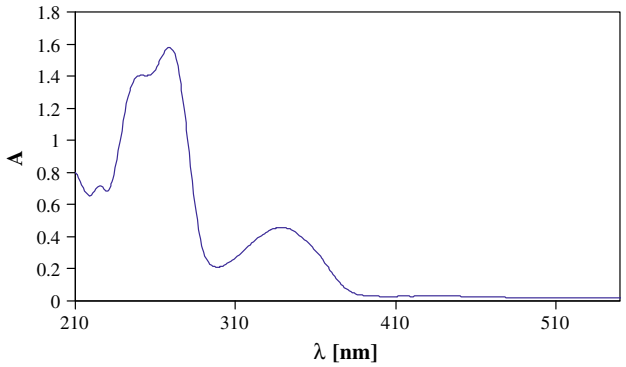


Fig. 6 UV spectrum of (**1**) in ethanol

2.782(9)–2.992(9) Å. This leads to the formation of 2D hydrogen-bonded sheets extending in the *ab* plane, which are stacked in the *c* axis direction (Fig. 2). Similar to the cation in the previously reported crystal structure of bis(tyrammonium) sulfate dihydrate (Kolev et al. 2009c), the 2-(phenylethyl)ammonium cations in **1** exhibit pseudo *T* and *G trans* configurations. In other (2-phenylethyl)ammonium salts (Fig. 3), *T trans* conformers are generally observed. In our case, one of the cations in the structure exhibits the lowest recorded value of the ϕ_1 (Scheme 1) dihedral angle leading to the *pseudo G trans* conformer, which is a unique case (Fig. 3), but typical for tyrammonium cations in the crystals. In the unit cell, the mean planes of the phenyl rings of the crystallographically non-equivalent cations are tilted at an angle of ca. 75.4° to one another.

The interpretation of the IR spectrum of compound studied is difficult within the whole middle IR-spectroscopic region, due to the strong overlapping effects of the bands corresponding to stretching OH modes (ν_{OH}) of hydrogensquarate anions and water, with the highest frequency maximum being at 3,407 cm^{-1} (Fig. 4). The Evan's hole effect of this hydrogen bonded system is observed at 833 cm^{-1} (Fig. 2) (Koleva et al. 2009b). The bands at 1,805 and 1,652 cm^{-1} are typical for the $\nu^{s}_{C=O}$ and $\nu^{as}_{C=O}$ vibrations of the hydrogensquarate anions. In the IR spectrum in Fig. 4, we can define the band of out-of-plane vibrations of benzene ring of the cation within the 800–600 cm^{-1} IR region. The elimination of the band at 695 cm^{-1} (**4**-γ_{Ar}) leads to disappearance of the maximum at 742 cm^{-1} (**11**-γ_{CH}) of same symmetry class (Fig. 5). However, the observed multicomponent character of these bands is a result of the Davydov splitting effect (Koleva et al. 2009b), typical for IR spectra of crystals with differently oriented molecules in the unit cell.

The UV spectrum of **1** in ethanol (Fig. 6) is characterized by series of bands of the benzene fragment in the β-phenylethylammonium cation, i.e. K- and B-bands at 218 nm ($\varepsilon = 12\ 312$ l $mol\ l^{-1}\ cm^{-1}$) and 260 nm ($\varepsilon = 988$ l $mol^{-1}\ cm^{-1}$). The low intensity maximum at 330 nm ($\varepsilon = 762$ l $mol^{-1}\ cm^{-1}$) belongs to the $n \rightarrow \pi^*$ transition of the hydrogensquarate species.

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References

Abdi M, Zouari F, Salah AB (2004) catena-(bis(b-Phenylethylammonium) (m2-chloro)-tetrachloro-thallium). Solid State Sci 6:739

Abdi M, Zouari F, Chniba-Boudjada N, Bordet P, Ben Salah A (2005) 2-(Phenylethyl)ammonium tetrabromothallate(iii). Acta Crystallogr 61E:m240

Blessing RH (1995) An empirical correction for absorption anisotropy. Acta Cryst A51:33

Ebina A, Nishikiori S, Iwamoto T (1994) bis(2-Phenylethylammonium) tetracyano-nickel(ii) *N*,*N*-dimethylaniline solvate. Chem Commun 233

Groh M, Spengler R, Burzlaff H, Zouari F, Salah AB (1997) catena-(bis(b-Phenylethylammonium) bis(m2-chloro)-dichloro-cadmium). Acta Crystallogr 53C:1199

Hlel F, Smiri L (1999) bis(2-Phenylethylammonium) dihydrogendiphosphate. Solid State Sci 1:321

Holmes C, Moak J, Eldadah B, Zimmerly E, Sharabi Y, Goldstein DS (2005) Dopamine contamination of infused tyramine. Clin Chem 51(9):1733

Huh Y, Kim J, Kweon S, Kuk W, Hwang C, Hyun J, Kim Y, Park Y (2006) bis(Phenylethylammonium) tetrabromo-zinc(ii). Curr Appl Phys 6:219

Ishida T, Yamamoto K, Inoue M (1983) 1-(2-Carboxyethyl)-uracil phenethylamine. Bull Chem Soc Jpn 56:955

Ivanova BB, Arnaudov MG, Bontchev PR (2004) Linear-dichroic infrared spectral analysis of Cu(I)-homocysteine complex. Spectrochim Acta 60(4)A:855

Ivanova BB, Tsalev DL, Arnaudov MG (2006) Validation of reducing-difference procedure for the interpretation of non-polarized infrared spectra of *n*-component solid mixtures. Talanta 69:822

Ivanova BB, Simeonov VD, Arnaudov MG, Tsalev DL (2007) Linear-dichroic infrared spectroscopy—validation and experimental design of the orientation technique as suspension in nematic liquid crystal. Spectrochim Acta 67A:66

Kolev T, Koleva BB, Spiteller M (2007) Spectroscopic, theoretical and structural characterization of hydrogensquarates of L-threonyl-L-serine and L-serine. Amino Acids 33:719

Kolev T, Zareva S, Mayer-Figge H, Spiteller M, Sheldrick WS, Koleva BB (2009a) L-Leucinamide hydrogensquarate: spectroscopic and structural elucidation. Amino Acids (in press). doi: 10.1007/s00726-008-0189-4

Kolev T, Koleva BB, Spiteller M, Sheldrick WS, Mayer-Figge H (2009b) Synthesis, spectroscopic and structural elucidation of sympathomimetic amine, tyrammonium dihydrogenphosphate. Amino Acids 36:185

Kolev T, Spiteller M, Koleva B (2009b) Spectroscopic and structural elucidation of amino acid derivatives and small peptides: experimental and theoretical tools. Amino Acids (mini review). doi:10.1007/s00726-008-0220-9

Kolev T, Koleva B, Spiteller M, Sheldrick WS, Mayer-Figge H (2009d) Synthesis, spectroscopic and structural elucidation of tyrosinamide hydrogensquarate monohydrate. Amino Acids 36:195

Kolev T, Koleva B, Seidel RW, Mayer-Figge H, Spiteller M, Sheldrick W (2009e) Tyrammonium 4-nitrophthalate dihydrate: structural and spectroscopic elucidation. Amino Acids 36:29

Koleva BB, Kolev T, Simeonov V, Spassov T, Spiteller M (2008) Linear polarized IR-spectroscopy of partial oriented solids as a colloid suspension in nematic liquid crystal—new tool for structural elucidation of the chemical compounds. J Inclusion Phenomenon 61:319

Koleva B, Spiteller M, Kolev T (2009a) Polarized spectroscopic elucidation of *N*-acetyl-L-cysteine, L-cysteine, L-cystine, L-ascorbic acid and a tool for their determination in solid mixtures. Amino Acids. doi:10.1007/s00726-008-0189-4

Koleva BB, Kolev T, Seidel RW, Spiteller M, Mayer-Figge H, Sheldrick WS (2009b) Self-assembly of hydrogensquarates: crystal structures and properties. J Phys Chem A 113:3088

Mitzi DB (1999) catena-(bis(bis(2-Phenylethylammonium) bis(m2-chloro)-dichloro-lead(ii))). J Solid State Chem 145:694

Mitzi DB, Medeiros DR, Malenfant PRL (2002) catena-(bis((2-Phenylethyl)ammonium) tetraiodostannate perfluorobenzene solvate). Inorg Chem 41:2134

Rademeyer M, Billing DG, Lemmerer A (2006) catena-(2-Phenylethylammonium (m3-chloro)-dichloro-mercury(ii)). Acta Crystallogr 62E:m1716

Sheldrick GM (2008) A short history of SHELX. Acta Cryst A64:112

Tchapkanov A (2008) 1, 8-Dinitro-4, 5-dihydroxyantraquinone—solid-state linear-polarized IR-spectroscopy of oriented colloid particles as a suspension in nematic liquid crystal. Spectrochim Acta 71A:1481–1484

Tchapkanov A, Zareva S (2008) alpha-Pyridoin tautomerism—reducing difference infrared spectral analysis. Polish J Chem 83:467–476

Tsoucaris G (91961) b-Phenylethylamine hydrochloride. Acta Crystallogr 14:909

Willett RD (1990) catena-(bis(2-Phenylethylammonium) bis(m2-chloro)-dichloro-copper(ii)). Acta Crystallogr 46C:565

Yesilel OZ, Odabasoglu M, Ölmez H, Büyükgüngör O (2006) Supramolecular organization of organoammonium squarates. Z Naturforsch 61b:1243–1248

Yesilel OZ, Pasaoglu H, Yilan O, Büyükgüngör O (2007) Syntheses, spectral, thermal and structural characterization of 2-hydroxyanilinium and 2-amino-3-hydroxypyridinium squarates. Z Naturforsch 62b:823–828

Yesilel OZ, Odabasoglu M, Büyükgüngör O (2008) Supramolecular squarate and hydrogensquarate compounds with 4-amino-1, 2, 4-triazole, 2-aminothiazole and 2-aminobenzimidazole. J Mol Struct 874:151–158

Zouari F, Salah AB (2004) bis(2-Phenylethylammonium) tetrabromocadmium. Solid State Sci 6:847–860