of H_2SO_4 with $Os_3(CO)_{12}$, however, gives the cationic species $HOs_3(CO)_{12}^+$ and $HOs(CO)_5^+$.[16] Protonation of $H_3Os_3(CO)_9(\mu_3\text{-CH})$ with H_2SO_4 presumably occurs on the Os–C bond;[17,18] the evolved gas is predominantly methane.[19] MO calculations on the analogous $H_3Ru_3(CO)_9(\mu_3\text{-CY})$ clusters show that the HOMO is mainly Ru–C in character.[22]

Phosphoric acid does not react with $H_3Os_3(CO)_9(\mu_3\text{-CH})$ under mild conditions. However, addition of trifluoromethanesulfonic acid leads to gas evolution and a yellow solution. The species present in solution have not yet been characterized but presumably involve complexes of the $CF_3SO_3^-$ ion.[23] Addition of P_4O_{10}-saturated phosphoric acid to this solution, followed by dilution with water, produces a light yellow precipitate. Analytical and mass spectral data are consistent with the expected phosphate complex,[24] but the IR spectrum clearly shows that it is best formulated as a hydrogen phosphate species, i.e., $H_2Os_3(CO)_9(\mu_3\text{-}O_3POH)$. In particular, a strong, H-bonded OH stretch occurs at 3400 cm^{-1} and a band appropriate for a P=O stretch is absent.[25] A similar bonding mode has been observed for layered metal phosphates, e.g., $\alpha\text{-Zr(HPO}_4)_2\cdot H_2O$[26] and $(VO)_2H_4P_2O_9$.[27]

These oxyanion complexes are of interest not only as unique molecular examples of the tridentate, triply bridging coordination mode but also as models for the interaction between metal clusters and oxide supports. In particular, they are a suggestive representation for the "decoration" of metal particles by MO_x moieties, which has been proposed to be involved in the strong metal–support interaction (SMSI).[28] Furthermore, they may be related to the oxyanion species identified as adsorbed on platinum electrodes.[29] The structural and reactivity implications of these "hard–soft" complexes are being pursued.

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Supplementary Material Available: Tables of final positional parameters and anisotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

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(15) Deeming, A. J.; Underhill, M. *J. Organomet. Chem.* **1972**, *42*, C60.

(16) Deeming, A. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. A* **1970**, 2967.

(17) The ^{1}H NMR spectrum of $H_3Os_3(CO)_9(\mu_3\text{-CCH}_3)$ in neat FSO_3H showed four apparent singlets at δ 5.35 (3 H), −12.85 (1H), −16.62 (2 H), and −16.81 (1 H): Bryan, E. G.; Jackson, W. G.; Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Schorpp, K. T. *J. Organomet. Chem.* **1976**, *108*, 385. The authors interpreted the spectrum in terms of the species $H_4Os_3(CO)_9(\mu_3\text{-CCH}_3)^+$, but we suggest that the signal at δ −12.85 is more likely due to a C··H··Os bridge, i.e., to C–Os protonation.[18]

(18) Keister has shown that protonation of $H_3Ru_3(CO)_9(\mu_3\text{-CCH}_3)$ occurs at an Ru–C bond: Bower, D. K.; Keister, J. B., unpublished results.

(19) GC analysis showed also a significant amount of ethane and trace amounts of propane, butane, and pentane. Generation of methane by protonation of methylidyne complexes has been observed previously.[20,21]

(20) Holt, E. M.; Whitmire, K. H.; Shriver, D. F. *J. Organomet. Chem.* **1981**, *213*, 125.

(21) DeMiguel, A. V.; Isobe, K.; Bailey, P. M.; Meanwell, N. J.; Maitlis, P. M. *Organometallics* **1982**, *1*, 1604.

(22) Sherwood, D. E., Jr.; Hall, M. B. *Organometallics* **1982**, *1*, 1519.

(23) A species isolated from this solution has been characterized as $H_2Os_3(CO)_9(O_3SCF_3)_2$: Frauenhoff, G. R.; Shapley, J. R., unpublished results.

(24) Anal. $(C_9H_3O_{13}POs_3)$ C, H, Os. Mass spectrum (^{192}Os), m/z 926 (M$^+$) plus fragment ions. ^{1}H NMR (acetone-d_6) δ −12.45 (d, ^3J(P–H) = 3.2 Hz). IR (CH_2Cl_2) ν(CO), 2133 (m), 2100 (s), 2072 (vs), 2033 (s), 1996 (m) cm^{-1}.

(25) (a) Christol, C.; Christol, H. *J. Chem. Phys.* **1965**, *62*, 246. (b) Verkade, J. G.; Reynolds, L. T. *J. Org. Chem.* **1960**, *25*, 663.

(26) Troup, J. M.; Clearfield, A. *Inorg. Chem.* **1977**, *16*, 3311.

(27) Torardi, C. C.; Calabrese, J. C. *Inorg. Chem.* **1984**, *23*, 1310.

(28) For the original identification of the SMSI effect, see: (a) Tauster, S. J.; Fung, S. C.; Garten, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 170. (b) Tauster, S. J.; Fung, S. C. *J. Catal.* **1978**, *54*, 29. For interpretation of SMSI effects as MO_x decoration, see: (c) Santos, J.; Phillips, J.; Dumesic, J. A. *J. Catal.* **1983**, *81*, 147. (d) Resasco, D. E.; Haller, G. L. *J. Catal.* **1983**, *82*, 279. (e) Rieck, J. S.; Bell, A. T. *J. Catal.* **1985**, *95*, 88 and references therein.

(29) Zelenay, P.; Habib, M. A.; Bockris, J. O'M. *J. Electrochem. Soc.* **1984**, *131*, 2464. Habib, M. A.; Bockris, J. O'M. *Ibid.* **1983**, *130*, 2510.

On the Origins of Stereoselectivity in "Chelation Controlled" Nucleophilic Additions to β-Alkoxy Aldehydes: Solution Structures of Lewis Acid Complexes via NMR Spectroscopy

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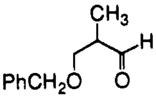
The area of "acyclic stereochemical control" has assumed a position of prominence in organic synthetic methodology in recent years. Many bond-forming processes utilized in this context have exploited "anti-Cram" or "chelation-controlled" phenomena[1] to obtain high levels of diastereofacial selectivity in nucleophilic additions to carbonyl compounds. Despite the amazing number of impressive examples that exploit such a phenomenon, i.e., presumed conformational biasing of substrate prior to reaction, no general study of the structures of such intermediates has been reported to date.[2] Our own interests in the mechanistic details and stereochemical course of additions of certain "storable organometallics"[3,4] to carbonyl compounds has prompted us to initiate a long-range program directed toward obtaining a fundamental understanding of this process, part of which requires a knowledge of the structures of putative complexed intermediates derived from alkoxy carbonyl compounds *in solution*. The results of some of our initial investigations are sufficiently compelling and relevant to the progress of much current research that we report them in this format.

Of crucial importance to this first report is the realization that, with β-alkoxy aldehydes **1** and **2**, attack of certain allylsilanes or stannanes (in the presence of bidentate Lewis acids) apparently occurs preferentially from the face opposite the methyl groups.[5] There is no obvious explanation for this result, particularly since all literature interpretations position the C_2 or C_3 substituents in pseudoequatorial positions in the presumed intermediate complex.[6] We record herein the resolution of this issue and the first direct experimental evidence regarding the origins of diastereofacial selectivity in such systems, via variable-temperature NMR spectroscopy of the complexes formed with aldehydes **1** and **2** with $TiCl_4$, $SnCl_4$, and $MgBr_2\text{–}OEt_2$ (Figure 1).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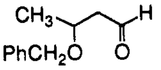
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We begin with the results for **1** with $TiCl_4$. ^{1}H and ^{13}C NMR spectra[7] were recorded at various temperatures (−80, −60, −40,

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(1) For a recent review of "chelation vs. nonchelation" in such reactions, note: Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 556–569.

(2) (a) Reetz has observed the complex formed from $TiCl_4$ and 2-methoxycyclohexanone by ^{1}H NMR: Reetz, M. T.; Kesseler, K.; Schmidtberger, S.; Wenderoth, B.; Steinbach, R. *Angew. Chem. Suppl.* **1983**, 1511–1516. (b) For a recent X-ray crystallographic analysis of the $TiCl_4$ complex of the acrylate derivative of ethyl lactate, which undergoes asymmetric Diels–Alder reactions, note: Poll, T.; Metter, J. O.; Helmchen, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 112–114.

(3) Kozikowski, A. P.; Stein, P. D. *J. Am. Chem. Soc.* **1985**, *107*, 2569–2571.

(4) (a) Keck, G. E.; Boden, E. P. *Tetrahedron Lett.* **1984**, *25*, 265–268. (b) Keck, G. E.; Boden, E. P. *Tetrahedron* Lett. **1984**, *24*, 1879–1882. (c) Keck, G. E.; Abbott, D. E. *Tetrahedron Lett.* **1984**, *25*, 1883–1886. (d) Keck, G. E.; Abbott, D. E.; Boden, E. P.; Enholm, E. J. *Tetrahedron Lett.* **1984**, *25*, 3927–3930.

(5) (a) Reetz, M. T.; Jung, A. *J. Am. Chem. Soc.* **1983**, *105*, 4833–4885. (b) Kiyooka, S.; Heathcock, C. H. *Tetrahedron Lett.* **1983**, *24*, 4765–4768. (c) Reetz, M. T.; Kesseler, K.; Jung, A. *Tetrahedron Lett.* **1984**, 729–732. (d) Heathcock, C. H.; Kiyooka, S.; Blumenkopf, T. A. *J. Org. Chem.* **1984**, *49*, 4214–4223. (e) Note also ref 4b. Our own unpublished observations on "1,3-asymmetric induction" will be reported separately.

(6) Note ref 1 and references therein.

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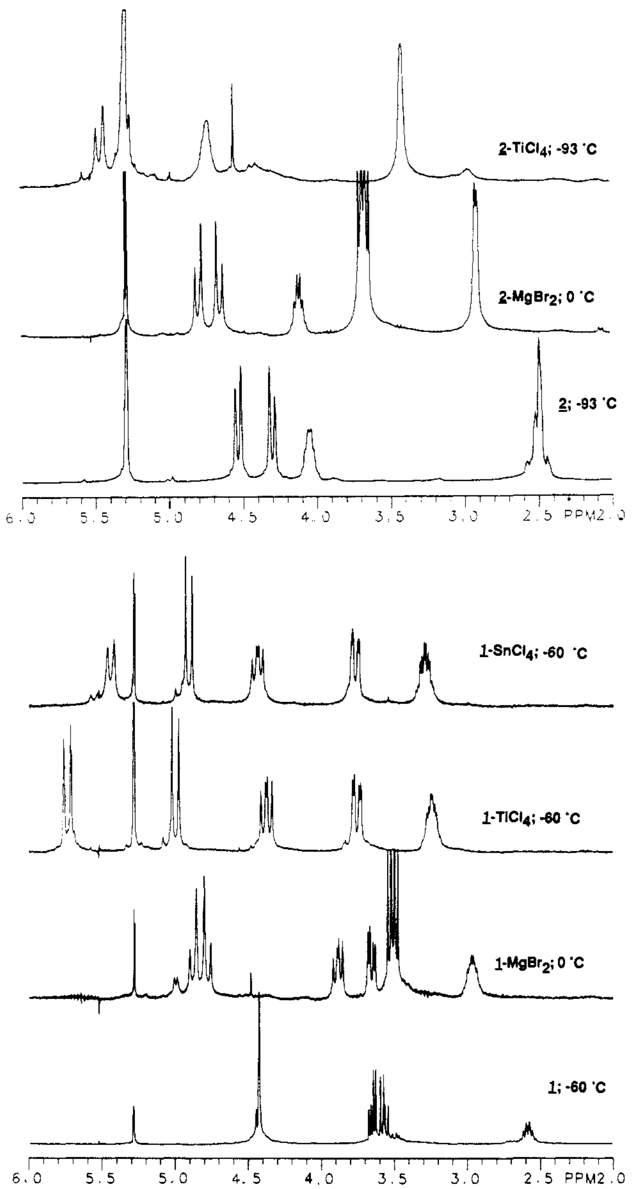

Figure 1. ^1H NMR spectra of **1** and **2** and their complexes with $MgBr_2$-OEt_2, $SnCl_4$, and $TiCl_4$ (2.0–6.0 ppm only) at selected temperatures. The large peak at ca. 5.3 δ is due to residual protium in the CD_2Cl_2 solvent; the large resonance at ca. 3.6 δ in the $MgBr_2 \cdot OEt_2$ spectra is due to ether; the chemical shift is somewhat variable due presumably to residual (uncomplexed) ether and averaging between free and bound ether.

and -20 °C) with varying stoichiometry of $TiCl_4$ to substrate (0.5, 1.0, and 2.0 equiv). The results clearly show that (a) a 1:1 complex is formed and (b) this species is quite rigid and essentially "conformationally locked", as the spectra for the complex were temperature-independent from -80 to -20 °C.[8] Moreover, from the observed coupling constants (J_{ax-ax} = 9.7 Hz, J_{ax-eq} = 3.5 Hz) for the C_2 methine to the diastereotopic methylene group at C_3, it is clear that the methyl group at C_2 occupies an equatorial (or pseudoequatorial) position. Chemical shift and coupling data are summarized in Table I, as are the data obtained with $SnCl_4$ and $MgBr_2$–OEt_2, which lead to parallel conclusions regarding the conformation of the complexes.[9]

Table I. ^1H NMR Spectral Data for Lewis Acid Complexes of **1**

H	δ	Δδ	mult	J/Hz
		$TiCl_4$		
C_1	9.87	-0.27	s (br)	
C_2	3.25	-0.66	m	
C_3	3.76	-0.19	dd	13.1, 3.5
C_3'	4.38	-0.74	dd	13.1, 9.7
C_4	5.00	-0.58	d	13.9
C_4'	5.74	-1.32	d	13.9
CH_3	1.35	-0.34	d	7.7
		$MgBr_2$		
C_1	9.68	-0.08	d	1.2
C_2	2.95	-0.36	m	
C_3	3.62	-0.50	dd	11.2;3.9
C_3'	3.91	-0.27	dd	11.2;7.9
C_4	4.78	-0.36	AB q	13.0
CH_3	1.09	-0.08	d	7.5
		$SnCl_4$		
C_1	9.61	-0.01	d	1.5
C_2	3.28	-0.69	m	
C_3	3.68	-0.11	dd	13.1, 3.5
C_3'	4.46	-0.82	dd	13.1, 8.8
C_4	4.82	-0.44	d	13.1
C_4'	5.39	-0.97	d	13.1
CH_3	1.24	-0.23	d	7.9
		None		
C_1	9.60		d	1.5
C_2	2.59		m	
C_3	3.57		dd	9.1, 6.5
C_3'	3.64		dd	9.1, 4.5
C_4	4.42		s	
CH_3	1.01		d	7.0

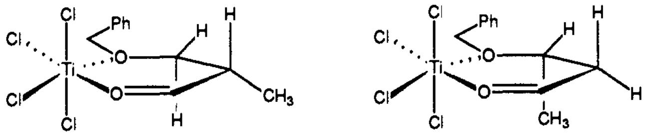

Figure 2. Approximate solution structures for the $TiCl_4$ complexes[11] of **1** and **2** as determined by NMR spectroscopy.

With the isomeric β-benzyloxy aldehyde **2**, the results were strikingly different. First of all, with $SnCl_4$, **2** could not be induced to yield a single species even at temperatures as low as -93 °C. Instead, a series of extremely broad resonances for both complexed and uncomplexed species is observed which sharpen as the temperature is lowered; even at -93 °C, however, the width at half-height for the aldehydic proton is ca. 30 Hz (as compared to ca. 1 Hz with **1**). With $TiCl_4$, the formation of a discrete bidentate complex was observed; again, complex formation was favored at lower temperatures and line widths also become narrower with decreasing temperature (Figure 2). In this case, the C_2 methylene protons appear as a singlet ($w_{1/2}$ = 10 Hz, as compared to 3 Hz for the aldehydic proton) at -93 °C (conditions under which line broadening is still significant although complexation is essentially complete) but the CH_3 group can still be observed as a doublet (J = 7 Hz). It thus appears that there can be no large coupling constants (cf. the 9.7-Hz coupling in the case of **1**) to this methylene group. Irradiation of the methyl group collapsed the multiplet for the C_3 methine to a broad triplet with a ca. 4.7 Hz coupling to the diastereotopic methylene protons at C_2.

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(7) (a) The ^{13}C NMR spectra proved less useful than the proton spectra in establishing bidentate chelation, as upfield shifts resulting from steric compression tend to mask charge-induced downfield shifts at most carbons.[7b] However, ^{13}C NMR spectroscopy was much more reliable than ^1H NMR in revealing complexation to the aldehyde oxygen, and these spectra also provided additional evidence that a single species was in fact present in each case. (b) Fratiello, A.; Kubo, R.; Chow, S. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1205–1209.

(8) (a) Considerable decomposition was noted at temperatures above -40 °C. (b) All spectra were recorded on a Varian XL spectrometer operating at 300 and 75 MHz for ^1H and ^{13}C, respectively. Solutions were 0.1 M with respect to substrate in CD_2Cl_2. All reagents were carefully purified and handled by techniques appropriate for air- and moisture-sensitive materials.

(9) Complexation studies with isobutyraldehyde and benzyl isobutyl ether as models for the aldehyde and ether portions of **1** further support the interpretation of the above data as resulting from bidentate chelation. With $SnCl_4$, complexation of benzyl isobutyl ether was highly temperature-dependent, with complexation favored at lower temperatures.

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 ^{1}H 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.

Acknowledgment. This research was supported by the National Institutes of Health (through Grant GM-28961), to whom we are most grateful. We also thank the National Institutes of Health, the National Science Foundation, and the University of Utah Institutional Funds Committee for funding for the purchase of the spectrometer used in this work.

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(10) ^{1}H 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)$_2$X,[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)$_2$AuI$_2$ has the highest T_c ($\sim$5 K) at *ambient pressure*,[2,3] and β-(ET)$_2$I$_3$ has the highest T_c ($\sim$8 K) under a *non*hydrostatic pressure of 1.3 kbar.[4-6]

Table I. H-Bonding Interaction Geometries for Several β-(ET)$_2$X 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)$_2$X 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)$_2$X salts based upon theoretical calculations.[9] Also, the donor–anion interactions in the modulated phase[15] of β-(ET)$_2$I$_3$ ($T < 200$ K) appear to be correlated to the modulation, which is unique in that β-(ET)$_2$I$_3$ 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)$_2$X 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)$_2$X 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)$_2$X 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)$_2$X salts.[11,12] In these

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* Author to whom correspondence should be addressed.

(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.

(2) Wang, H. H.; Beno, M. A.; Geiser, U.; Firestone, M. A.; Webb, K. S.; Nuñez, L.; Crabtree, G. W.; Carlson, K. D.; Williams, J. M.; Azevedo, L. J.; Kwak, J. F.; Schirber, J. E. *Inorg. Chem.* **1985**, *24*, 2465.

(3) Carlson, K. D.; Crabtree, G. W.; Nuñez, L.; Wang, H. H.; Beno, M. A.; Geiser, U.; Firestone, M. A.; Webb, K. S.; Williams, J. M. *Solid State Commun.* **1986**, *57*, 89.

(4) Murata, K.; Tokumoto, M.; Anzai, H.; Bando, H.; Saito, G.; Kajimura, K.; Ishiguro, T. *J. Phys. Soc. Jpn.* **1985**, *54*, 1236.

(5) Laukhin, V. N.; Kostyuchenko, E. E.; Sushko, Yu. B.; Shchegolev, I. F.; Yagubski, E. B. *JETP Lett.* (*Engl. Transl.*) **1985**, *41*, 81.

(6) Schirber, J. E.; Azevedo, L. J.; Kwak, J. F.; Venturini, E. L.; Leung, P. C. W.; Beno, M. A.; Wang, H. H.; Williams, J. M. *Phys. Rev. B* **1987**, *33*.

(7) Mori, T.; Kobayashi, A.; Sasaki, Y.; Kobayashi, H.; Saito, G.; Inokuchi, H. *Chem. Lett.* **1984**, 957.

(8) Whangbo, M-H.; Williams, J. M.; Leung, P. C. W.; Beno, M. A.; Emge, T. J.; Wang, H. H.; Carlson, K. D.; Crabtree, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 5815.

(9) Whangbo, M.-H.; Williams, J. M.; Leung, P. C. W.; Beno, M. A.; Emge, T. J.; Wang, H. H. *Inorg. Chem.* **1985**, *24*, 3500.

(10) For the van der Waals radii used here (2.15 Å for I, 1.95 Å for Br, 1.80 Å for Cl, and 1.20 Å for H), see: Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960; p 260.

(11) Emge, T. J.; Leung, P. C. W.; Beno, M. A.; Wang, H. H.; Firestone, M. A.; Webb, K. S.; Carlson, K. D.; Williams, J. M.; Venturini, E. L.; Azevedo, L. J.; Schirber, J. E. *Mol. Cryst. Liq. Cryst.* **1986**, *132*, 363.

0002-7863/86/1508-3849$01.50/0