Volume 25
Number 4
February 12, 1986

Inorganic Chemistry

Communications

Synthesis, Electrical Properties, and Crystal Structure of the First Organic Metal–Solid Electrolyte Hybrid: $(\mathrm{BEDT\text{-}TTF})_3\mathrm{Ag}_x\mathrm{I}_8$ ($x \sim 6.4$)

Sir:

We have recently reported[1] the crystal and band-electronic structures of (BEDT-TTF)$Ag_4(CN)_5$, (BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene, $C_{10}S_8H_8$, or simply "ET"). This material is the first conducting organic radical-cation salt that contains a *polymeric* anion. The crystal structure consists of a loosely packed *three-dimensional* donor network with interspersed cross-linked anionic silver cyanide "necklaces". In this paper, we describe the preparation, crystal structure, and electrical properties of ET silver iodide, $(ET)_3Ag_xI_8$ ($x \sim 6.4$). This new synthetic metal is the first to possess a truly *two-dimensional* polymeric anion, one which combines the structural features of both an organic electronic conductor and an inorganic solid electrolyte (ionic conductor).

Experimental Methods. $(ET)_3Ag_xI_8$ was prepared electrochemically (Pt electrodes) at a current density of 0.5 $\mu A/cm^2$ from a methylene chloride solution containing 1.4 mM ET (Strem Chemical Co.) and 6 mM $[K(18\text{-crown-}6)]_2Ag_4I_6$ (the crystal structure of this novel cluster compound will be published elsewhere[2]). The use of a crown ether salt, made by refluxing AgI with 1 equiv of 18-crown-6 in a saturated aqueous KI solution, constitutes a new approach to electrocrystallization reactions. The title compound can also be synthesized at a significantly higher current density (10 $\mu A/cm^2$) from a 1,1,2-trichloroethane solution of 1.5 mM ET and 23 mM $(n\text{-}Bu_4N)AgI_2$, made from AgI and $(n\text{-}Bu_4N)I$ in acetonitrile, but the crystals so obtained are of inferior quality.

The crystal structure[3] was solved by use of direct methods and Fourier techniques. It consists of alternating anion and cation donor layers (see Figure 1). The anion, in this case, constitutes a double layer of iodide ions, separated by roughly two ionic radii (2 × 2.16 Å), with rows of disordered silver cations located at interstitial sites. The silver ions are clustered along channels parallel to $3a + b$, inside the iodide double layer (see Figure 2). Most interstitial sites possess distorted-tetrahedral geometry. The refined populations of the 20 silver atom sites add to 6.44 (4). The stoichiometry is further confirmed by the agreement between the absorption coefficient calculated from the composition, 66.6 cm^{-1}, and that obtained from a set of ψ-scans, 62 cm^{-1}.

Nonrandomly disordered silver ions have been found in several ternary silver iodides, e.g., $RbAg_4I_5$,[4] $(C_5NH_6)Ag_5I_6$,[5] or $[(CH_3)_4N]_2Ag_{13}I_{15}$.[6] The high-temperature α-phase of AgI also exhibits similar disorder of the silver ions.[7] All of these salts show high ionic electrical conductivity, α-AgI being historically the first example.[8] Ionic conductors and the structural aspects of silver iodide based solid electrolytes have been reviewed.[9,10]

The network of ET donor molecules contains three molecular stacks. Two are related by inversion symmetry, whereas the third stack is crystallographically independent. The stacks are only loosely packed, with all S···S contacts within a column well above the sum of two sulfur van der Waals radii (~3.6 Å). Much shorter S···S contacts, which are responsible for the electronic conductivity of ET-based conductors,[11] are found between stacks, as shown in Figure 1. The S···S contacts drawn in Figure 1 are in the range 3.35–3.65 Å. This network is well suited for the two-dimensional conductivity usually observed in $(ET)_2X$, X = monovalent anion, materials. The charge calculated for each ET molecule in $(ET)_3Ag_xI_8$ ($x = 6.44$) is $(8 - x)/3 = +0.52$ (2), or $+^1/_2$ within the accuracy of our measurement. All contacts between the ET donor layer and the silver iodide anionic layer are through ethylene group hydrogen–iodide interactions.

Figure 3 shows the resistivity[12] for one of the samples on a log scale vs. temperature below 300 K. The behavior appears rather unusual in that (1) there is a broad region centered on 180 K where the resistivity increases by about a factor of 3 upon cooling, (2) the resistivity is nearly flat down to 100 K, and (3) below 100 K the behavior becomes activated with an activation energy of about 400 K. The following tests at 30, 150, and 300 K failed to discern any ionic component to the conductivity above 0.1%:

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(1) Geiser, U.; Wang, H. H.; Gerdom, L. E.; Firestone, M. A.; Sowa, L. M.; Williams, J. M.; Whangbo, M.-H. *J. Am. Chem. Soc.* **1985**, *107*, 8305.

(2) Wang, H. H.; Donega, K. M.; Geiser, U.; Williams, J. M. to be submitted for publication.

(3) X-ray data were collected on a Nicolet P3/F diffractometer, and the triclinic unit cell data (space group $P\bar{1}$, $Z = 2$) are as follows: a = 4.4357 (12) Å, b = 16.873 (7) Å, c = 21.115 (7) Å, α = 96.49 (3)°, β = 91.57 (2)°, γ = 93.47 (3)°, V = 1566.4 (9) $Å^3$, ρ_{calcd} = 3.04 g/cm^3. Diffraction data (θ–2θ scan, Mo Kα radiation, graphite monochromator, λ = 0.71073 Å) were collected at 298 K in the range $4° < 2\theta < 54°$, and 7552 reflections were averaged ($R_{av}(F)$ = 3.1%) to yield 6804 independent reflections, which were corrected for absorption (μ = 66.6 cm^{-1}), with T_{min} = 0.27 and T_{max} = 0.83. Full-matrix least-squares refinement (iodine, sulfur, and carbon atoms anisotropic, except for one ethylene group of ET; silver atoms with one common isotropic thermal parameter, silver atom site occupancies refined with a total of 358 parameters) yielded $R(F)$ = 7.5% and $R_w(F)$ = 7.4% (GOF = 3.63). Peaks on the final difference map of less than 2.8 $e/Å^3$ may be interpreted as additional, partially occupied silver atom sites.

(4) Geller, S. *Science* (*Washington, D.C.*) **1967**, *157*, 310.

(5) Geller, S.; Owens, B. B. *J. Phys. Chem. Solids* **1972**, *33*, 1241.

(6) Geller, S.; Lind, M. D. *J. Chem. Phys.* **1970**, *52*, 5854.

(7) Strock, L. W. *Z. Phys. Chem., Abt. B* **1934**, *25*, 441; **1936**, *31*, 132.

(8) Tubandt, C.; Lorenz, E. *Z. Phys. Chem., Stoechiom. Verwandtschaftsl.* **1914**, *87*, 513.

(9) Wiedersich, H.; Geller, S. In Eyring, L., O'Keeffe, M., Eds. "The Chemistry of Extended Defects in Non-Metallic Solids"; North-Holland: Amsterdam, **1970**, p 629.

(10) Geller, S. *Acc. Chem. Res.* **1978**, *11*, 87.

(11) For a review, see: Williams, J. M.; Beno, M. A.; Wang, H. H.; Leung, P. C. W.; Emge, T. J.; Geiser, U.; Carlson, K. D. *Acc. Chem. Res.* **1985**, *18*, 261.

(12) The electrical conductivity was measured at ambient pressure on two crystals with nearly identical results. A linear four-probe configuration along the needle (a) axis was used. Contacts were attached with silver paint on evaporated gold pads.

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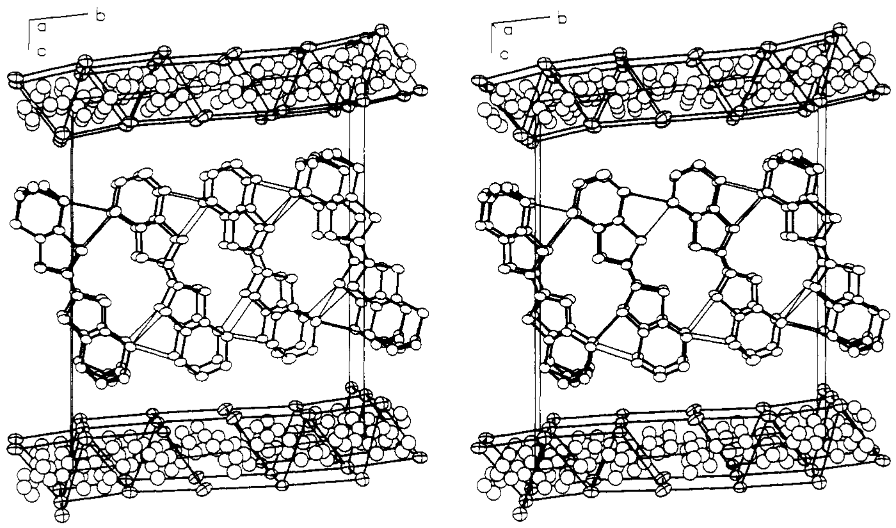

Figure 1. Stereoview of the unit cell of $(ET)_3Ag_xI_8$ ($x \sim 6.4$) along the *a* axis. The figure shows one layer of the two-dimensional ET donor-molecule network (center) with S···S contacts (3.35–3.65 Å), indicated by thin lines, and two silver iodide layers (top and bottom).

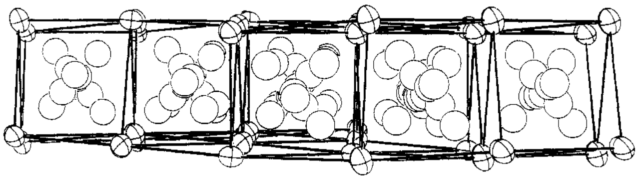

Figure 2. Edge-on view of the silver iodide polyanion layer in $(ET)_3Ag_xI_8$ ($x \sim 6.4$), along $3a + b$. The lines drawn between the iodide ions (with principal ellipses shown) are shorter than 4.65 Å. Silver atom positions within the iodide anion channels are shown as open circles. Similar cation-containing channels are found in numerous solid electrolytes.[10]

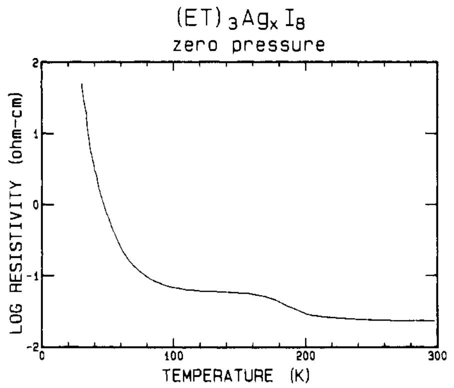

Figure 3. Electrical resistivity (logarithmic scale) along the needle axis (*a*) of $(ET)_3Ag_xI_8$ ($x \sim 6.4$) as a function of temperature. Metallic conductivity is observed at room temperature ($\sigma \simeq 50\ \Omega^{-1}\ cm^{-1}$).

(1) A dc current (100 μA) was applied for an extended period in order to see polarization effects. No change to within our resolution (0.1%) was observed after 20–30 min. This test assumes that the electrodes are at least partially blocking to ionic transport, a reasonable assumption for the type of contacts we employed. (2) No frequency dependence of the resistivity from 0 to 20 kHz was observed. (3) An uncalibrated heating of one sample above 300 K produced an *increase* in the resistivity, contrary to the expectation for ionic transport. Thus, the electrical conductivity is metallic at room temperature ($\sigma = 50\ \Omega^{-1}\ cm^{-1}$).

Conclusions. $(ET)_3Ag_xI_8$ is the first hybrid synmetal–solid electrolyte. However, the high electrical conductivity is dominated by the electronic contribution, at least near room temperature. This is not surprising, since the highest room-temperature ionic conductivity in silver iodide based solid electrolytes measured is 0.27 $(\Omega\ cm)^{-1}$ in $RbAg_4I_5$.[13,14] Furthermore, even smaller silver ion mobility is expected in $(ET)_3Ag_xI_8$, because the silver ions are confined to parallel channels, whereas transport along all directions is possible in $RbAg_4I_5$. We are currently investigating the nature of the 180 K anomaly and the low-temperature properties of $(ET)_3Ag_xI_8$.

Acknowledgment. Work at Argonne National Laboratory and Sandia National Laboratories is sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under Contracts W-31-109-Eng-38 and KC020202, respectively.

Supplementary Material Available: Tables of crystal structure data collection and refinement parameters (Table X1) and final atomic positions with anisotropic temperature factors and silver ion occupancy parameters (Tables X2 and X3) (3 pages). Ordering information is given on any current masthead page.

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(13) Raleigh, D. O. *J. Appl. Phys.* **1970**, *41*, 1876.

(14) Owens, B. B.; Argue, G. R. *J. Electrochem. Soc.* **1970**, *117*, 898.

(15) K.M.D. and B.A.A. are student research participants sponsored by the Argonne Division of Educational Programs from St. Michael's College, Winooski, VT, and Wittenberg University, Springfield, OH.

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Received December 20, 1985

Molecular Structure of a Nickel(II) Complex with Phenolate-Appended Cyclam

Sir:

The phenol-pendant cyclam **1** was recently synthesized via a novel "recycle" of coumarin with linear the tetraamine 1,9-diamino-3,7-diazanonane.[1] The structurally appropriate positioning of its phenol for apical coordination has been implied by the formation of stable complexes with Fe^{II} and Fe^{III} in aqueous solutions. Furthermore, the phenolate coordination appears to render the higher oxidation state of iron more stable.[1] The new ligand **1** may provide a simplified model for the study of phenolate

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