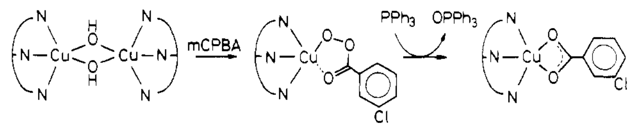
Scheme I



scribed as tetragonal. In accord with the binuclear structure, **2** shows strong antiferromagnetic properties; it is EPR silent in CH_2Cl_2 at -196 °C. ^1H NMR ($CDCl_3$, -40 °C, ppm): -51 (s, br, 2 H, OH), 1.34 (s, br, 36 H, *Me*$_2$CH), 1.70 (s, br, 36 H, *Me*$_2$CH), 2.91 (br, 6 H, Me_2CH), 3.85 (s, br, 6 H, Me_2CH), 12.66 (s, br, 6 H, pz).

When a solution of **2** in pentane was treated with a ca. 2-equiv amount of mCPBA at -20 °C, a slight color change from blue to greenish blue was noted within ca. 10 min. Removal of the unreacted mCPBA by filtration followed by evaporation at -20 °C afforded **1** as a thermally unstable solid[8] that exhibited the characteristic IR band at 1640 cm^{-1} assigned to the acyl carbonyl group (Figure 2). The frequency is ca. 100 cm^{-1} down-shifted as compared with that of free mCPBA (1735 cm^{-1}). Fe(mCPBA)TTPPP[9] (TTPPP = 5,10,15,20-tetrakis(2,4,6-triphenylphenyl)porphyrinate), in which the acyl carbonyl group is not coordinated by the iron, shows a band at 1744 cm^{-1}. Hence, the acyl carbonyl group is suggested to coordinate to copper, and **1** is ascribed to a pentacoordinated complex with a N_3O_2 ligand donor set. The structure is also supported by the EPR spectrum, which is typical for a square-pyramidal mononuclear copper(II) complex ($g_\parallel = 2.27$, $g_\perp = 2.07$, and $A_\parallel = 160$ G at -196 °C in CH_2Cl_2).

Complex **1** is moderately stable at -20 °C (the half-life time in CH_2Cl_2 is ca. 0.5 h), although it decomposes at room temperature even in the solid. When PPh_3 was added to a solution of **1** at -20 °C, an instantaneous color change to green took place with the quantitative formation of $OPPh_3$. The solids obtained by the evaporation of the resulting solution exhibited the characteristic new band at 1515 cm^{-1}, as shown in Figure 2. The band is attributable to the carbonyl group of the benzoato complex $Cu(mCBA)(HB(3,5\text{-}iPr_2pz)_3)$[10] (**3**), of which the crystal structure is shown in Figure 3.

As described above, **1** readily oxidizes PPh_3. However, the oxidizing capability is apparently less than that of free mCPBA. For instance, **1** did not react with cyclohexene at -20 °C, whereas free mCPBA oxidizes cyclohexene to cyclohexene oxide under comparable reaction conditions. The addition of protons to the reaction solution of **1** did not affect the result. The low reactivity of **1** is in striking contrast to the high reactivity of Fe(mCPBA)(TTPPP). The iron complex undergoes heterolytic cleavage by H^+ to give an oxoiron(IV) porphyrin π-cation-radical complex,[11] which is extremely effective for the oxo-transfer reaction of cyclohexene even at a low temperature. Therefore, the occurrence of a heterolytic O-O bond cleavage to form an oxocopper(III) cation or oxocopper(IV) intermediate (which is expected to show the high oxo-transfer reactivity) seems unlikely in the present system, although such a reaction is suggested as an elemental step in the enzymatic oxidations catalyzed by dopamine β-hydroxylase.[4]

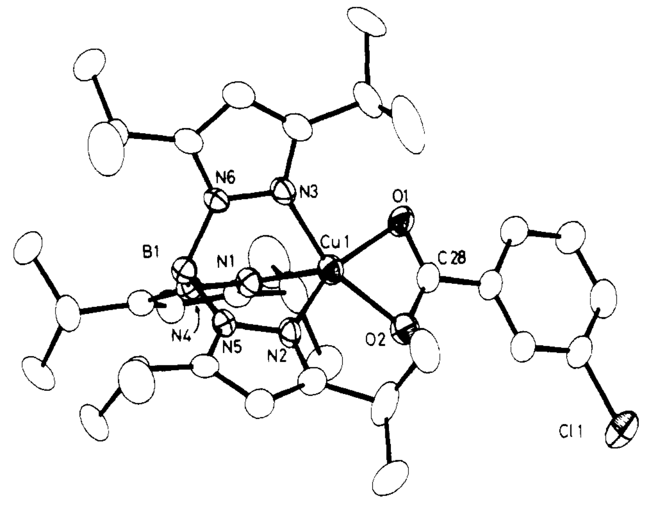


Figure 3. ORTEP view of **3**. Selected bond distances (Å) and bond angles (deg): Cu1-N1, 2.171 (9); Cu1-N2, 1.977 (8); Cu1-N3, 1.980 (9); Cu1-O1, 2.043 (7); Cu1-O2, 2.013 (8); O1-C28, 1.246 (15); O2-C28, 1.252 (14); O1-Cu1-O2, 64.7 (3); O1-C28-O2, 120.6 (10).

Acknowledgment. We thank Dr. K. Toriumi for his kind help in the final refinements of the X-ray analysis of **2**. Financial support for this study by the Ministry of Education, Science and Culture of Japan (Grants 62430018 and 1607003) is gratefully acknowledged. N.K. is also grateful to the Kawakami Memorial Foundation for financial support.

Supplementary Material Available: For **2** and **3**, text covering crystallographic details, figures showing fully labeled ORTEP structures, and tables of atomic coordinates, thermal parameters, bond distances, and bond angles (32 pages); tables of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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[8] Isolation of **1** as a pure crystalline solid has been unsuccessful so far, owing to the instability of **1** and the contamination of **3**.

[9] Groves, J. T.; Watanabe, Y. *Inorg. Chem.* **1987**, *26*, 785.

[10] An authentic sample of **3** was obtained by the reaction of $Cu(HB(3,5\text{-}iPr_2pz)_3)^3$ with mCPBA. Anal. Calcd for $C_{34}H_{50}N_6BO_2CuCl$: C, 59.65; H, 7.36; 12.28. Found: C, 59.60; H, 7.40; N, 12.25. EPR (CH_2Cl_2, -196 °C): $g_\parallel = 2.29$, $g_\perp = 2.06$, $A_\parallel = 141$ G. UV-vis (CH_2Cl_2): 757 nm (ε 130). **3** (MW 684.62) crystallized in the monoclinic space group $P2_1/n$ with $a = 15.887$ (2) Å, $b = 18.783$ (2) Å, $c = 12.531$ (2) Å, $\beta = 96.06$ (2)°, $V = 3718$ (1) Å^3, and $Z = 4$ for 2759 observed reflections ($2\theta < 45°$; $F_o > 3\sigma(F_o)$) taken on a Rigaku AFC-5 diffractometer at 25 °C. The structure was refined by a full-matrix least-squares method to final residuals $R = 6.29\%$ and $R_w = 6.05\%$. Hydrogen atoms on the boron, the pyrazole rings, and the tertiary positions of the iPr groups were calculated. The other hydrogen atoms were not included in the calculation.

[11] Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7834. An acylperoxoplatinum complex was also reported to be effective for an oxo-transfer reaction of cyclohexene: Chen, M. J. K.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1977**, 204.

Soluble and Volatile Alkoxides of Bismuth. The First Structurally Characterized Bismuth Trialkoxide: $[Bi(\mu\text{-}\eta^1\text{-}OCH_2CH_2OMe)_2(\eta^1\text{-}OCH_2CH_2OMe)]_\infty$

We and others[1] are interested in bismuth alkoxides as potential precursors for solution-phase and vapor-phase syntheses of bismuth-containing oxide superconductors. Mehrotra and Rai previously described the synthesis of simple alkoxides of bismuth(III) according to eq 1.[2] The compounds were reported to

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[1] (a) Sauer, N. N.; Garcia, E.; Salazar, K. V.; Ryan, R. R. *Abstracts of Papers*, 197th National Meeting of the American Chemical Society, Dallas, TX; American Chemical Society: Washington, DC, 1989; INOR-251. (b) Sauer, N. N.; Garcia, E.; Ryan, R. R. *Abstracts of Papers*, 198th National Meeting of the American Chemical Society, Miami Beach, FL; American Chemical Society: Washington, DC, 1989; INOR-256. (c) For related bismuth-amide chemistry see: Clegg, W.; Compton, N. A.; Errington, R. J.; Norman, N. C.; Wishart, N. *Polyhedron* **1989**, *8*, 1579.

[2] Mehrotra, R. C.; Rai, A. K. *Indian J. Chem.* **1966**, *4*, 537.

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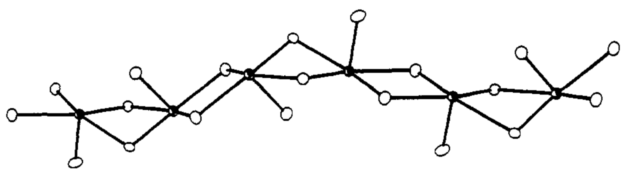

Figure 1. View of the $[\mathrm{Bi}(\mu\text{-O})_2\mathrm{O}]_\infty$ central skeleton from the crystal structure of $\mathrm{Bi(OCH_2CH_2OMe)_3}$ (**2**) showing the one-dimensional connectivity. Oxygen atoms are represented by open ellipsoids, and bismuth atoms by hatched, shaded ellipsoids.

have poor solubilities in organic solvents and to sublime in very low yields.

$$\mathrm{BiCl_3} + 3\ \mathrm{MOR} \xrightarrow{-3\ \mathrm{MCl}} \mathrm{Bi(OR)_3} \qquad (1)$$

M = Li, Na; R = Me, Et, i-Pr

More recent work established that the trialkoxides (specifically the isopropoxides) of yttrium(III),[3] indium(III),[4] and ytterbium(III)[4] are unstable with respect to the oxo-centered pentanuclear compounds $\mathrm{M_5(\mu_5\text{-}O)(\mu_3\text{-}OR)_4(\mu_2\text{-}OR)_4(OR)_5}$. Related instabilities of bismuth(III) trialkoxides with respect to oxo alkoxides might account for the poor volatilities cited above. Consequently, we sought to confirm the isolability of bismuth trialkoxides as earlier claimed[2] and to improve their solubility and volatility.

We now report several soluble and volatile bismuth trialkoxides prepared by alcoholyses of $\mathrm{Bi(NMe_2)_3}$[5] (eq 2). The crystal structure of $\mathrm{Bi(OCH_2CH_2OMe)_3}$ (**2**) has been determined, which to our knowledge provides the first structural characterization of a bismuth trialkoxide. A preliminary account of the thermolytic and hydrolytic decomposition of representative examples to bismuth oxides is also given.

$$\mathrm{Bi(NMe_2)_3} + 3\ \mathrm{ROH} \xrightarrow{-3\ \mathrm{HNMe_2}} \underset{\mathbf{1\text{-}5}}{\mathrm{Bi(OR)_3}} \qquad (2)$$

R = i-Pr (**1**), 80%

$\mathrm{CH_2CH_2OMe}$ (**2**), 89%

$\mathrm{CH_2CH_2NMe_2}$ (**3**), 79%

$\mathrm{CHMeCH_2NMe_2}$ (**4**), 50%

$\mathrm{CMe_2Et}$ (**5**), 80%

The trialkoxides prepared according to eq 2 were purified by recrystallization, generally from hydrocarbons, and characterized by chemical and spectroscopic analyses.[6] Our observations regarding the low solubility and volatility of isopropoxide **1** parallelled those of Mehrotra and Rai,[2] and chemical analyses were consistent with empirical formula Bi(O-*i*-Pr)$_3$, not a bismuth oxo alkoxide. As we previously found for the alkoxides of Cu(II)[7,8] and Zn(II),[9] the use of potentially chelating or bulky alkoxide ligands resulted in higher solubilities and volatilities. Each of **2**–**5** was readily soluble in common organic solvents, and **3**–**5** sublimed with fair to excellent recovery in the range of 60–90 °C at 10^{-4} Torr. The methoxyethoxide **2** was not volatile. The lower sublimation yields[6] of **1**, **3**, and **4** compared to **5** presumably result from thermal degradation to less volatile, higher molecular weight species, perhaps polynuclear oxo compounds.

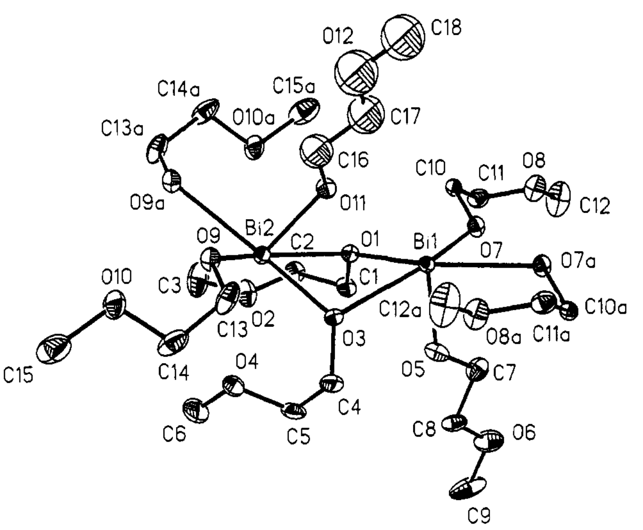

Figure 2. View of the asymmetric unit in the crystal structure of Bi(OCH$_2$CH$_2$OMe)$_3$ (**2**). Selected distances (Å): Bi(1)–O(1), 2.21 (1); Bi(1)–O(3), 2.56 (1); Bi(1)–O(5), 2.07 (2); Bi(1)–O(7), 2.20 (1); Bi(1)–O(7A), 2.54 (1); Bi(2)–O(1), 2.58 (1); Bi(2)–O(3), 2.21 (1); Bi(2)–O(9), 2.20 (1); Bi(2)–O(9A), 2.53 (1); Bi(2)–O(11), 2.11 (1); Bi(1)–Bi(2), 3.641 (3); Bi(1)–Bi(1), 3.953 (3); Bi(2)–Bi(2), 3.975 (3). Selected angles (deg): O(1)–Bi(1)–O(3), 73.0 (3); O(1)–Bi(1)–O(5), 89.4 (4); O(1)–Bi(1)–O(7), 85.2 (3); O(3)–Bi(1)–O(7A), 133.0 (3); O(7)–Bi(1)–O(7A), 67.4 (4); O(1)–Bi(2)–O(3), 72.7 (3); O(1)–Bi(2)–O(9A), 129.9 (3); O(1)–Bi(2)–O(11), 72.2 (4); O(3)–Bi(2)–O(9), 88.4 (4); O(9)–Bi(2)–O(9A), 65.8 (4).

Crystals of **2** suitable for single-crystal X-ray diffraction were obtained from benzene.[10] The structure comprises one-dimensional alkoxide-bridged chains, as shown in Figures 1 and 2. In the solid state all of the terminal and bridging ligands have dangling rather than chelating configurations. However, the good solubility and dimeric molecular complexity (in benzene) of **2** suggest that chelation through ether oxygens occurs to some extent in solution.

The asymmetric unit contains two bismuth atoms, each having a distorted square-pyramidal coordination provided by one terminal and four bridging alkoxides. The chains are constructed from a series of basal-edge-shared square pyramids with the apical sites alternating in an up–down–up–down fashion. The terminal ligands, which are in the apical positions, have the shortest Bi–O distances of 2.07 (2) and 2.11 (1) Å. The Bi–O separations in the asymmetric bridges fall into two sets; the shorter Bi–O distances range from 2.20 (1) to 2.21 (1) Å, and the longer Bi–O distances range from 2.53 (1) to 2.58 (1) Å. Presumably, a stereochemically active lone pair occupies the sixth octahedral vertex at each Bi center.

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[3] Poncelet, O.; Sartain, W. J.; Hubert-Pfalzgraf, L. G.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1989**, *28*, 263.

[4] Bradley, D. C.; Chudzynska, H.; Frigo, D. M.; Hursthouse, M. B.; Mazid, M. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1258.

[5] Ando, F.; Hayashi, T.; Ohashi, K.; Koketsu, J. *J. Inorg. Nucl. Chem.* **1975**, *37*, 2011.

[6] Syntheses were carried out in hydrocarbon solvents at room temperature with reaction times of several minutes. Satisfactory elemental analyses were obtained. ^{1}H NMR (δ; benzene-d_6, 300 MHz): **2**, 5.08 (t, ^3J = 4.5 Hz, 6 H), 3.51 (t, ^3J = 4.5 Hz, 6 H), 3.22 (s, 9 H), resonances broadening progressively and substantially upon cooling to −85 °C, but not decoalescing; **3**, 5.12 (t, ^3J = 5.0 Hz, 6 H), 2.40 (t, ^3J = 5.1 Hz, 6 H), 2.12 (s, 18 H); **4**, 4.82–4.53 (m, 3 H), 2.43–2.17 (m, 3 H), 2.12 (s, 18 H), 2.07–1.98 (m, 3 H), 1.35 (d, ^3J = 6.1 Hz, 9 H); **5**, 1.63 (q, ^3J = 7.3 Hz, 6 H), 1.35 (s, 18 H), 1.04 (t, ^3J = 7.3 Hz, 9 H). Molecular complexity (*n*, cryoscopic in benzene): **2**, 2.1 (1); **3**, 1.5 (2); **4**, 1.1 (1); **5**, 1.2 (1). Sublimation point (°C (yield); 10^{-4} Torr): **1**, 92 (10%); **3**, 85 (38%); **4**, 90 (54%); **5**, 63 (>90%).

[7] Goel, S. C.; Kramer, K. S.; Gibbons, P. C.; Buhro, W. E. *Inorg. Chem.* **1989**, *28*, 3619.

[8] Goel, S. C.; Kramer, K. S.; Chiang, M. Y.; Buhro, W. E. *Polyhedron*, in press.

[9] Goel, S. C.; Chiang, M. Y.; Buhro, W. E. Submitted for publication in *Inorg. Chem.*

[10] Crystal data for **2**: $\mathrm{C_{18}H_{42}Bi_2O_{12}}$, M_r = 868.5, triclinic, $P\bar{1}$, a = 10.849 (8) Å, b = 12.041 (9) Å, c = 13.11 (1) Å, α = 66.57 (6)°, β = 73.54 (6)°, γ = 66.71 (5)°, V = 1427 (2) Å^3, T = 295 K, Z = 2, D_c = 2.022 g cm^{-3}, λ(Mo Kα) = 0.71073 Å. Of the 6549 unique intensities measured, 3627 with $F_o > 6.0\sigma(F_o)$ yielded $R(F)$ = 0.0497 and $R_w(F)$ = 0.0588.

Comparisons can be made to the structure of α-Bi_2O_3,[11,12] which possesses two symmetrically distinct bismuth atoms, Bi(1) and Bi(2). Bi(1) has five nearest-neighbor oxides in a distorted square-pyramidal arrangement with a lone pair directed toward the remaining 6-fold vertex.[11] Bi(2) is octahedrally coordinated.[11] The Bi–O separations about Bi(1) in α-Bi_2O_3 closely resemble the Bi–O separations in **2**.[12] The shortest Bi–O distance in α-Bi_2O_3 is to the apical oxide, 2.13 Å. In the basal set there are two shorter, 2.21 and 2.22 Å, and two longer Bi–O distances, 2.55 and 2.63 Å, parallelling the pattern shown by **2**. In many Bi(III) oxy compounds the Bi centers are surrounded by five or six nearest neighbors at distances of 2.1–2.7 Å.[13]

Solutions of **2** in methoxyethanol (0.2 M) remained homogeneous after addition of up to 12 molar equiv of H_2O. When such solutions were brought to reflux, metastable β-Bi_2O_3 formed as a crystalline yellow precipitate.[14] In contrast, the room-temperature hydrolysis of **2** in THF (0.2 M) with stoichiometric quantities of water rapidly gave a gelatinous precipitate, which collapsed to an amorphous powder with continued stirring. Finally, the *tert*-pentoxide **5** was selected for thermolysis studies; its superior volatility makes it the best candidate for a vapor-deposition source compound. Thermal decomposition under a N_2 stream at 200 °C followed by a 600 °C anneal gave a mixture of α-Bi_2O_3 (major) and γ-Bi_2O_{3+x} (minor).[15]

In summary, bismuth trialkoxides are stable, isolable compounds and have good solubility and volatility in examples with appropriate bulky or chelating alkoxide ligands. The compounds are hydrolytic and thermolytic precursors to bismuth oxides. Efforts to use them in the preparation of bismuth-containing superconductors are in progress.[16]

Note Added in Proof. Professor L. G. Hubert-Pfalzgraf, Université de Nice, has informed us that our groups independently solved the structure of **2** at approximately the same time.

Acknowledgment. W.E.B. and M.A.M. warmly thank Dr. Subhash C. Goel for ideas, advice, and encouragement. Support was provided by the National Science Foundation under Grant No. DMR-8914196. The Washington University X-Ray Crystallography Facility was funded by the NSF Chemical Instrumentation Program (Grant CHE-8811456). The Washington University High-Resolution NMR Service Facility was funded in part by NIH Biomedical-Research-Support Shared-Instrument Grant 1 S10 RR02004 and a gift from the Monsanto Co.

Supplementary Material Available: Listings of the details of the data collection, final positional and equivalent isotropic thermal parameters, bond distances, bond angles, calculated hydrogen atom parameters, and anisotropic thermal parameters (7 pages); a listing of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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(14) (a) Medernach, J. W.; Snyder, R. L. *J. Am. Ceram. Soc.* **1978**, *61*, 494. (b) Note that data in JCPDS File 18-244 are incorret.[14a]

(15) α-Bi_2O_3: JCPDS File 14-699. γ-Bi_2O_{3+x}: JCPDS File 6-312.

(16) A reviewer has suggested an alternate description of the structure of **2**: The one short and two medium Bi–O separations identify a pyramidal $Bi(OR)_3$ repeat unit, made polymeric by the two additional, long (weak) Bi–O bridges. These weak bridges possess the attributes of "secondary bonding" as defined by Alcock.[17]

(17) Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 2.

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Molecular Identities in First-Principles Self-Consistent-Field Band Electronic Structures of the Organic Superconducting Salts β-$(BEDT\text{-}TTF)_2X$ ($X^- = I_3^-, AuI_2^-, IBr_2^-$)

Organic donor molecule bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or simply ET) gives rise to a number of ambient-pressure 2:1 superconducting salts, which include the β-phase salts β-$(ET)_2X$ ($X^- = I_3^-$, AuI_2^-, and IBr_2^-, for which the superconducting transition temperature T_c = 1.4,[1] 5.0,[2] and 2.8 K,[3] respectively), the κ-phase salts κ-$(ET)_2X$ ($X^- = I_3^-$ and $Cu(NCS)_2^-$, for which T_c = 3.6[4] and 10.4 K,[5] respectively), and θ-$(ET)_2I_3$ (T_c = 3.6 K[6]). A structural pattern common to all these salts is that they have layers of donor molecules ET alternating with layers of anions in one crystallographic direction (i.e., the *c* direction).[7] With the formal oxidation states $(ET)_2^+$ and X^- for the 2:1 salts $(ET)_2X$, it is expected that the ET layers are primarily responsible for the partially filled band, and hence for the metallic properties, of $(ET)_2X$. In agreement with this prediction, the electrical conductivities of the superconducting $(ET)_2X$ salts are much greater in the plane of the ET layers.[1] Thus the electronic structures relevant for their normal metallic states are well described by extended Hückel tight-binding (EHTB) band calculations[8] on a single ET layer. In calculations of Mori et al.,[9] this EHTB band calculation is simplified by calculating only those bands resulting from the HOMO's of ET molecules on the basis of the overlap integrals between the HOMO's of nearest-neighbor ET molecules. Concerning the nature of the partially filled bands of the superconducting 2:1 salts, the regular EHTB[8] and its simplified[9] approaches provide similar results since these bands are essentially made up of the HOMO's of ET molecules. Thus the highest occupied (HO) bands are half-filled, as expected from the formal oxidation state $(ET)_2^+$, and their Fermi surfaces have a simple shape of a distorted circle[8,9] or overlapping distorted circles.[6b,10]

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