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(2-Azoniaethyl)guanidinium dichloride – A promising phase-matchable NLO material employing a simple hydrogen bond acceptor in its structure

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ABSTRACT

(2-Azoniaethyl)guanidinium dichloride (**AEGCl**), a salt of a functional guanidine derivative, was prepared and characterised by single-crystal and powder X-ray diffraction analysis, elemental analysis and by NMR, UV–Vis and vibrational spectroscopy. The crystal structure of **AEGCl**, which crystallises with the symmetry of the chiral space group $P2_1$, is built up *via* simple and multicentred N—H···Cl hydrogen bonds and further supported by C—H···Cl contacts. The compound is thermally robust and exhibits promising NLO properties with powder SHG efficiency better than potassium dihydrogen phosphate. In contrast, (2-azoniaethyl)guanidinium salts with inorganic oxoanions such as (2-azoniaethyl)guanidinium dinitrate and diperchlorate, synthesised for a comparison, form centrosymmetric crystal assemblies having several structurally independent "molecules" in their structures.

1. Introduction

The search for new non-linear optical (NLO) materials is nowadays motivated by their wide applications ranging from harmonic frequency generation, sum- and difference-generation, light-by-light and stimulated light scattering, optical power limiting to optical computing and data storage [1]. Highly polarisable organic molecules [2] are among prospective building blocks for crystal engineering [3,4] of NLO materials. In this regard, H-bonded salts prepared from suitable organic molecules are particularly attractive because the organic molecules (cations) in their structures typically act as the carriers of the non-linear optical properties, while the anions can aid in suppressing the preferred centrosymmetric arrangement through formation of hydrogen-bonded arrays and, furthermore, remarkably increase chemical and thermal stability of the resulting materials. This concept was successfully employed in the preparation of non-centrosymmetric crystalline materials containing hydrogen-anions derived from inorganic acids that act as H-bond donors [5–7]. Besides, there has been reported a considerable number of analogous materials containing fully deprotonated inorganic anions, which can only act as H-bond acceptors [7–9]. Building upon this strategy, we have decided to evaluate the structural role of the simplest common inorganic H-bond acceptor – the chloride anion – in a family of selected guanidine-based materials, whose crystal packing will be thus mainly influenced by the nature of the used cation.

The guanidine molecule and especially its corresponding monoprotonated cation represent interesting examples of flat rigid molecules showing extensive π-electron delocalisation [10]. Guanidinium(1+) cation is an almost ideal example of an octupolar (*i.e.*, exhibiting three-fold rotational symmetry) building block for the design of molecular NLO materials [11,12]. In addition to salts resulting from inorganic and organic acids and unsubstituted guanidine [13–15], there have been reported several examples of unique crystalline materials based on guanidine derivatives such as arginine salts [16] showing excellent NLO properties as well as interesting molecular crystals resulting from biguanide [7,17], carbamoylguanidine [18,19] and aminoguanidine [20,21]. The attractiveness of this type of materials arises mainly from various $\chi^{(2)}$ and $\chi^{(3)}$ nonlinear laser effects they often exhibit [12,22].

In this contribution, we report the synthesis and detailed characterisation of (2-azoniaethyl)guanidinium dichloride, a novel stable crystalline material showing favourable non-linear optical properties.

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2. Experimental

2.1. Materials and methods

Starting *N*-Boc-1,2-diaminoethane was purchased from Alfa-Aesar. Methanol was dried with a Pure Solv 5 solvent purification system (Innovative Technology, USA). Other reagents and solvents were used as received from commercial sources (Sigma-Aldrich, solvents from Lachner, Czech Republic). NMR spectra were recorded with a Varian Unity INOVA 400 spectrometer (^{1}H at 399.95 MHz, ^{13}C at 100.58 MHz) at 298 K. Chemical shifts are given relative to internal tetramethylsilane. Electrospray ionisation (ESI) mass spectra were obtained on a Bruker Esquire 3000 (low resolution) or a Waters Q-Tof micro (high resolution) spectrometers using solutions in HPLC-grade methanol.

FTIR spectra of polycrystalline samples were recorded on a Thermo Nicolet Magna 6700 FTIR spectrometer (4 cm^{-1} resolution, Happ–Genzel apodization) in the 400–4000 cm^{-1} range using transmission (Nujol and Fluorolube mulls, KBr windows) and DRIFTS (samples diluted by grinding with IR spectroscopy-grade KBr) techniques. FT Raman spectra of polycrystalline sample were recorded on a Thermo Nicolet Magna 6700 FTIR spectrometer equipped with a Nicolet Nexus FT Raman module (4 cm^{-1} resolution, Happ-Genzel apodization, 1064 nm Nd:YVO_4 laser excitation, 450 mW power at the sample) in the range 150–3700 cm^{-1}.

Powder X-ray diffraction patterns were measured at the room temperature using a Philips X'pert PRO MPD diffractometer (Bragg–Brentano geometry, ultrafast X'Celerator detector and Cu Kα radiation, λ = 1.5418 Å). The data were analysed by FullProf software [23]. The theoretical diffraction patterns were calculated from the single-crystal X-ray diffraction data using PLATON program [24].

DSC measurements were carried out with Perkin Elmer Pyris Diamond DSC and DSC 7 instruments in the range 90–490 K (nitrogen and helium atmosphere was used above and below 298 K, respectively; heating rate: 10 K min^{-1}). Approximately 20 mg of a finely ground sample was placed in a hermetically sealed aluminium pan.

UV–Vis spectrum of **AEGCl** was recorded on an Agilent Cary 4000 UV–Vis spectrometer equipped with a diffuse reflectance accessory (Internal DRA-900) in the spectral range 190–900 nm with 0.5 nm resolution. A powdered sample was placed between two QS windows.

2.2. Computational details

Geometry optimisation of selected isolated cations derived from guanidine, aminoguanidine and (2-aminoethyl)guanidine (Fig. 1) were performed (Gaussian 09W software [25]) using the closed-shell restricted density functional theory (DFT) method using Becke's three-parameter hybrid functional [26] combined with the Lee–Yang–Parr correlation functional (B3LYP) [27] with the 6-311+G(d,p) basis set, applying tight convergence criteria and an ultrafine integration grid. The choice of this basis set was due to its flexibility and the fact that diffuse *p* function on the hydrogen atoms tends to compensate the anharmonic effects of the CH and NH stretches [28]. Furthermore, this basis set allows for a direct comparison with the results of previous studies [18,19,29]. The geometry optimisations, also yielding the molecular energies, were followed by calculations of the first hyperpolarisability components (Table 1). The visualisation of the results was carried out with the GaussView [30] program package.

2.3. X-ray structure determination

Full-set diffraction data ($\pm h \pm k \pm l$; θ_{max} = 27.5°, data completeness = 96.9%) were collected with a Kappa CCD (Nonius) diffractometer equipped with an Apex II CCD detector (Bruker) and a Cryostream Cooler (Oxford Cryosystems) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and were corrected for absorption by the methods incorporated in the diffractometer software (multi-scan routine [31], transmission coefficients in the range 0.77–0.90). The phase problem was solved by direct methods (SHELXS97 [32]) and the structure was refined by full-matrix least-squares routine based on F^2 (SHELXL97 [32]). The non-hydrogen atoms were refined with anisotropic displacement parameters. The CH hydrogens were included in their calculated positions and refined as riding atoms while the hydrogen atoms residing on the nitrogen atoms were identified on the difference electron density maps and refined similarly with U_{iso}(H) set to 1.2U_{eq}(N).

Selected crystallographic data are as follows: $C_3H_{12}N_4Cl_2$, M = 175.07, monoclinic, space group $P2_1$ (no. 4), a = 4.4825(5) Å, b = 7.2665(8) Å, c = 12.6326(13) Å, β = 91.700(3)°, V = 411.29(8) Å^3, T = 150(2) K, Z = 2, 2620 diffractions were measured of which 1576 were independent (R_{int} = 1.69%) and 1440 observed [$I > 2\sigma(I)$ criterion]. The final R and $wR(F^2)$ were 2.27% and 4.70% for the observed diffractions, and 2.49% and 4.75% for all data. Flack parameter = −0.03(6). Residual electron density: 0.23 and −0.22 e Å^{-3}.

Geometric data and all structural drawings were obtained with a recent version of the PLATON program [24]. The numerical values were rounded with respect to their estimated deviations (ESDs). Parameters for atoms in constrained positions are given without ESDs.

2.4. SHG measurements

SHG measurements on **AEGCl** were performed using the modified Kurtz-Perry powder method [33]. The samples were irradiated with 160 fs laser pulses generated at an 82 MHz repetition rate by a Ti:sapphire laser (MaiTai, Spectra Physics) at 800 nm. For quantitative determination of the SHG efficiency, the intensity of back-scattered laser light at 400 nm generated in the sample was measured by a grating spectrograph with a diode array (InstaSpect II, Oriel) and the signal was compared with that produced by a potassium dihydrogen phosphate (KDP) standard. The initial experiments were performed on a powdered sample (100–150 μm particle size) loaded into a 5 mm glass cell by using a mechanical vibrator. The measurements were repeated on different areas of the same sample and the results were averaged. This experimental procedure minimizes the signal fluctuations induced by sample packing. Finally, the measurements were performed also with size-fractioned samples (particle size: 25–45, 45–63, 63–75, 75–100, 100–125, and 125–150 μm).

2.5. Synthesis of Boc-protected (2-aminoethyl)guanidine

A two-necked round-bottom flask was charged with *N*-Boc-1,2-diaminoethane (2.00 g, 12.5 mmol) and a stirring bar, flushed with argon and sealed with a rubber septum. The starting material was dissolved in absolute methanol (16 mL) and the resulting solution was treated with a mixture of *O*-methylisourea hydrogen sulphate (3.89 g, 22.6 mmol), water (16 mL) and triethylamine (4.2 mL, 44 mmol) while stirring and cooling in an ice bath. The colour of the reaction mixture changed from colourless to light yellow upon the addition. After the addition, the reaction mixture was stirred at room temperature overnight and evaporated under vacuum. The oily residue was triturated with absolute ethanol (2 × 20 mL under sonication) to afford a white solid, which was mixed with absolute ethanol (30 mL) and stirred at 273 K (ice bath) for another 1 h. Then, the solid product was filtered off, washed with absolute ethanol and dried under vacuum to afford the crude reaction