slow, and solutions containing an excess of the lithium ion showed two ^{7}Li signals. These results are very similar to the ones we had previously obtained with lithium cryptates in nonaqueous solutions.[9]

Plots of observed ^{7}Li chemical shifts vs. (ligand)/(Li^+) mole ratio are shown in Figure 1. Formation constants and limiting chemical shifts for the complexed lithium ion were calculated from these data by using previously described techniques.[10] The results are shown in Table I. Values of some formation constants, obtained previously in nonaqueous solutions, are given for comparison.[11]

It is interesting to note that the stabilities of the complexes in the melt and in nonaqueous solvents follow the order 15C5 > 12C4 > 18C6. The fact that 18C6 forms the weakest complex is not surprising in view of the large disparity between the ionic diameter and the size of the cavity. It is surprising, however, that 15C5 forms more stable complexes than 12C4 since, according to the literature, its cavity size is considerably larger than the Li^+ ion.[12]

It seems reasonable to expect that the lithium ion enclosed in the two-dimensional cavity of a crown ether also remains bonded to one or even two chloride ions. Crystal structure studies on crown ether complexes abound with examples where the complexed cation has either one or two anions as near neighbors. For example, in the LiNCS·12C4 complex, the Li^+ ion is coordinated to the NCS^- counterion,[13] and in the $LiNO_3$·B14C4 complex, it is coordinated to the nitrate ion,[14] while in the $Mg(NCS)_2$·B15C5 complex, the cation is coordinated to two anions, one above and one below the macrocyclic plane.[15] The likelihood of a Li^+–Cl^- bond is much less for the C211 complex, where Li^+ is enclosed in a three-dimensional cavity. Studies on the nature and the structures of macrocyclic complexes of lithium in molten salts are being continued in our laboratory.

Initial studies by ^{23}Na and ^{133}Cs NMR on sodium chloride and cesium chloride in the melts showed that the two salts are essentially insoluble in the basic media. However, CsCl is soluble in acidic melts to the extent of approximately 0.25 mol %. The ^{133}Cs chemical shift remains essentially constant between 50 and 60 mol % of $AlCl_3$ but then changes rapidly and shifts upfield some 20 ppm in the 67 mol % mixture. It is quite obvious that the immediate environment of the Cs^+ ion undergoes a substantial change somewhere between 60 and 67 mol % of $AlCl_3$. One possible explanation would be that, with melt compositions in excess of 60 mol % $AlCl_3$, the interaction of Cs^+ with $Al_2Cl_7^-$ begins to predominate over that with $AlCl_4^-$.

Addition of crown ethers to the CsCl solution in acidic melts changed very little the ^{133}Cs resonance, indicating only a minor change in the cationic environment. It is interesting to note, however, that the addition of 18C6 to a CsCl suspension in a basic melt (45 mol % $AlCl_3$) resulted in a ^{133}Cs signal some 50 ppm upfield from the ^{133}Cs resonance in a 60% $AlCl_3$–(BP)Cl melt. This behavior is very similar to the one described by Pedersen,[16] where $KMnO_4$ was solubilized in benzene by the addition of dicyclohexano-18C6.

Preliminary studies have shown that NaCl is soluble in the acidic melt. In a 51 mol % $AlCl_3$ melt a rather broad line (approximately 100 Hz) appeared about 6 ppm upfield from the reference. There is a slight (approximately 2 ppm) upfield shift when the melt composition is changed from 60 to 67 mol % of $AlCl_3$. The addition of B15C5 to NaCl solution in a 51 mol % melt results in a very large broadening of the signal, which indicates the formation of the B15C5·Na^+ complex.

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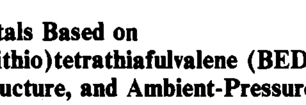
Synthetic Metals Based on Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF): Synthesis, Structure, and Ambient-Pressure Superconductivity in $(BEDT\text{-}TTF)_2I_3$

Sir:

Very recently we reported[1] the synthesis and detailed crystal structures (at 298 and 125 K) of two isostructural derivatives of BEDT-TTF,[2] or "ET", i.e., $(ET)_2ReO_4$ and $(ET)_2BrO_4$.



BEDT-TTF
(ET)

These materials comprise a new *structural*[1] class of electrical conductors of which $(ET)_2ReO_4$ was, until very recently, reportedly the only S-based organic superconductor[3] ($T_c \simeq 2.0$ K) when under an applied pressure of $\simeq$4 kbar. It was suggested that $(ET)_2X$ systems having this structural type, i.e., a predominance of shorter *inter*chain vs. intrachain (stacking) S–S interaction distances (the former less than the van der Waals S-atom radius sum of 3.6 Å), might hold the promise of a rich variety of electrical properties including potentially new superconductors.[1] On the basis of two consecutive reports[4,5] it appears that $(ET)_2I_3$ is a member of this new structural class, but more importantly, that this salt is the first *ambient-pressure* S-based organic *super*conductor (four-probe resistivity measurements, $T_c \simeq 1.4$–1.5 K).[4] To date, the only ambient-pressure organic superconductor has been *Se*-based $(TMTSF)_2ClO_4$,[7] ($T_c \simeq 1.2$ K). However, numerous crystalline phases of $(ET)_2I_3$ have been reported[5,6] with electrical

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[2] BEDT-TTF or "ET" is bis(ethylenedithio)tetrathiafulvalene, $C_{10}S_8H_8$.

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[5] Kaminskii, V. F.; Prokhorova, T. G.; Shibaeva, R. P.; Yagubskii, E. B. *Zh. Eksp. Teor. Fiz., Pis'ma Red.* **1984**, *39*, 15. The reported crystal data are as follows: $a = 6.609$ (1), $b = 9.083$ (1), $c = 15.267$ (2) Å; $\alpha = 85.63$ (2), $\beta = 95.62$ (2), $\gamma = 70.22$ (2)°; $V_c = 852.2$ Å^3; $Z = 1$. While no positional or refinement parameters are reported in this reference, the structural projections and associated description convince us that the distorted-hexagon phase and the superconducting[4] needle or flake phases have the same structure.

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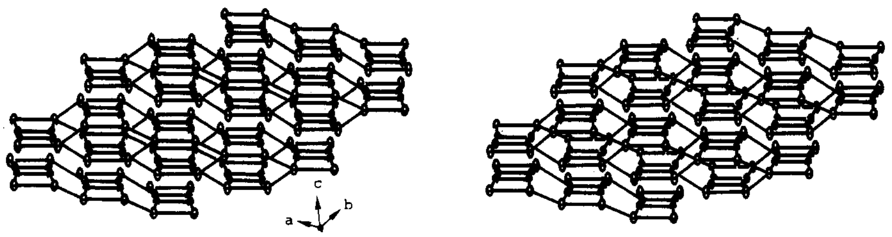

Figure 1. Stereoview of all short (<3.60 Å) intermolecular *inter*stack S–S interactions in $(ET)_2I_3$, which form a "corrugated sheet" network. This network is quite different from that observed in $(TMTSF)_2X$ conductors but very similar to that found in superconducting $(ET)_2ReO_4$.[1]

properties ranging from metallic[4,6] to insulating[4,6] to superconducting.[4] In order to clarify these reports, we have electrocrystallized[8] a different crystalline morphology for $(ET)_2I_3$ (distorted-hexagon-shaped crystals) from a different solvent (1,1,2-trichloroethane, TCE, rather than benzonitrile, which previously[5] yielded "flakes" and needles) and investigated both the crystal structure and superconductivity of the crystals formed. In this communication we report the unusual crystal structure at 298 K, which establishes that this new material is a member of the unique structural class recently described[1] having a novel 2-dimensional "corrugated sheet" network with short, *inter*stack S–S interaction distances that form the basis for the anisotropic electrical properties. In addition, we report the existence of ambient-pressure superconductivity, detected inductively, in the new distorted-hexagon phase of $(ET)_2I_3$, thereby presenting independent confirmation of this phenomenon in an S-based organic conductor.[10]

Crystals of $(ET)_2I_3$ were prepared by the electrochemical oxidation (Pt electrodes) of ET, at constant temperature (23.4 °C), in the presence of $(n\text{-}Bu_4N)I_3$ as supporting electrolyte.[8] The ET–X, ($X = BrO_4^-$, ReO_4^-) systems are notorious for yielding different crystalline phases having different *stoichiometries* all during one electrocrystallization cycle.[1,3] However, only one unsolvated (ET–X) phase with 2:1 stoichiometry is produced for $X = BrO_4^-$ or ReO_4^-. To the best of our knowledge, the ET–I_3^- system is the first case in which more than one 2:1 phase having *different* crystallographic and electrical properties can be produced on the same electrode during a growth cycle. In the previous report[5] it is stated that three types of crystals were grown from benzonitrile, viz. two as "flakes" and one as needles. One type of flake exhibited a metal–insulator (M–I) transition at ~140 K while the other type, and the needles, displayed superconductivity (critical temperature (T_c) of 1.4–1.5 K). No crystal data were given for the material having a 140 K metal–insulator transition, but we believe this phase of $(ET)_2I_3$ corresponds to that of Bender et al.,[6] which also has an M–I transition at 140 K. We find two types of crystals from TCE: large intergrown thin plates and distorted-hexagon-shaped plates/blocks. The large thin plates have crystal unit cell parameters identical with those reported by Bender et al.[6] and do not exhibit superconductivity at ambient pressure ($T \geq 0.4$ K), while the distorted hexagons have crystallographic structure[11] in general agreement with that of the superconducting flakelike phase just reported,[4,5] and are superconducting at ambient pressure (vide infra).

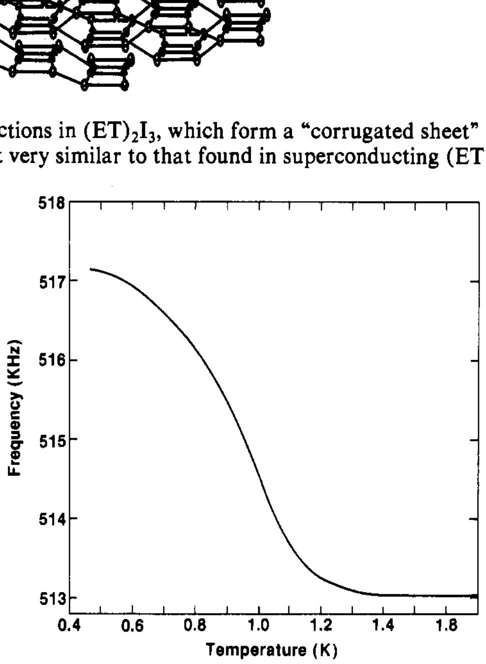

Figure 2. Change in resonant frequency of the RF coil with temperature for the distorted-hexagon plates of $(ET)_2I_3$. The onset of superconductivity, detected inductively,[12,13] was established to be 1.40 ± 0.02 K for both the distorted-hexagon crystal phase and those with needle morphology.

In $(ET)_2I_3$, as in $(ET)_2X$, $X = BrO_4^-$, ReO_4^-, the ET molecules are nonplanar and somewhat dimerized and form loosely connected "stacks" along the crystallographic (110) diagonal axis. The I_3^- anions form chains with a relatively short intermolecular I–I distance of 4.211 (1) Å. The intermolecular *intra*stack S–S contact distances are all greater than

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(6) Bender, K.; Dietz, K.; Endres, H.; Helberg, H. W.; Henning, I.; Keller, H. J.; Schafer, H. W.; Schweitzer, D. *Mol. Cryst. Liq. Cryst.* **1984**, *107*, 45. None of the details of the electrocrystallization procedure, or solvent used, were given. The lattice parameters were given as $a = 9.211$ Å, $b = 10.850$ Å, $c = 17.488$ Å, $\alpha = 96.95°$, $\beta = 97.97°$, $\gamma = 90.75$, and $V_c = 1717$ Å^3, i.e., approximately *double* the unit cell volume of the superconducting $(ET)_2I_3$ crystals. The phase of Bender et al. has a unit cell that is very similar to that found in $(ET)_2X$, $X = ReO_4^-$ and BrO_4^- (see ref 1).

(7) Bechgaard, K.; Carneiro, K.; Rasmussen, F. B.; Olsen, M.; Rindorf, G.; Jacobsen, C. S.; Pedersen, H. J.; Scott, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2440. TMTSF is tetramethyltetraselenafulvalene.

(8) BEDT-TTF (ET) was synthesized as previously described.[1] Preparation of $(n\text{-}Bu_4N)I_3$ was based on a similar literature procedure[9] with the following modifications: 5.00 g of $(n\text{-}Bu_4N)I$ (13.5 mmol) was suspended in 120 mL of 1.7 M KI solution at 60 °C and 3.44 g of I_2 (13.6 mmol) was slowly added. The resulting mixture was stirred for 10 min and was cooled to room temperature. The resulting black solid mass of $(n\text{-}Bu_4N)I_3$ was filtered and twice recrystallized as deep purple needles from absolute methanol. Approximately 6.54 g of product (78% yield) was obtained; mp 70–71 °C. Anal. Calcd (Found) for $(n\text{-}Bu_4N)I_3$: C, 30.84 (30.57); H, 5.82 (6.21); N, 2.25 (2.21); I, 61.09 (60.80). Dark brown thin plates (or "flakes") and thick distorted-hexagon-shaped plates of $(ET)_2I_3$ were grown electrochemically in 1,1,2-trichloroethane at 1 μA/cm^2 current density with 1.3 mM ET and 40 mM $(n\text{-}Bu_4N)I_3$ at 23 °C. Some very small bronze-colored flakes were also observed upon initial mixing of the above solutions. Detailed characterization of the large dark brown flakes is in progress, and at this stage we find some are the Bender et al.[6] phase on the basis of X-ray measurements. Among these other phases, needle-shaped crystals of $(ET)_2I_3$ were also obtained when benzonitrile was used as solvent. The needle-shaped crystals (from benzonitrile) and distorted-hexagon-shaped crystals (from TCE) have very similar crystal unit cell lattice constants.

(9) Silvestrori, P.; Rallo, F. *Gazz. Chim. Ital.* **1979**, *109*, 295.

(10) We have also electrocrystallized needle crystals of $(ET)_2I_3$ from benzonitrile, which have crystal lattice constants very similar to those of our distorted-hexagon phase and which we find are also superconducting with $T_c = 1.40 \pm 0.02$ K, identical with that of the distorted-hexagon crystals.

(11) X-ray data at 298 K were collected on a Syntex $P2_1$ diffractometer. The triclinic crystals (space group $P\bar{1}$, $Z = 1$) have unit cell lattice parameters (298 K) $a = 6.615$ (1) Å, $b = 9.100$ (1) Å, $c = 15.286$ (2) Å, $\alpha = 94.38$ (1)°, $\beta = 95.59$ (1)°, $\gamma = 109.78$ (1)°, and $V_c = 855.9$ (2) Å^3. For $(ET)_2I_3$ (298 K) in the range $3° < 2\theta < 65°$ 9426 measurements were corrected for absorption ($\mu = 36.7$ cm^{-1}, $T_{min} = 0.29$, $T_{max} = 0.49$) and averaged to give 5785 unique data ($R_{av} = 0.04$); of these 4142 reflections with $F_{obsd} > 3\sigma$ (F_{obsd}) were used in the final full-matrix least-squares analysis. The initial structure solution (Patterson methods) yielded the iodine atom positions, and subsequent cycles of Fourier and least-squares analysis calculations yielded $R(F) = 0.06$, $R_w(F) = 0.06$.

the van der Waals S-atom radius sum of 3.60 Å (shortest intrastack distance 3.759 (1) Å).[11] One of the ethylene groups of the ET molecule is disordered. The corresponding "corrugated sheet" network of S–S interactions, through which electrical conduction likely occurs, and which lie principally along the *a* and *b* axes, is shown in Figure 1. The four shortest interstack interaction distances range from 3.574 (1) to 3.599 (1) Å. Preliminary X-ray investigations at 125 K reveal satellite reflections for all zones of diffraction vectors, indicating the presence of a complex modulated superstructure for at least the I_3^- anions. A full structural study at 125 K is presently under way.

While the previous workers[4] used four-probe resistivity measurements to identify ambient-pressure superconductivity in $(ET)_2I_3$, we have used RF penetration depth measurements,[12,13] performed as a function of temperature in a pumped helium cryostat containing either ^3He or ^4He. Temperatures were determined by vapor phase pressure thermometry. Measurements in superfluid ^4He showed the onset temperature for bulk superconductivity in the distorted-hexagon-shaped crystals to be 1.40 ± 0.02 K (see also ref 10). Separate measurements in pumped ^3He show, as illustrated in Figure 2, a broad transition that is not complete at the lowest temperature obtained, 0.44 K. Qualitatively, the RF frequency vs. temperature data are similar to those for slow-cooled $(TMTSF)_2ClO_4$, which we have also determined.[14] The onset temperature in the $(ET)_2I_3$ salt is slightly lower than that reported earlier from four-probe resistivity measurements. This difference is consistent with a broad transition width, which allows a low-resistance filament to be detected resistively before the superconductivity in the bulk of the sample can be detected inductively. Details of the RF penetration depth measurements of the superconducting transition temperature and critical magnetic field are given elsewhere.[14] Finally, a number of new $(ET)_x(I_yBr_z)$ derivatives are presently being characterized which are ambient-pressure superconductors. The transition temperatures, measured by RF penetration depth, range from 2.3 K to, in one sample, 4.2 K.

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Registry No. $(ET)_2I_3$, 89061-06-3; ET, 66946-48-3; $(n\text{-}Bu_4N)I_3$, 13311-45-0.

Supplementary Material Available: Table of final positional parameters and anisotropic temperature factors at 298 K (1 page). Ordering information is given on any current masthead page.

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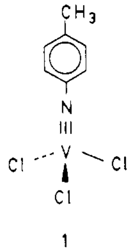
Preparation, Chemistry, and ^{51}V NMR Spectroscopy of (*p*-Tolylimido)vanadium(V) Complexes

Sir:

Despite the current interest in transition-metal organoimido species, there are only a few well-characterized vanadium(V) organoimido complexes.[1] Moreover, there has been virtually no chemistry reported for these compounds since the majority of them are thermally unstable and often decompose to yield polymeric materials. We now report our preparation, characterization, and preliminary chemical investigations of (*p*-tolylimido)vanadium trichloride, $V(Ntol)Cl_3$ (**1**), a readily prepared, thermally stable species that provides a convenient entry into vanadium(v) organoimido chemistry.[2]



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In a typical preparation, a solution of *p*-tolyl isocyanate (60 mmol) in octane (10 mL) was added, under an N_2 atmosphere, to a solution of $VOCl_3$ (40 mmol) in octane (50 mL) and refluxed for 3 h, resulting in copious evolution of CO_2 and forming a dark green solution.[3] After removal of solvent and drying at 110 °C in vacuo overnight, the dark residue was sublimed at 130 °C (10^{-4} torr) onto a water-cooled probe to yield 9.1 g (87%) of **1** as large, glistening purple-black crystals.[4] The mass spectrum of **1** (determined at 35 °C) reveals only the expected mononuclear isotopomers to be present. While all of the complexes described herein possess excellent thermal stability, they all are exceedingly moisture sensitive; their solutions acquire an intense violet color immediately upon exposure.

$V(Ntol)Cl_3$, with a formal 12-electron configuration, behaves as a Lewis acid and readily forms addition complexes with donor ligands. Thus, dissolution of **1** in THF, followed by slow admission of hexane, affords orange crystalline $V(Ntol)Cl_3(THF)$.[5] The reaction of **1** with PPh_3 in CH_2Cl_2 similarly yields $V(Ntol)Cl_3(PPh_3)$ as khaki-colored microcrystals.[6] The isolation of these monoadducts is surprising, given the electron deficiency of **1** and in view of the chemistry

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(1) (a) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123. (b) Burger, H.; Smrekar, O.; Wannagat, U. *Monatsh. Chem.* **1964**, *95*, 292. (c) Slawisch, A. *Z. Anorg. Allg. Chem.* **1970**, *374*, 291. (d) Nugent, W. A.; Harlow, R. L. *J. Chem. Soc., Chem. Commun.* **1979**, 342. (e) Nugent, W. A. *Inorg. Chem.* **1983**, *22*, 965. (f) Bradley, D. C.; Hursthouse, M. B.; Jelfs, A. N. M.; Short, R. L. *Polyhedron* **1983**, *2*, 849.
(2) A related species, $V(NC_6H_5)Cl_3$, was reported by Slawisch[1c] to be polymeric. $V(NC_6H_5)Cl_3$ has also been mentioned by Bradley and co-workers,[1f] but no details were given and the compound was apparently contaminated with phenyl isocyanate.
(3) For other examples of the use of isocyanates in the preparation of organoimido complexes see, e.g.: (a) Kolomnikov, I. S.; Koreshkov, Y. C.; Lobeeva, T. S.; Volpin, M. E. *J. Chem. Soc., Chem. Commun.* **1970**, 1432. (b) Bradley, D. C.; Hursthouse, M. B.; Malik, K. M. A.; Nielson, A. J. *Ibid.* **1981**, 103. (c) Pederson, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 7483.
(4) Anal. Calcd for $C_7H_7NCl_3V$: C, 32.04; H, 2.69; N, 5.34. Found: C, 32.25; H, 2.91; N, 5.62. ^1H NMR ($CDCl_3$, 25 °C): δ 7.33 (q, 4 H, J_{AB} = 7.8 Hz, $C_6H_4CH_3$), 2.53 (s, 3 H, $C_6H_4CH_3$).
(5) Anal. Calcd for $C_{11}H_{15}NOCl_3V$: C, 39.49; H, 4.52; N, 4.19. Found: C, 39.48; H, 4.63; N, 4.15. ^1H NMR ($CDCl_3$, 25 °C): δ 7.42 (q, 4 H, J_{AB} = 8.3 Hz, $C_6\mathit{H}_4CH_3$), 4.34 (t, 4 H, $\overline{OC\mathit{H}_2(CH_2)_2C}\mathit{H}_2$), 2.55 (s, 3 H, $C_6H_4C\mathit{H}_3$), 2.06 (quintet, 4 H, $\overline{OCH_2(C\mathit{H}_2)_2C}H_2$).
(6) Anal. Calcd for $C_{25}H_{22}NPCl_3V$: C, 57.22; H, 4.23; N, 2.67. Found: C, 57.43; H, 4.46; N, 2.69. ^1H NMR ($CDCl_3$, 25 °C): δ 7.65–7.38 (m, 15 H, $P(C_6H_5)_3$), 7.13 (q, 4 H, J_{AB} = 8.2 Hz, $C_6\mathit{H}_4CH_3$), 2.47 (s, 3 H, $C_6H_4C\mathit{H}_3$).

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