Even more definitive evidence regarding the preferred conformation of bidentate chelates derived from **2** was obtained for the case of $MgBr_2$ as Lewis acid; a discrete bidentate chelate with very narrow ^1H NMR lines was observed at 0 °C. Irradiation of the methyl group collapsed the six-line multiplet for the C_3 methine to a triplet with $J = 5$ Hz. These results require that the C_3 C-H bond essentially bisects the H-C-H angle at C-2, i.e., that the methyl group at C_3 occupies an axial (or pseudoaxial) orientation in the complexes formed from **2** and $TiCl_4$ or $MgBr_2$.[10]

It is now clear why "chelation-controlled" additions to **2** are characterized by high levels of diastereofacial selectivity. Apparently, relief of $A^{1,3}$-like interactions between the C_3 methyl group and the benzyl group on oxygen is responsible for the conformation of chelates derived from **2** in solution; no significant 1,3-diaxial interactions are present to disfavor this conformation. For the first time, the stereochemistry of Lewis acid mediated additions to materials such as **1** and **2** can be interpreted on a rational basis—one based upon experiment rather than hypothesis.

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(10) ^1H NMR chemical shifts for the complexes formed from **2** with $MgBr_2$–OEt_2 and $TiCl_4$ are summarized here, as are chemical shift differences relative to **2** at the same temperature (12.3 and −93 °C, respectively): $MgBr_2$——C_1 9.85 (−0.13), C_2, $C_{2'}$ 2.91 (−0.30, −0.44), C_3 4.11 (−0.08), C_4 4.65 (−0.24), $C_{4'}$ 4.79 (−0.24), CH_3 1.23 (0.01); $TiCl_4$——C_1 10.10 (−0.39), C_2, $C_{2'}$ 3.41 (−0.91), C_3 4.73 (−0.70), C_4 5.28 (−0.73), $C_{4'}$ 5.46 (−0.91), CH_3 1.21 (0.03).

(11) (a) The aldehydic proton is omitted for clarity. (b) Only the indicated relationships at C_2 and C_3 are stereochemically significant.

Neutron Diffraction Evidence for Unusual Cohesive H-Bonding Interactions in β-(BEDT-TTF)$_2$X Organic Superconductors

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In order to determine the nature and exact geometries of the interionic interactions that are responsible for crystal cohesion between the sheetlike networks of radical cation molecules and the halide-containing anions in the *layered* organic conductors of the type β-$(ET)_2X$,[1] we have undertaken low-temperature (20 K) neutron diffraction studies of the $X^- = AuI_2^-$ and I_3^- salts. For these synthetic organic superconductors, β-$(ET)_2AuI_2$ has the highest T_c (~5 K) at *ambient pressure*,[2,3] and β-$(ET)_2I_3$ has the highest T_c (~8 K) under a *non*hydrostatic pressure of 1.3 kbar.[4-6]

Table I. H-Bonding Interaction Geometries for Several β-$(ET)_2X$ Salts Derived from 20 K Neutron Data and Low-Temperature X-ray Data[a]

$X^- = AuI_2^-$, 20 K neutrons			$X^- = AuI_2^-$, 120 K X-rays	
contact	dist/Å	angle/deg	dist/Å	angle/deg
H102···I	2.966 (4)	147.8 (3)	3.03	141.8
H81···I	3.132 (4)	148.3 (3)	3.13	153.9
H71···I	3.146 (4)	122.6 (3)	3.20	120.0
H92···I	3.154 (4)	136.6 (3)	3.27	129.6
H102···I	3.222 (4)	123.3 (3)	3.24	127.2
$X^- = I_3^-$, 20 K neutrons[15]			$X^- = I_3^-$, 9 K X-rays	
contact	dist/Å	angle/deg	dist/Å	angle/deg
H81···I	3.082 (7)	140.9 (6)	3.03	147.3
H82···I	3.179 (7)	131.1 (6)	3.17	131.6

$X^- = IBr_2^-$, 9 *K* X-rays			$X^- = ICl_2^-$, 120 K X-rays		
contact	dist/Å	angle/deg	contact	dist/Å	angle/deg
H102···Br	2.89	132.7	H71···Cl	2.59	168.2
H81···Br	2.90	154.4	H102···Cl	2.63	167.2
H102···Br	2.94	136.3	H91···Cl	2.77	129.9
H82···Br	3.14	126.8	H81···Cl	2.88	117.1
H92···Br	3.18	128.2	H92···Cl	2.91	140.5

[a] The observed C-H bond distances derived from our neutron diffraction data average 1.09 (1) Å. For the X-ray results, the H atom coordinates were calculated by using C-H bond distances of 1.09 Å and sp^3 geometries.

It has been shown that a direct relationship exists between the two-dimensional (2D) electrical behavior and the crystal structures of the β-$(ET)_2X$ salts, because of their sheetlike networks of strongly interacting ET molecules.[7-9] However, the crystal packing interactions between the 2D ET molecule networks and the adjacent, parallel layers of X^- anions are not well understood. The donor–anion interactions may be bonding (i.e., attractive), as expected for Coulombic interactions between counterions, or nonbonding (i.e., repulsive), as previously found for donor–donor interactions in β-$(ET)_2X$ salts based upon theoretical calculations.[9] Also, the donor–anion interactions in the modulated phase[15] of β-$(ET)_2I_3$ ($T < 200$ K) appear to be correlated to the modulation, which is unique in that β-$(ET)_2I_3$ contains the largest triatomic anion, I_3^-, in this series of materials. Of particular importance to the investigation of donor–anion interactions in these salts is the precise description of significant intermolecular contacts. The relationship between electrical properties and anion size for the β-$(ET)_2X$ conductors, where X^- is a linear triatomic anion, is examined here in terms of the donor–anion interactions.

Because of the molecular environment at the interface between the ET molecule network and the anion layer in β-$(ET)_2X$ salts, the *only* short intermolecular contacts between ET donors and X^- anions (i.e., interatomic distances less than the sum of the van der Waals radii[10]) are of the H···X type. Thus, it is imperative to obtain precise H atom positions, which can be derived only from neutron diffraction data, to accurately compare the donor–anion interactions for the various β-$(ET)_2X$ superconductors. The approximate coordination of *five* nearby H atoms to each terminal halide atom of the X^- anion is observed by use of neutron or X-ray data for all of the superconducting β-$(ET)_2X$ salts.[11,12] In these

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(1) The abbreviations "ET" and "BEDT-TTF" refer to the organic donor molecule bis(ethylenedithio)tetrathiafulvalene ($C_{10}H_8S_8$) as in: Mizuno, M.; Garito, A. F.; Cava, M. P. *J. Chem. Soc., Chem. Commun.* **1978**, 18.

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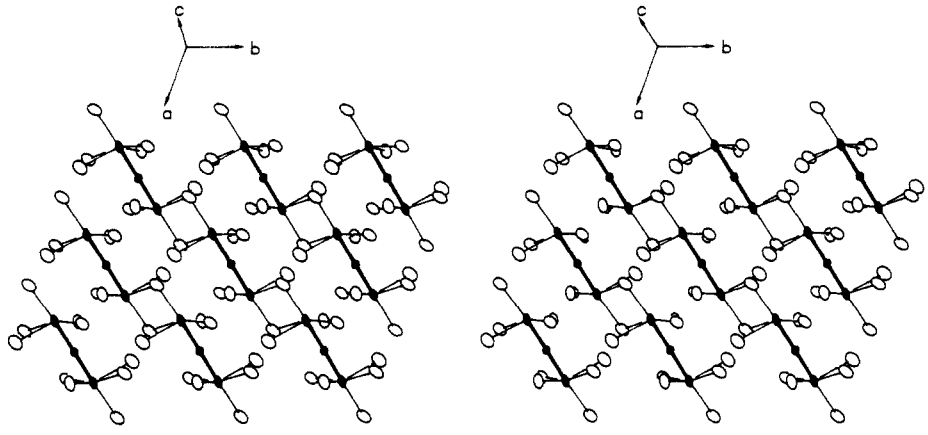

Figure 1. A stereoview of the *ab* plane of β-$(ET)_2AuI_2$ at 20 K shows the AuI_2^- anions and the numerous short H···I contacts (thin lines) with distances less than the van der Waals radii sum of 3.3 Å. The environment about each terminal I atom of the anions is nearly an octahedron of atoms. Thermal ellipsoids are known very precisely and are drawn at the 99% probability level.[16]

materials, there is a nearly octahedral environment of atoms about the terminal halogen atoms of the anion (see Figure 1). The shortest H···X distances and their corresponding C–H···X angles for several β-$(ET)_2X$ salts with X^- = linear anion are given in Table I. Although the most precise geometries in Table I are those obtained from neutron diffraction data, the low-temperature X-ray results agree surprisingly well, by comparison. Thus, the neutron diffraction experiments *verify* previous assumptions concerning the H···X geometries based upon low-temperature X-ray diffraction data. The H atom geometries that were calculated for the completely ordered structures of β-$(ET)_2IBr_2$[11] and β-$(ET)_2ICl_2$[12] from low-temperature X-ray data are also expected to be accurate (by comparison) and these parameters are included in Table I. The differences in the H···X interactions of the β-$(ET)_2X$ salts with X^- = AuI_2^-, IBr_2^-, and ICl_2^- are summarized as follows: (i) for the shortest H···X contacts in the above three salts, the angles about the H atoms, namely C–H···I, C–H···Br, and C–H···Cl, are largest for β-$(ET)_2ICl_2$ (approaching 180°) and are smallest for β-$(ET)_2AuI_2$; (ii) for longer contact distances in each of the above salts, the corresponding C–H···X angles are much smaller (i.e., approaching 120°); (iii) the H···Br, and H···Cl contact distances are as much as 0.38, 0.26, and 0.41 Å *shorter* than their respective van der Waals radii sums,[10] which is significant in comparison to the estimated errors for the values of the H···X distances derived from X-ray data (±0.1 Å or less). The above structural results confirm that the closest H···X contacts in the β-$(ET)_2X$ salts are the main contributors to the cohesive forces between the 2D ET molecule networks and the anions in these crystals and that these H···X interactions are similar to H-bonding interactions in other organic compounds.[13,14] The discovery of the very short H···I contacts in β-$(ET)_2AuI_2$ is surprising because such interactions are generally assumed to be weak.[13,14] In summary, there are important implications for the design and synthesis of new β-$(ET)_2X$ systems where the X_n^- anions contain halide (I, Br, Cl, F) atoms, namely, that H-bonding interactions of the type H···X play a major role in determing the crystal cohesive forces between donors and anions thereby controlling compound formation.

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Supplementary Material Available: Table S1, neutron data collection and refinement parameters; Table S2, atomic positional and thermal parameters for β-$(ET)_2AuI_2$ at 20 (neutron data) and 120 K (X-ray data); Table S3, atomic positional and thermal parameters for β-$(ET)_2I_3$ at 20 (neutron data) and 9 K (X-ray data); Table S4, atomic positional and thermal parameters for β-$(ET)_2IBr_2$ at 9 K (X-ray data) (6 pages). Ordering information is given on any current masthead page.

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Polyhedral Oligometallasilsesquioxanes (POMSS) as Models for Silica-Supported Transiton-Metal Catalysts: Synthesis and Characterization of $(C_5Me_5)Zr[(Si_7O_{12})(c\text{-}C_6H_{11})_7]$

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Heterogeneous silica-supported transition-metal compounds play an increasingly important role as catalysts in the petrochemical industry.[1] The commerical importance of such catalysts has stimulated an intense interest in the chemical processes which occur on the surface of heterogeneous catalysts. Although recent

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