Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Yutronic, N. , Merchán, J. , Jara, P. , Manríquez, V. , Wittke, O. and González, G.(2004) 'Single-crystal Anisotropic Proton Conductivity in the Clathrate of the Hydrogen-diquinuclidine Ion Inserted in a Polyanionic Thiourea-chloride Matrix', Supramolecular Chemistry, 16: 6, 411 — 414

To link to this Article: DOI: 10.1080/10610270412331286003

URL: http://dx.doi.org/10.1080/10610270412331286003

Supramolecular Chemistry, September 2004, Vol. 16 (6), pp. 411–414

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Single-crystal Anisotropic Proton Conductivity in the Clathrate of the Hydrogen-diquinuclidine Ion Inserted in a Polyanionic Thiourea–chloride Matrix

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Received (in Southampton, UK) 3 November 2003; Accepted 31 January 2004

The anisotropic proton conductivity of a large-sized single crystal of the supramolecular, commensurate host–guest inclusion compound constituted by a polyanionic thiourea–chloride matrix defining channels in which the diquinuclidinium cations $[Q_2H]^+$ are hosted is reported. Specimens in the millimetre scale display an anisotropy factor of about 100, with electrical conductivities along molecular channels of the order of $10^{-4}\,S\,cm^{-1}$ at room temperature.

Keywords: Inclusion compounds; Thiourea; Semiconductor crystals; Anisotropic properties

INTRODUCTION

Anisotropic conducting materials are of special interest because of their potential in the development of new, more efficient, miniature devices useful, for instance, in the fields of microelectronics and communications. In the search for anisotropic compounds relevant to such applications, obtaining ordered solids as oriented phases or as single crystals of appropriate size is an important but not always easy task. Molecular engineering, chemical recognition and the formation of low-dimension inclusion compounds are appropriate methods for achieving ordered phases [1]. The latter is indeed one of the more prominent properties of classical clathrates, which can lead to large anisotropic crystals. However, clathrates are generally insulators with no appreciable ionic or electronic conductivity.

Thiourea forms crystalline host–guest inclusion compounds in which a variety of guest molecules of appropriate size and shape are inserted in van der Waals cavities arising from an extensive hydrogen-bonded network of the thiourea molecules [2–9]. Although most of the reported thiourea clathrates are covalent species, there are a few examples of ionic compounds [10–15], including the salt $[(\text{quinuclidine})_2H]^+[(\text{thiourea})_2Cl]^-$, which we described recently [15]. In the present paper we report the anisotropic electrical conductivity of large-sized single crystals of this salt.

EXPERIMENTAL

The compound $[(\text{quinuclidine})_2H]^+[(\text{thiourea})_2Cl]^-$ was prepared by mixing stoichiometric amounts of quinuclidine (0.730 g, 6 mmol) and quinuclidine hydrochloride (0.970 g, 6 mmol) with a solution of thiourea (1.00 g, 13 mmol) in methanol. Mp 170°C. Anal. Found (Calcd.) for $C_{16}H_{35}ClN_6S_2$(%): C, 46.56 (46.75); H, 8.55 (8.53); N, 20.44 (20.46). Infrared spectra were measured on an FTIR Perkin Elmer 2000 instrument. Principal absorptions (cm^{-1}): 3341 s, 3283 s, 3180 sh, 3139 s, 2937 m, 2866 m, 2810 sh, 2690 w, 2164 m, 1610 s, 1489 w, 1485 m, 1437 s, 1333 m, 1280 w, 1165 m, 1084 m, 1048 m, 1003 w, 978 w, 865 w, 8825 w, 770 m, 744 m, 667 m, 601 s, 549 w, 493 s. Single-crystal diffraction analysis was carried out using a Siemens R3m/v X-ray diffractometer, with graphite-filtered Mo Kα radiation. Crystal dimensions: $0.44 \times 0.46 \times 0.54$ mm. Crystal data for one $C_{16}H_{35}ClN_6S_2$ unit, $M = 205.5$: monoclinic symmetry with space group ($C2/c$)

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ISSN 1061-0278 print/ISSN 1029-0478 online
DOI: 10.1080/10610270412331286003

(N 13); $a = 13.355(4)$, $b = 11.386(3)$, $c = 14.573(3)$ Å, $\beta = 99.13(3)°$, $V = 2187$ Å^3, $Z = 8$, $D_c = 1.248\,\mathrm{g\,cm^{-3}}$, $F(000) = 888$, $\mu(\mathrm{Mo\,K\alpha}) = 0.378\,\mathrm{mm^{-1}}$. Final reliability factors were $R = 0.036$ and $R_w = 0.048$ [17]. Electrical conductivities were measured by AC-impedance analysis in the $1–10^5$ Hz range using a PARC Electrochemical Impedance Analyser model 6310. Electrical contacts were provided by gold layers of thickness *ca* 0.2 μm evaporated onto both sides of the crystal or pellet. Robust single-crystal specimens were obtained by immersing the crystal in a block of epoxy resin, leaving uncovered only those sides used for the electrical contacts. Polycrystalline pellets were obtained by pressing the powder in a 0.65-cm diameter cylindrical die under pressure of 10.21 MPa. The measurement error of the instrument was 10^{-11} S.

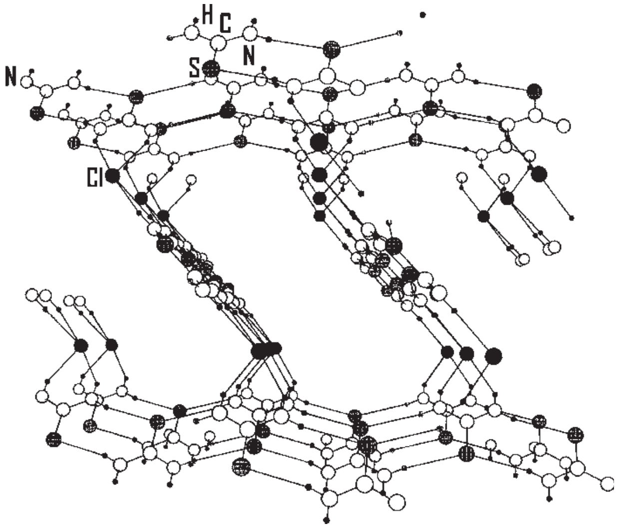

FIGURE 1 Transverse section of the $[(Q)_2H]^+[(TU)_2Cl]^-$ structure, showing hydrogen-bond linking thiourea units forming near-planar ribbons.

RESULTS AND DISCUSSION

Crystal Structure

Preliminary results on the salt $[(\mathrm{quinuclidine})_2\mathrm{H}]^+ \times [(\mathrm{thiourea})_2\mathrm{Cl}]^-$ have been reported previously [15]. The importance of the molecular arrangement in this supramolecular compound for understanding the anisotropic behaviour, observed macroscopically in the conductivity determinations described here, still deserves some additional comments. The complete structural determination of the product shows the presence of a supramolecular structure, which may be described as a host–guest inclusion compound in which a polyanionic matrix, made by hydrogen-bonded thiourea chains connected through chloride bridges, defines channels in which the diquinuclidinium $[Q_2H]^+$ counterions are hosted.

As shown in Fig. 1, near-planar thiourea molecular units are linked to each other by hydrogen bonds through their N—H protons *cis* to the sulfur atoms, generating thiourea ribbons. There is no direct connection between parallel thiourea ribbons; however, stacks of such ribbons are joined to perpendicular stacks, not directly, but through chloride ions. Such an arrangement defines cavities approximately 9.6 by 13.4 Å, with a cross-section of about 137 Å^2, in which the $[Q_2H]^+$ complex species are stacked with a periodicity of 11.3 Å (Fig. 2). The $[Q_2H]^+$ complex appears to be held in the host cavities only by weak van der Waals interactions. Indeed, the distances between the active centres in the complex (N atoms and N—H protons) and the matrix are always longer than 3 Å. Nevertheless, these interactions are strong enough to prevent free rotation of the cation.

The guest species $[Q_2H]^+$ corresponds to an adduct of a heterocyclic base with its conjugated cation in a symmetric linear arrangement $[\mathrm{Q—H—Q}]^+$, similar to one reported for diquinuclidinone [17]. The considerably short N—H distance (1.332 Å) in the compound described here is similar to that determined by neutron diffraction studies for the perchlorate salt of the diquinuclidinium homoconjugated cation [d(N—H) = 1.317 Å, ∠N—H—N = 175.7°] [17]. Some longer N—H distances are found for the layered compounds $[(\mathrm{quinuclidine})_2\mathrm{H}]^+[(\mathrm{urea})_2\mathrm{Br}]^-$ and $[(\mathrm{quinuclidine})_2\mathrm{H})]^+[(\mathrm{urea})_2\mathrm{I}]^-$ (1.360 and 1.380 Å, respectively) [18]

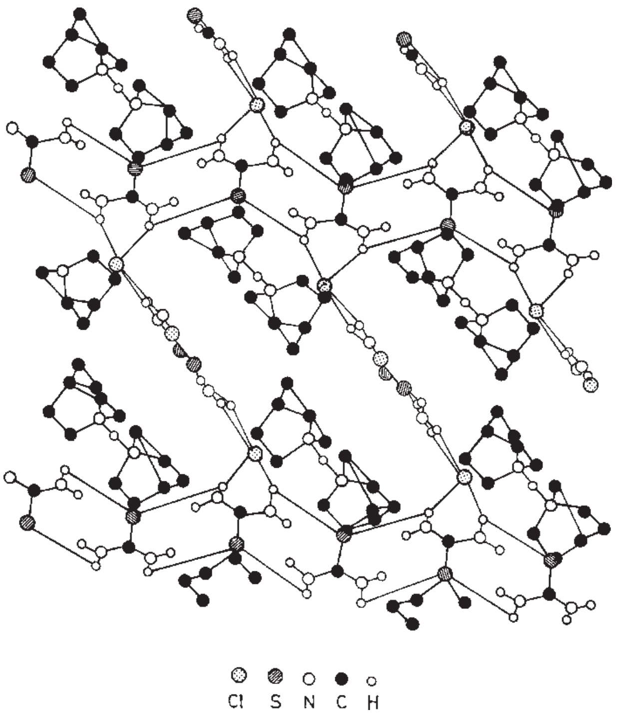

FIGURE 2 Transverse section of the $[(Q)_2H]^+[(TU)_2Cl]^-$ structure, showing cavities defined by the thiourea–chloride network, and position of the diquinuclidinium ions inside the cavities.

TABLE I Anisotropic electrical conductivity of single crystals of $[(Q)_2H]^+[(TU)_2Cl]^-$ in the presence of moisture[a]

	Electrical conductivity ($S\,cm^{-1}$)		
Crystal orientation[b]	25°C	40°C	60°C
Parallel	$(2.19 \pm 0.13) \times 10^{-4}$	$(4.08 \pm 0.23) \times 10^{-5}$	$(2.68 \pm 0.15) \times 10^{-5}$
Perpendicular	$(2.42 \pm 0.16) \times 10^{-6}$	$(9.74 \pm 0.63) \times 10^{-7}$	$(2.54 \pm 0.17) \times 10^{-7}$

[a] Conductivity of pressed microcrystalline powder at 25°C: $4.33 \times 10^{-8}\ S\,cm^{-1}$. [b] Parallel and perpendicular to crystal channel.

and for the recently reported bichannel compound $[(quinuclidine)_2H]^+[(urea)_5Cl]^-$ (1.353 Å) [19].

Although the bridging H atom in $[Q_2H]^+$ in $[(quinuclidine)_2H]^+[(thiourea)_2Cl]^-$ appears to be located in the crystallographic symmetry centre, it shows a rather high thermal motion, with the largest principal axis making a 150° angle to the N—N direction. The root-mean-square displacement of the proton along the hydrogen-bond axis is indicative of a disordered arrangement with two closely spaced sites for the bridged hydrogen. Such a dual location for the hydrogen atom is indeed predicted for this kind of system from an *ab initio* study of the $[NH_3—H—NH_3]^+$ complex [20] from which the existence of a double-well potential for proton transfer is deduced. Furthermore, vibrational analysis of this hypothetical species predicts absorption at $668\,cm^{-1}$ for the symmetric N···N stretching mode, and at 2798 and $1260\,cm^{-1}$ for the antisymmetric ion transfer vibrations. Corresponding features are indeed apparent in the IR spectrum of $[Q_2H]^+$, in which a low-frequency continuum threshold at $550\,cm^{-1}$ and another characteristic frequency at $2937\,cm^{-1}$ have been observed [21]. Thus, besides the quinuclidine absorption (at 1866 and $2937\,cm^{-1}$) and the characteristic stretching modes of the thiourea network (observed normally at 1095 and between 3169 and $3367\,cm^{-1}$), a relatively intense absorption band at $2164\,cm^{-1}$ and a weak absorption at $549\,cm^{-1}$ are clearly seen.

Electrical Conductivity

The aim of this work was to study the occurrence of anisotropic transport features in this particular ionic compound. From the structure of the compound discussed above, the occurrence of an anisotropic proton conductor, in which in at least one of the crystalline directions the charge will be transported by proton migration, is expected. As shown in Table I, electric conductivity along the channel axis is significantly higher than that along the perpendicular axis, and both are much greater than in pellets obtained by pressing the microcrystalline powder. The observed anisotropy ratio of approximately 100 should correspond to the difference between migration in two ways, one along the channels, and the other, somewhat more difficult, through the thiourea–chloride network.

A small amount of water, which is not detectable in either elemental microanalysis or TG measurements, is necessary to observe the electrical conductivity in this compound. In fact, under vacuum or in an argon atmosphere, the conductivity of the materials was so low that it could not be measured. Moreover, the presence of moisture is also necessary for obtaining robust pressed pellets. In the absence of moisture, cohesiveness between the crystals is not enough for obtaining self-supporting specimens, regardless of the applied pressure. In the case of single crystals, conductivity is also reversibly switched by the presence of water. The observed conductivity, however, appears to be independent of the degree of humidity. We suggest that in the case of large single crystals the role of water is to repair defects in the relatively fragile lattice, allowing the appearance of the macroscopic, long-range effects. Microcrystalline samples, obtained by pressing the powder in air, show an electrical conductivity of $(4.33 \pm 0.15) \times 10^{-8}\ S\,cm^{-1}$.

The importance of crystalline order for proton transport commented on above is also seen in the dependence of conductivity on temperature. Resistivity increases with increasing temperature, this effect being somewhat more pronounced for parallel conductivity. Apparently, temperature-induced disorder is, in this temperature range, more important for hindering conductivity than the natural increase expected for normal activated proton transport.

Supplementary Data

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 100256. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

Financial support by FONDECYT (Grant 1010891) is gratefully acknowledged.

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