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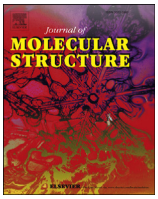

Crystal structure, phase transition and conductivity study of two new organic – inorganic hybrids: $[(CH_2)_7(NH_3)_2]X_2$, X = Cl/Br

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ABSTRACT

Two hybrids 1,7-heptanediammonium di-halide, $[(C_7H_{20}N_2]X_2$,X = Cl/Br crystallize in monoclinic *P*2$_1$/*c*, Z = 4. $[(C_7H_{20}N_2]Cl_2$: a = 4.7838 (2) Å, b = 16.9879 (8) Å, c = 13.9476 (8) Å, β = 97.773 (2)°, V = 1203.58(10) Å^3, D = 1.137 g/cm^3, λ = 0.71073 Å, R = 0.052 for 1055 reflections with $I > 2\sigma(I)$, T = 298(2) K. $[(C_7H_{20}N_2]Br_2$: a = 4.7952 (10) Å, b = 16.9740 (5) Å, c = 13.9281 (5) Å, β = 97.793 (2)°, V = 1203.83(6) Å^3, D = 1.612 g/cm^3, λ = 0.71073 Å, R = 0.03 for 1959 reflections with $I > 2\sigma(I)$ T = 298(2) K. Asymmetric unit cell of $[(C_7H_{20}N_2]X_2$,X = Cl/Br, each consist of one heptane-1,7-diammonium cation and two halide anions. The organic hydrocarbon layers pack in a stacked herring-bone manner, hydrogen bonded to the halide ions. Lattice potential energy is 1568.59 kJ/mol and 1560.78 kJ/mol, and cation molar volumes are 0.295 nm^3 and 0.300 nm^3 for chloride and bromide respectively. DTA confirmed chain melting transitions for both hybrids below T ~ 340 K. Dielectric and ac conductivity measurements ($290 < T$ K < 410; $0.080 < f$ kHz<100) indicated higher conductivity and activation energy of bromide for $T > 340$ K. Cross over from Jonscher's universal dielectric response at low temperatures $T < 340$ K to super-linear power law for $T > 340$ K is observed. At high temperatures halide ion hopping in accordance with the jump relaxation model prevails.

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1. Introduction

Recently, organic-Inorganic hybrid (OI) materials have attracted much attention due to their interesting structure, optical and electrical properties [1]. The class of hybrid materials is very large showing different structures and properties that promise wide applications in different fields. Alkylene-diammonium dihalide hybrids, $[(CH_2)_n(NH_3)_2]X_2$; n = 2, …6 and X = Cl/Br show several interesting structural phase transitions, they mimic lipid bilayer, being solids they provide an excellent model for the study of transport in cell membranes [2]. Besides these hybrids are precursor ligands in transition metal complexes [3] and have structure-directing properties in the synthesis of a number of nanoparticles [4,5]. Room temperature crystal structure determination of the chlorides and bromides where n = 2, 3, 4, 5 and 6 [6–16] crystallize in monoclinic system with space group *P*2$_1$/*c* except for bromide with n = 2 (space group *C*2/*m*), at 100 K [8] and the chloride where n = 5 which is orthorhombic with space group *Pbam* [12]. To the best of our knowledge, no structure analysis or physical properties concerning n = 7 hybrids were reported. This is most likely due to difficulty in growing single crystal of anhydrous 1,7 -heptanediammonium hybrids. It is worth noting that for n = 8 and 10 only hydrated hybrids were obtained [17]. In this article we report synthesis, characterization, single crystal structure analysis, phase transitions and conductivity study of chloride and bromide hybrids where n = 7. Differential thermal scanning (290 K < T < 580 K) and impedance spectroscopy (290 K < T < 410 K) in the frequency range 100 Hz - 100 kHz were used to study the phase transitions and electric transport properties of the two samples 1,7-heptane-diammonium crystals $[(CH_2)_7(NH_3)_2]X_2$, X = Cl/Br, henceforth C7C and C7B.

2. Experimental

Samples were synthesized by adding slight excess 30% HCl/HBr to 1,7- diaminoheptane. The resulting solution is heated to 70 °C for 1 h. Slow cooling to room temperature yields colorless solids. The solids were washed with a 1:1 solution of ethanol and methylene chloride. Samples were re-dissolved in ethanol and re-crystallized twice. Colorless prismatic and needle crystals were grown from

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ethanol solution kept in vacuum desiccator for 6 months, for chloride and bromide hybrids respectively. Chemical analysis and ir absorption spectrum (in the range 400 cm^{-1}–4000 cm^{-1}) were carried out at the micro analysis center at university of Cairo.

The elemental analysis showed the percent of carbon = 39.50% (40.46%), 29.30% (28.78%) and hydrogen = 10.12% (9.701%), 6.50% (6.902%) for C7Cl and C7Br respectively; theoretical values are given in brackets.

The IR spectrum was obtained using FTIR 1650 Perkin Elmer spectrometer. The IR and the chemical analysis results confirmed formation of the two samples with chemical formula $[(CH_2)_7(NH_3)_2]\ X_2$, X = Cl/Br.

Differential thermal scanning (DSC) measurements were carried out on a Shimadzu thermal scanner model DSC-50 at 10 °C/min. Powdered crystals weighing 2.5 mg were used. Measurements were performed in a flow of dry nitrogen gas at a rate of 50 ml/min. The data were calibrated with the melting transition of Indium at 157 °C.

X-ray crystallographic data were collected on Enraf-Nonius 590 Kappa CCD single crystal diffractometer with graphite monochromator using MoKα (λ = 0.71073 Å). The intensities were collected at room temperature using φ-ω-scan mode. The cell refinement and data reduction were carried out using Denzo and Scalepak programs [18]. The crystal structure was solved by the direct method using SIR92 program [19] which revealed the positions of all non-hydrogen atoms and refined by the full matrix least square refinement based on F^2 using maXus package [20]. The temperature factors of all non-hydrogen atoms were refined anisotropically, then hydrogen atoms were introduced as a riding model with C—H = 0.96 and refined isotropically. Molecular graphics were prepared using ORTEP Program [21].

Ac conductivity is measured using computer controlled SR-830 lock-In amplifier. A home built cryostat was used. Temperature was measured using a copper constantan thermocouple. Well ground crystallites were pressed in the form of a disc 1.0 cm in diameter and 1.2 mm thickness under a pressure of 2.4 kPa. The surfaces were coated with Ag paste to ensure good electrical contacts. The sample chamber was evacuated for 12 h prior to measurements to ensure moisture free atmosphere. Several virgin samples were measured to ensure reproducibility of results.

3. Results and discussion

3.1. Crystal structure

The two isomorphous hybrids crystallize in monoclinic $P2_1/c$ with 4 molecules/unit cell each. Lattice spacing are a = 4.7838 (2) Å, 4.79520 (10) Å, b = 16.9879 (8) Å, 16.9740 (5) Å, c = 13.9476 (8) Å, 13.9281 (5) Å, β = 97.773 (2)°, 97.793(2)°, V = 1203.58 (10) $Å^3$, 1203.83 (10) $Å^3$ for chloride and bromide respectively as listed in Table 1 along with data collection parameters and refinement. Table 2 lists the fractional atomic coordinates and equivalent isotropic thermal parameters. Table 3 lists the anisotropic displacement parameters ($Å^2$). The selected bond length and bond angles and dihedral angles are listed in Table 4. Table 5 lists the hydrogen bonds geometry of the two samples.

As can be seen from Table 4, for C7C the chains deviate slightly from planarity. It is expected that as the temperature increases conformation changes will take place, which would lead to phase transitions.

Fig. 1a is an ORTEP view of the atoms where X = Cl/Br and Fig. 1b shows ORTEP view of molecular arrangement in the unit cell of C7B. The cation exists in an ideal fully extended conformation in layers and lies on a mirror plane. The chains extend in a zigzag structure of seven carbon atoms with two NH_3 cations attached at chain ends which are hydrogen bonded to the halide anion. Each two parallel chains are connected to each other forming a couple via halide ion Cl(2)/Br(2). The nearly perpendicular couples are connected via Cl(1)/Br(1). Fig. 1c depicts molecular arrangement and hydrogen bond net-work of C7Cl along a-axis. It reveals the occurrence of four short N—Cl non-bonded contacts, three of these contacts may be ascribed to charge-assisted hydrogen-bond formation and the fourth is a short contact directed approximately along the extension of the C—N bond. Three, H3A, H3B, and H3C, have values within the range of the hydrogen bond distance 2.393 Å, 2.254 Å and 2.289 Å respectively.

Table 1
X-ray data collection parameters and refinement, of C7C and C7B at 298 K.

	a. (C7C)	b. (C7B)
Formula	$C_7H_{20}N_2Cl_2$	$C_7H_{20}N_2Br_2$
M_r	207.784	292.059
Space group	Monoclinic $P2_1/c$	Monoclinic $P2_1/c$
a	4.7838 (2)Å	4.79520 (10)Å
B	16.9879 (8)Å	16.9740 (5)Å
C	14.9476 (8)Å	14.9281 (5)Å
β	97.773 (2)°	97.793 (2)°
V	1203.58 (10)$Å^3$	1203.83 (6)$Å^3$
Z	4	4
D_x	1.147 Mg m^{-3}	1.612 Mg m^{-3}
λ	0.71073	0.71073
$θ_{max}$	27.48°	27.48°
μ	0.70 mm^{-1}	6.69 mm^{-1}
Measured reflections	2756	5182
Independent reflections	3088	2993
Observed reflections	1055	1959
Criterion	I > 3.00 sigma(I)	I > 3.00 sigma(I)
R_{int}	0.052	0.030
H	−6 →6	−6 →6
K	0 → 21	0 → 21
L	−19 → 19	−19 → 19
R(all)	0.185	0.072
R(gt)	0.093	0.041
w*R*(ref)	0.266	0.080
w*R*(all)	0.276	0.086
S(ref)	2.278	1.613
$Δ/σ_{max}$	0.037	0.016
$Δρ_{max}$	0.98e$Å^3$	0.96e$Å^3$
$Δρ_{min}$	−1.32e$Å^3$	−0.81e$Å^3$
w*R*(gt)	0.266	0.080

It is worth mentioning that hydrogen bond length of H—Cl1 is shorter than H—Br1 while the opposite is true where the H—Br2 is slightly longer than the hydrogen bond attached to H—C12 as listed in Table 5. The average bond length N—C = 1.511 (Å), C—C = 1.51 (Å), C—H = 0.960 (Å) are in the acceptable range with previously reported similar hybrids [6–16].

3.2. Lattice potential energy, molecular and cation volume

Estimation of lattice potential energy U (pot) for the general type of the hybrids of M_pX_q can be obtained using Eq. (1) below [22]:

$$U(pot) = \sum n_i z^2 \left[\alpha/V^{1/3} + \beta\right] \tag{1}$$

where α and β are appropriate fitting coefficients chosen according to the stoichiometry of the hybrid, n_i is the number of ions with a charge z_i in the formula unit, V_m is the molecular volume.

For MX_2 (1:2) hybrids, the lattice potential energy is given by Ref. [22]:

$$U(pot) = \left|Z^+\right|\left|Z^-\right|\upsilon\left[\alpha\Big/V^{1/3} + \beta\right] \tag{2}$$

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