Characterization of Trimethylammonium Iodide and 7,7,8,8-Tetracyano-*p*-quinodimethane Reaction Product. A One-Dimensional "Metal-Like" Complex

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Abstract: The highly conducting metallic green appearing reaction product of trimethylammonium iodide and 7,7,8,8-tetracyano-*p*-quinodimethane, TCNQ, has been characterized by elemental analysis, x-ray diffraction, thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), Raman scattering, anisotropic dc conductivity, and electron spin resonance (ESR). The elemental analysis on 13 samples [45.96 (10) C, 3.66 (9) H, 17.81 (11) N, and 32.49 (18) I] and Raman active mode at 105 cm^{-1} are consistent with the charge transfer formulation: $(NMe_3H)^+(I_3^-)_{1/3}(TCNQ)^{2/3-}$ (**1**) and consequently a one-third filled band for this one-dimensional complex. DSC and TGA data characterize **1** to be thermally stable with respect to iodine loss up to 225 °C; however, in open vessels decomposition to NMe_3(g), HI(g), and TCNQ^0 occurs at higher temperatures. Refinement of 25 reflections from a single crystal reveal that **1** possesses a monoclinic unit cell [a = 13.874 (9), b = 6.441 (3), c = 19.084 (6) Å, β = 105.85 (4)°, and V = 1640.7 (5) Å^3]. The room temperature conductivity is ~20 Ω^{-1} cm^{-1} and the anisotropic conductivity ratio is ~400. The complex exhibits metallic-like conductivity above 240 K. An abrupt simultaneous change in both temperature dependent conductivity and ESR line width is observed at 160 K. The ESR derivative peak to peak line width is ~225 mG at 160 K and ~500 ± 50 mG at 295 K. The isotropic nearly free electron g value (g = 2.003 ± 0.0005), however, appears to remain temperature independent.

The study of linear chain inorganic and organic complexes has received considerable attention in recent years due to the observation of a number of novel anisotropic phenomena such as high conductivity and in some cases a metallic state.[1-13] Halogen oxidation of inorganic[1] and organic[10-13] complexes has led to the formation of various types of one-dimensional (1-D) materials which exhibit a wide array of physical properties. For example, chlorine oxidation of potassium tetracyanoplatinate(II)[14] leads to the isolation of the well characterized 1-D metal $K_2Pt(CN)_4Cl_{0.30}\cdot 3H_2O$, whereas bromine oxidation of dibromodiammineplatinum(II) leads to the formation of the semiconducting $[Pt^{II}Br_2(NH_3)_2][Pt^{IV}(NH_3)_2Br_4]$[15] complex which contains alternating divalent and tetravalent platinum complexes.[16] Bromine and/or iodine oxidation of bis(diphenylglyoximato)nickel(II)[17,18] leads to the formation of a nonstoichiometric semiconducting[19] complex, i.e., $Ni(HDPG)_2X_y$ ($y \lesssim 1.15$),[20] which is consistent with 1-D strands of both bis(diphenylglyoximato)nickel[21] and trihalide.[20,21]

Halogen oxidation of organic molecules may also lead to the formation of novel highly conducting species. Oxidation of planar aromatic organic molecules, e.g., tetrathiofulvalene,[11] tetraselenotetracene,[12a] tetrathiotetracene,[12b] and benzophenothiazines,[13] may result in the formation of novel highly conducting nonstoichiometric complexes containing radical cations. In contrast to this type of reaction, TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane) oxidation of iodide salts, eq 1, frequently leads to the formation of molecular solids containing one-dimensional (1-D) chains of TCNQ radical anions, TCNQ^{z-}, eq 2.[9b,10,20,22]

$$3\ \mathrm{Cation}^+\ I^- + 2TCNQ \rightarrow 2TCNQ^- + 2\ \mathrm{Cation}^+ + \mathrm{Cation}^+\ I_3^- \quad (1)$$

$$TCNQ^- + \mathrm{Cation}^+ + xTCNQ \rightarrow \mathrm{Cation}(TCNQ)_{1+x} \quad (2)$$

The TCNQ oxidation of $NMe_3H^+I^-$, as reported by Cougrand et al.,[23] however, leads to the formation of a novel tertiary component material of $(NMe_3H)(I)(TCNQ)$, **1**, stoichiometry. This complex contains 1-D chains of both TCNQ and halogen.[23] We were interested in studying the stoichiometry and thermal properties of this novel tertiary component complex to ascertain the TCNQ/X ratio and whether or not thermally activated iodine loss could be effected without structural modification [as observed[20] for $M(HDPG)_2X_y$]. This might enable the preparation of an isomorphous series of materials containing a variable amount of iodine so that the physical properties could be monitored as a function of energy band filling. Herein we report the stoichiometry, thermal properties, Raman spectra, electrical conductivity, and ESR of **1**.

Experimental Section

Commercially available acetonitrile,[10a] hydriodic acid, hydrobromic acid, trimethylamine (25% in methanol), and bromine were used as obtained. TCNQ was purified via Sohxlet extraction with anhydrous dichloromethane under purified nitrogen. Trimethylammonium halide was prepared prior to use by addition of stoichiometric amounts of amine and hydrohalic acid. The iodide salt crystallized from the reaction vessel and was air dried, whereas the bromide salt required evaporation of the solvent. In a typical preparation of **1**, 25 mL of acetonitrile solutions, containing 753 mg of $NMe_3H^+I^-$ (4.0 mmol) and 408 mg of TCNQ (2.0 mmol), respectively, were mixed together. Upon standing overnight at −8 °C 521 mg (58%) of product separated as long needle crystals. Recrystallization was effected from a minimum amount of acetonitrile. By slower cooling, larger highly reflecting green crystals were isolated. Elemental analyses are reported as obtained from Galbraith and Spang Laboratories. Computer evaluation of the elemental analyses was carried out using both the Coordination Compound Analysis Program[24a] and Chemical Analysis Program.[24b]

X-ray powder diffraction data were obtained on a tungsten calibrated Philips diffractometer using monochromatic Cu Kα radiation. Comparison of the observed powder diffraction data with literature values was facilitated with the aid of the Powder Pattern Program.[25] Single crystal unit cell parameters were obtained from Molecular Structures Corp. from refinement and Delanic reduction of 25 reflections. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were recorded at 20°/min with a du Pont 900 differential thermal analyzer using a low temperature cell and a du Pont 951 thermal gravimetric analyzer. The crystal structures of the complex were monitored during the DSC scans by quenching samples and obtaining x-ray scattering data in a Philips diffractometer.

Room temperature anisotropic dc conductivity measurements were made by the Montgomery method[26] as previously reported.[27] Temperature dependent single crystal conductivity (13 Hz) measurements were performed using a PAR Model 124A lock-in amplifier. Care was taken to assure agreement between dc and ac (13 Hz) measurements. Temperature variation was obtained using a Janis Research Co. Super Varitemp Dewar. ESR measurements were recorded from deoxygenated single crystals as a function of temperature by a previously published procedure.[28] The ESR tube was filled with dry deoxygenated nitrogen. Low temperature measurements were made with the use of a Varian V4540 variable temperature controller. The effect of modulation on line shape was studied in detail to preclude any possibility of modulation broadening of the very narrow ESR lines observed in the crystal. Sample temperature was independently calibrated by using a platinum resistance standard. The backscattered Raman spectrum was measured on a pressed neat pellet in a Spex Ramalog double monochromator system using the 6471-Å line from a Spectra-Physics krypton laser. The incident laser power was kept sufficiently attenuated so that no damage to the surface was detectable by microscopic examination. Data was taken from 20 to 2600 $\mathrm{cm^{-1}}$ at a rate of 60 $\mathrm{cm^{-1}}$ $\mathrm{min^{-1}}$ with a spectral slit width ≤ 2 $\mathrm{cm^{-1}}$.

Results and Discussion

The reaction product[23] of trimethylammonium iodide and TCNQ is $(\mathrm{NMe_3H})(\mathrm{I})(\mathrm{TCNQ})$. Evaluation[24] of 13 elemental analyses obtained from seven independently prepared samples show that the analyses of **1** are usually best fitted by a $(\mathrm{NMe_3H})(\mathrm{I})(\mathrm{TCNQ})$ formulation, Table I.[29,30] Thus, the complex is stoichiometric and unlike the nonstoichiometric $\mathrm{TTF(X)}_{\sim 0.7}$ (X = Br, I)[11] and $\mathrm{Ni(HDPG)_2X}_y$ (X = Br, I; $y < 1.15$)[20] complexes. Attempts were made to synthesize the bromo analogue of **1**. The reactions of (1) $\mathrm{NMe_3H^+Br^-}$, (2) $\mathrm{NMe_3H^+I^-}$, $\mathrm{Br_2}$, and (3) $\mathrm{NMe_3H^+I^-}$, $\mathrm{NMe_3H^+Br^-}$, with TCNQ were attempted. Reaction 1 failed because TCNQ does not oxidize bromide, and the products isolated from reactions 2 and 3 did not possess any bromine as determined by elemental analysis. Thus, the bromo analogue of **1** could not be made.

The form of the halogen in the 1-D channel was evaluated by a comparison of the reported monoclinic unit cell *b* axis length[23] (parallel to the halogen chain) with the calculated effective halogen length for $\mathrm{I^-}$, $\mathrm{I_2}$, $\mathrm{I_3^-}$,[20] and $\mathrm{I_5^-}$. An occupied iodine channel of **1** with the reported[23] *b* axis length of 6.444 Å is estimated[20] to be filled with either 0.75 $\mathrm{I^-}$, 0.92 $\frac{1}{2}\mathrm{I_2}$, 0.96 $\frac{1}{3}\mathrm{I_3^-}$, or 1.04 $\frac{1}{5}\mathrm{I_5^-}$ per TCNQ. The latter occupancies are in good agreement with respect to the observed value of 1.00. Because of this slight discrepancy and small variations in the observed powder diffraction traces (vide infra) compared to the calculated traces[25] for the monoclinic structure,[23] single crystal unit cell parameters for **1** were obtained. The observed cell constants were $a = 13.874$ (9), $b = 6.441$ (3), $c = 19.084$ (6) Å, $\beta = 105.85$ (4)°, and $V = 1640.7$ (5) Å^3. This observed unit cell transforms into a cell of $a = 20.301$ (13), $b = 6.441$ (3), $c = 13.874$ (9) Å, and $\beta = 115.26$ (5)° which is in good agreement with previously reported data[23] except for β, which is $\approx 1°$ smaller in value.

In order to verify the $\mathrm{I_3^-}$ or $\mathrm{I_5^-}$ assignment the Raman spectrum was measured. The major feature of the Raman spectrum is a very strong, sharp line at 105 $\mathrm{cm^{-1}}$ with an apparent overtone at 212 $\mathrm{cm^{-1}}$. This absorption is assigned to the triiodide anion.[31,32] Using similar analysis of their Raman spectra Marks et al.[33,34] identified the iodine species in one-dimensional phthalocyanine[34] and glyoximato[21,33] complexes as triiodide and pentahalide. The higher frequency features in the spectrum (predominantly >1000 $\mathrm{cm^{-1}}$) are consistent with the known Raman spectrum of TCNQ.[35] Thus, from charge conservation **1** is best described by $(\mathrm{NMe_3H})^+(\mathrm{I_3^-})_{1/3}(\mathrm{TCNQ})^{2/3-}$ and possesses a 0.33 filled band.

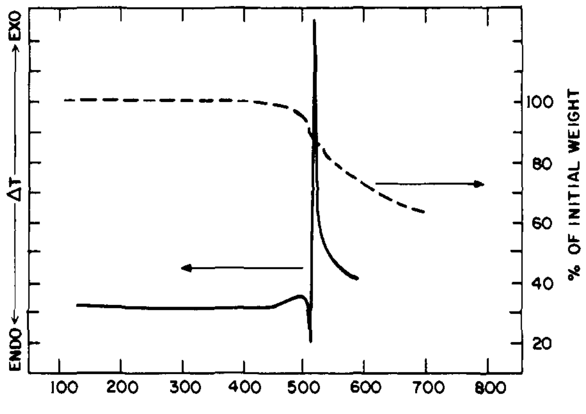

Figure 1. Differential scanning calorimetry and thermal gravimetric traces of **1** taken at 20° $\mathrm{min^{-1}}$.

In accord with the precedent of the thermally activated halogen loss (without a structural modification) from $\mathrm{M(HDPG)_2X}_y$[20] (M = Ni, Pd; X = Br, I) attempts were made to expel halogen,

$$\underset{\mathbf{1}}{(\mathrm{NMe_3H})^+(\mathrm{I_3^-})_{1/3}(\mathrm{TCNQ})^{2/3-}} \not\xrightarrow[\Delta]{} \underset{\mathbf{2}}{n\mathrm{I_2} + (\mathrm{NMe_3H})^+(\mathrm{I})_{1-2n}{}^{1/3-}(\mathrm{TCNQ})^{(2+2n)/3-}} \quad (3)$$

and form an isomorphous series of complexes, **2**, which would allow for the subtle study of the physical properties as a function of TCNQ band filling (Fermi energy). In order to study the feasibility of forming **2** the thermal properties of **1** were evaluated. Figure 1 depicts the thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) traces for **1** at a heating rate of 20° $\mathrm{min^{-1}}$. The DSC trace indicates no phase transitions are present between −173 °C and the melting endotherm at ~242 °C and the decomposition above the melting point. TGA data shows that **1** loses weight above 100 °C and exhibits an inflection point in the trace at the melting point; however, the positions and/or relative intensities of the observed x-ray reflections were not observed when samples were quenched at temperatures up to 225 °C. Thus, although the TGA and DSC data are consistent with iodine loss, the x-ray data strongly suggests that iodine is not lost upon thermal treatment. Visual analysis of samples heated for extended periods of time in an open vessel clearly show decomposition to a yellow residue. For example, heating **1** at 175 °C for 3 h resulted in a 25% weight loss and a crystalline residue which was yellow and metallic green in appearance. The diffraction pattern of the residue indicated that the yellow substance was $\mathrm{TCNQ^0}$[36] and the green reflecting substance was undecomposed **1**. Thus, it is concluded that **1** decomposes via the equation

$$\mathbf{1} \xrightarrow[\Delta]{} \mathrm{HI(g)} + \mathrm{NMe_3(g)} + \mathrm{TCNQ^0} \quad (4)$$

in an open container. In the closed vessel used in DSC traces, decomposition of **1** was not observed as there was no crystallographic evidence for $(\mathrm{NMe_3H})_2(\mathrm{TCNQ})_3$,[37] or unknown reflections which could be characteristic $\mathrm{NMe_3H^+I^-}$ or $\mathrm{NMe_3H^+I_3^-}$ due to a reaction between amines and TCNQ.[9b,38]

The single crystal anisotropic dc conductivity of **1** was measured at room temperature using the Montgomery technique.[26] The results indicated that $\sigma_{\parallel}/\sigma_{\perp} \sim 400$ where $\sigma_{\parallel}$ is the conductivity parallel to the needle axis and $\sigma_{\perp}$ is the conductivity perpendicular to the needle axis and in the broad face of these needle shaped crystals. Since the unit cell deviates from orthorhombic symmetry, caution must be exercised in its interpretation; nonetheless, **1** possesses a large anisotropic conductivity which is characteristic of various one-dimensional organic[8] and inorganic[1] substances.

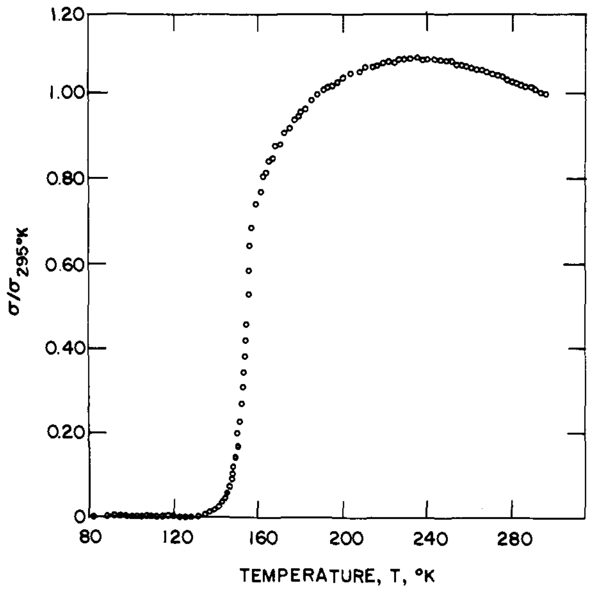

Figure 2. Temperature dependence of electrical conductivity at 13 Hz of a typical sample of **1**. The plotted values are normalized to the conductivity at 295 K.

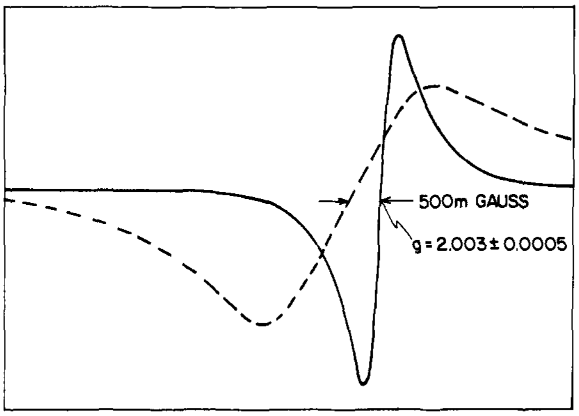

Figure 3. Room temperature ESR spectra of **1** (solid line). The coal pitch standard is depicted by the dashed line.

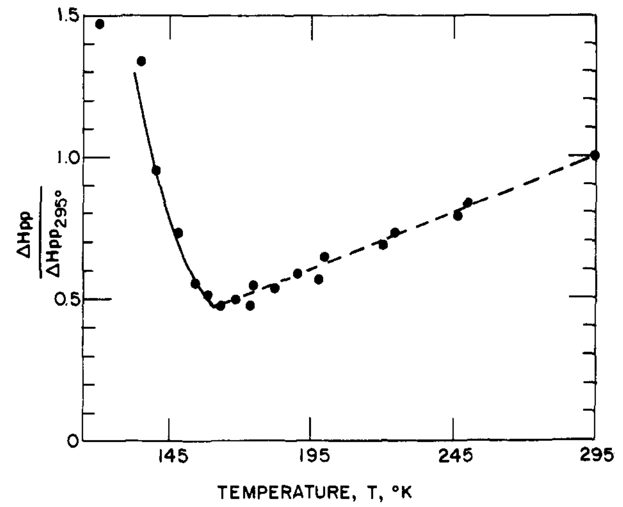

Figure 4. The temperature dependence of the normalized derivative peak to peak line width of **1**. The line width at 295 K is 500 ± 50 mG, while at 160 °C it is ~225 mG.

The temperature dependence of the conductivity parallel to the needle axis was measured using the four probe technique between room temperature and 60 K on many crystals prepared from independent syntheses. There were significant variation in behavior observed, ranging from results similar to the data previously reported by Cougrand et al.[23] to "metal-like" behavior. The room temperature $\sigma_{\|}$ of our highest conducting crystals is ~30 $(\Omega\ \mathrm{cm})^{-1}$ compared with the previously reported value of ~1 $(\Omega\ \mathrm{cm})^{-1}$. Also, as shown in Figure 2, the conductivity parallel to the needle axis of these crystals *increases* as the temperature is decreased below room temperature, reaching a maximum of $1.08\sigma_{\|295\mathrm{K}}$ at ~240 K. It then decreases until 160 ± 1 K when it starts to continuously decrease at a much more rapid but continuous rate. These results indicate a "metal-like" behavior above 240 K and an abrupt but reversible change at 160 K. Previously a semiconducting behavior was reported above and below the abrupt transition reported[23] to be at 150 K. In accord with the perspective of Epstein et al.[39] the transition at 160 K appears to be a semiconductor to semiconductor transition, i.e., variations in $\sigma(T)$ for $T > 160$ K can be accounted for by a temperature dependent mobility varying with sample quality.

The room temperature ESR spectrum of single crystals of **1** is depicted in Figure 3. The spin density was estimated by direct comparison with a calibrated coal pitch sample. The average value obtained for several crystals ~10^{19} spins/cm^3 is somewhat smaller than the number density calculated from published susceptibility data.[23] Spin counting errors could, however, easily arise from approximations introduced in making the filling factor and line shape corrections. Complex **1** exhibits a temperature independent isotropic g factor of nearly the free electron value, i.e., $g = 2.003 \pm 0.0005$. The g value and high spin density are commonly observed in other paramagnetic TCNQ charge transfer salts.[40] The derivative peak to peak line width, ΔH_{pp}, was determined to be 500 ± 50 mG at 295 K. Complex **1** exhibits a complex temperature dependent derivative peak to peak line width between 113 and 295 K, Figure 4. Between 295 and 160 K the line width decreases approximately linearly to a minimum value of ~225 mG. Below 160 K the line width increases nonlinearly while the spin density appears to progressively decrease as the temperature is lowered. ESR and conductivity data suggest a reversible transition occurs at 160 K which is not observed in DSC traces. Furthermore, there is no significant hysteresis observed in either measurement near 160 K. Further detailed physical measurements and interpretation will be reported later.

Summary

The reaction of $\mathrm{NMe_3H^+I^-}$ and $\mathrm{TCNQ^0}$ leads to the formation of $\mathrm{(NMe_3H)^+(I_3^-)_{1/3}(TCNQ)^{2/3-}}$ which exhibits metallic-like conductivity above 240 K. The complex, unlike other polyiodide containing materials, is thermally stable with respect to iodine loss; however, thermal treatment in an open vessel leads to decomposition to $\mathrm{TCNQ^0}$ and presumably HI(g) and $\mathrm{NMe_3(g)}$. The room temperature $\sigma_{\|}$ and anisotropic conductivity ratio are ~20 Ω^{-1} cm^{-1} and ~400, respectively. The temperature dependent conductivity in some samples is "metal-like" between 240 K and room temperature. This dependence is also at variance with a previous report in the literature; however, the sharp reversible change in conductivity behavior at 160 ± 1 K is in qualitative agreement with the previous report at 150 K. The temperature dependent free electron ESR spectra are also consistent with an abrupt change in conductivity behavior at 160 K. The sharp ESR spectrum at room temperature is similar to previously reported $\mathrm{TCNQ^{z-}}$ spectra.

Note Added in Proof: Recently Delhaes et al. report that **1** contains $\mathrm{I_3^-}$.[41]

Supplementary Materials Available: The observed elemental analysis of **1** (Table I) is listed (2 pages). Ordering information is given on any current masthead page.

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(29) Previously elemental analyses of 46.8 C, 3.9 H, 18.7 N, and 32.5 I were reported.[23] The sum is 101.9%, the data is reported to 0.1%, and duplicate analysis on independently prepared samples were not reported. Utilizing these results and the Chemical Analysis Program[24b] no reasonable fit could be obtained unless two elements deviated from a calculated percentage by greater than 0.5%. The lowest standard deviation obtained for a formulation [i.e., $(NMe_3H)(I)_{0.96}(TCNQ)$] was ~7 times greater than that obtained for $(NMe_3H)(I)_{1.04}(TCNQ)$ with the data reported herein.

(30) Besides the 13 samples reported in Table I, excellent agreement for the C, H, N, and I elemental analysis was obtained between the pair of independently prepared samples and the values calculated for the 1.04 I/TCNQ stoichiometry. The standard deviations between these samples are $^1/_{15}$ and $^1/_{28}$ times as large as the differences between the calculated elemental percentages for 1.04:1 I/TCNQ and 1.00:1 I/TCNQ for carbon and iodine, respectively. Thus, $(NMe_3H)I_{1.04\pm0.01}(TCNQ)$ is the best description of the stoichiometry for these two samples. A noncommensurate amount of halogen has been reported for other systems. Halogen and seleno- or thiocyanogen oxidation of tetrathiofulvalene[11] leads to materials with a nonstoichiometric amount of halogens and pseudohalogens. This type of nonstoichiometry has also been recently reported for the bromine and iodine reaction product with $M^{II}(HDPG)_2$ (M = Ni, Pd; H_2DPG = diphenylglyoxime).[20]

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