

cycle and of the latter as a dioxygen storage protein that requires the ferrous state.

The present results show that reversible electron transfer to imidazole-MP8 is controlled by three electrostatic gates. Protonation of the heme propionate and deprotonation of the N-terminal amino group decrease the midpoint potential of the Fe(III)/Fe(II) couple because of changes in Coulombic interaction between these groups and the metal ion. This models equivalent electrostatic perturbations of the redox potential of various cytochromes where ionizing groups have been identified as a heme propionate ( $\Delta(pK_a) \approx 1$ ) or a noncoordinated His ( $\Delta(pK_a) \approx 0.4$ ) and means that electron uptake at one center is coupled to proton uptake at another as decreased charge on the metal ion raises the  $pK_a$  of these ionizing groups. MP-8 has previously proved a useful protein-free model for the peroxidase enzymes,<sup>30,31</sup> for studying reactions of protein-free heme-bound dioxygen,<sup>32</sup> and for delineating features of hemoprotein topology that control access to the heme.<sup>33</sup> The effects described here now provide a plausible mechanism for control of redox potentials and proton pumping by the cytochromes. Work with other MP8 derivatives and other small heme peptides that will further explore this hypothesis is planned and will be reported elsewhere.

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Department of Chemistry  
 University of the Witwatersrand  
 1 Jan Smuts Avenue  
 P.O. Wits  
 2050 Johannesburg  
 Republic of South Africa

Helder M. Marques

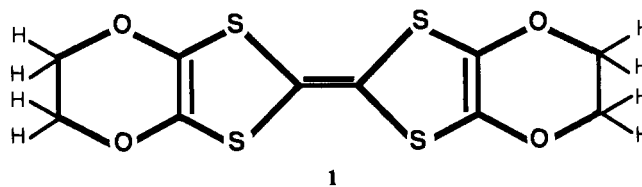
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### The First Ambient Pressure Organic Superconductor Containing Oxygen in the Donor Molecule, $\beta_m$ -(BEDO-TTF)<sub>3</sub>Cu<sub>2</sub>(NCS)<sub>3</sub>, $T_c = 1.06$ K

In this communication, we report the discovery of superconductivity in an organic charge-transfer salt containing an oxygen-bearing organic-donor molecule. A review of the literature<sup>1</sup> on organic conductors and superconductors reveals that all such superconductors are based on Se- or S-containing organic electron-donor molecules. In fact, an increasingly large number of *ambient-pressure organic superconductors* occur as the atomic number of the chalcogen atoms in the electron-donor molecule decreases from Se to S. So far, one ambient-pressure superconductor has been discovered in an all-Se-containing system, (TMTSF)<sub>2</sub>ClO<sub>4</sub> ( $T_c \approx 1.1$  K),<sup>2</sup> and at least nine such superconductors are found in S-containing systems based on BEDT-TTF.<sup>3</sup>

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 (3) For a summary see: Inokuchi, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1747. BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene.

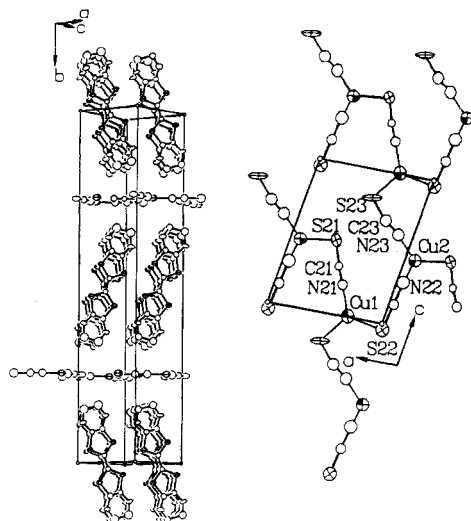
The latter system has yielded the highest transition temperature obtained thus far in an organic superconductor, for  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>,  $T_c \approx 10.4$  K.<sup>4</sup> If this trend continues one might expect to find a number of O-based organic superconductors, as appropriate organic electron-donor molecules are synthesized. As suggested by Wudl and co-workers,<sup>6a</sup> there may be a remote connection between oxygen containing organic superconductors and Cu–O high- $T_c$  superconductors.<sup>5</sup> In addition, according to BCS theory<sup>18</sup> (isotope effect), a lighter atom (oxygen) than S or Se in otherwise identical organic-donor molecules could cause  $T_c$  to rise in the lighter atom salt. Expanding on this possibility, we point out that the discovery of superconductivity in an oxygen-containing organic system could be important for systematically expanding the range of possible organic superconductors and for potentially establishing a link between organic superconductors and the recently discovered high-temperature oxide superconductors.<sup>5</sup> In fact, organic superconductors have many features in common with the high- $T_c$  oxide superconductors; viz., both are layered compounds, both have short anisotropic superconducting coherence lengths (type-II superconductors), and both have superconducting ground-states competing with magnetic instabilities. In this communication, we report the first organic superconductor based on the oxygen-bearing electron-donor molecule BEDO-TTF<sup>6,7</sup> [BEDO-TTF is bis(ethylenedioxy)tetrathiafulvalene, 1],



and a copper-containing inorganic anion. We describe herein the synthesis of this new material, its crystal structure, its characteristic ESR properties, inductive measurements of its superconducting transition, and its band electronic structure.

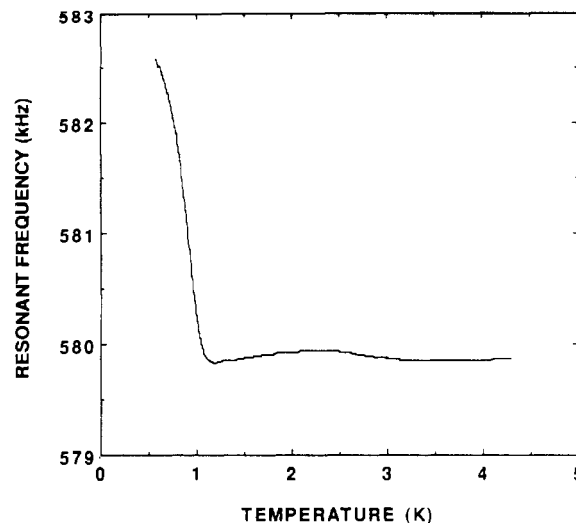
**Synthesis and ESR Study.** The salt, which we denote as  $\beta_m$ -(BEDO-TTF)<sub>3</sub>Cu<sub>2</sub>(NCS)<sub>3</sub>, was prepared by electrocrystallization of the organic donor BEDO-TTF<sup>6a</sup> (7.0 mg, 0.022 m mol), CuSCN (27.5 mg, 0.23 m mol), KSCN (22.1 mg, 0.23 m mol), and 18-crown-6 (~60 mg, 0.23 m mol) in 1,1,2-trichloroethane with 10% (vol) absolute ethanol at room temperature. Crystal growth was carried out in a drybox purged with nitrogen gas. The current density applied was 0.07  $\mu\text{A}/\text{cm}^2$ , and small black crystals were harvested after 25 days. Preliminary room-temperature ESR data indicate an anisotropic single line absorption in which the peak-to-peak line width varies from 17.5 to 27 G. No other line width was observed in several samples, indicating that the title compound is the only product formed under the above preparative conditions. An analysis of the copper content was carried out by use of an inductively coupled plasma/atomic emission spectrometer (ICP/AES). A similar, but well-defined, compound,  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>, was also analyzed for comparison; % Cu, found (calcd) = 6.53  $\pm$  0.33 (6.69). The result for  $\beta_m$ -(BEDO-TTF)<sub>3</sub>Cu<sub>2</sub>(NCS)<sub>3</sub>; % Cu, found (calcd) = 9.90  $\pm$  0.50 (10.06). Low-temperature single-crystal ESR studies revealed a monotonic decrease in line width from 12.6 G at 150 K to 1.5 G at 4.2 K, and the ESR spin susceptibility was approximately constant from 150 to 30 K, below which temperature a Curie-like impurity tail was observed. The Curie-like tail could be caused by chemical contamination from a magnetic impurity or by the formation of paramagnetic centers due to twinning or packing defects. The constant spin susceptibility (30–150 K) is consistent with the Pauli paramagnetism expected of a metallic specimen.

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**Figure 1.** Left: the unit cell for  $\beta_m$ -(BEDO-TTF) $_3$ Cu $_2$ (NCS) $_3$ , which contains two anion layers and two layers of BEDO-TTF molecules. The view is approximately down the  $a$  axis of the donor sublattice. Right: planar Cu $_2$ (NCS) $_3^-$  anion layers. The two independent Cu atoms have slightly different coordination.

**Structure.**<sup>7-10</sup> Examination of numerous  $\beta_m$ -(BEDO-TTF) $_3$ Cu $_2$ (NCS) $_3$  single crystals by use of X-ray diffraction techniques showed a diffraction pattern in which a strong (fundamental) sublattice, exhibiting consistent diffraction intensities, is interspersed with a commensurate superlattice (within our resolution) whose diffraction intensities vary from crystal to crystal.<sup>8</sup> The structure of the donor molecule layer, which may be derived from the diffraction intensities of the sublattice reflections,<sup>9</sup> consists of BEDO-TTF molecules located with the central carbon-carbon double bond on an inversion center. In this unit cell, all donor molecules in the same layer are related by unit cell translations. The donor molecule layers are separated by anions that are constrained to lie on a crystallographic mirror plane. In this model, a donor layer contains one-third of a Cu $_2$ (NCS) $_3^-$  anion unit; therefore, no reasonable anion model can be derived from the sublattice. For a type-1  $\beta_m$  crystal<sup>8</sup> with both sublattice (fundamental) and superlattice reflections, a reasonable model for the anion layers is obtained as shown in Figure 1.<sup>10</sup> The Cu $_2$ (NCS) $_3^-$  anion shown on the right side of Figure 1 is an infinitely connected planar 2-dimensional polymer. This result is in contrast to the Cu(NCS) $_2^-$  ribbons found in  $\kappa$ -(BEDT-TTF) $_2$ Cu(NCS) $_2$ , a superconducting salt that can be synthesized under conditions very similar to those described herein.<sup>4</sup> In the BEDO-TTF salt, the ribbons found in the BEDT-TTF salt are cross-linked by the elimination of half the terminal SCN $^-$  units



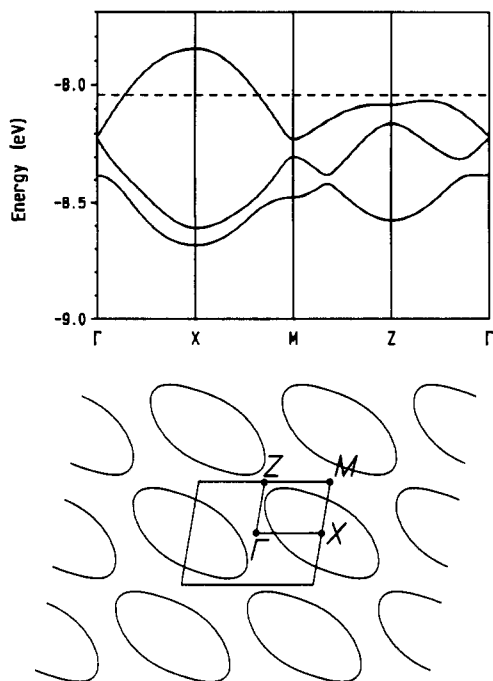
**Figure 2.** Resonant frequency as a function of temperature as determined by rf penetration depth measurements of  $\beta_m$ -(BEDO-TTF) $_3$ Cu $_2$ (NCS) $_3$  in zero applied magnetic field (derived  $T_c = 1.06 \pm 0.02$  K at ambient pressure).

and formation of bonds between the S atoms of the remaining terminal thiocyanate ions with the copper atoms of a neighboring chain. The zigzag chains found in  $\kappa$ -(BEDT-TTF) $_2$ Cu(NCS) $_2$  are still evident in the 2-dimensional anion of (BEDO-TTF) $_3$ Cu $_2$ (NCS) $_3$  (see Figure 1).

The donor-molecule layer depicted on the left side of Figure 1 is only slightly distorted from that derived from the sublattice reflections alone and is strikingly similar to that observed<sup>7</sup> for (BEDO-TTF) $_2$ AuBr $_2$ . Whereas the salts of BEDT-TTF exhibit great variety in donor molecule packing motifs,<sup>1a</sup> the salts of BEDO-TTF reported to date all possess very similar donor molecule packing patterns. An explanation for the occurrence of a single donor packing mode for BEDO-TTF salts is the existence of short C-H $\cdots$ O intermolecular hydrogen bonding contacts, which appear to favor a single intermolecular donor packing arrangement.<sup>11</sup>

Further investigations to determine the origin of the ( $h, k, l \pm 1/3$ ) superlattice reflections are planned. However, one possibility is that they arise from stacking faults similar to those described by Ravy et al.<sup>12</sup> for  $\kappa$ -(BEDT-TTF) $_2$ Cu(NCS) $_2$ . If that

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- (8) Two distinct patterns for the superlattice are observed. In the type-1  $\beta_m$  crystals, in addition to the sublattice (fundamental) reflections, weak commensurate satellite peaks are observed with indices of ( $h + 1/3, k, l + 1/3$ ) and ( $h - 1/3, k, l - 1/3$ ). In addition to these satellite reflections, type-2 crystals possess satellite reflections of the type ( $h, k, l \pm 1/3$ ). The fundamental (sublattice) and satellite reflections may be indexed on the monoclinic cells, with  $a = 7.2015$  (8) Å,  $b = 33.476$  (5) Å,  $c = 9.340$  (2) Å,  $\beta = 99.56$  (1) $^\circ$ , and  $V_c = 2220.5$  (5) Å $^3$  for  $\beta_m$ -type-1 crystals and  $a = 12.711$  (2) Å,  $b = 33.481$  (6) Å,  $c = 15.819$  (3) Å,  $\beta = 97.94$  (1) $^\circ$ , and  $V_c = 6667.8$  (1.2) Å $^3$  for type-2 crystals.
- (9) X-ray data for several black platelike crystals were collected on Syntex P2 $_1$  and Nicolet P3/F diffractometers. All exhibited a strong monoclinic sublattice,  $P2_1/m$ , with  $a = 4.237$  (1) Å,  $b = 33.481$  (6) Å,  $c = 5.273$  (1) Å,  $\beta = 97.94$  (1) $^\circ$ , and  $V_c = 740.8$  (2) Å $^3$ . In a preliminary report,<sup>7</sup> the subcell was identified as arising from the BEDO-TTF donor layers, but from the sublattice diffraction pattern alone, the composition of the anion layer could not be determined. Diffraction data ( $\omega$  scan, Mo K $\alpha$  radiation, graphite monochromator,  $\lambda = 0.7107$  Å), were collected in the range  $4^\circ < 2\theta < 50^\circ$ , corrected for absorption ( $\mu = 16.90$  cm $^{-1}$ , with  $T_{\min} = 0.73$  and  $T_{\max} = 0.88$ ) and averaged to yield 956 independent sublattice reflections. Full-matrix least-squares refinement (all non-hydrogen donor atoms refined with anisotropic temperature factors, anion coordinates fixed at the positions derived from the type-1 crystals, occupancy factors of  $1/3$ , and isotropic temperature factors, with 93 variable parameters) yielded  $R(F) = 6.8\%$ ,  $R_w(F) = 7.1\%$ , and GOF = 3.39. The unit cell contains two BEDO-TTF molecules and two anion layers.
- (10) Type-1 crystal  $\beta_m$ -(BEDO-TTF) $_3$ Cu $_2$ (NCS) $_3$  (unit cell, see ref 8), space group  $P2_1/m$ ,  $Z = 2$ . Diffraction data ( $\omega$  scan, Mo K $\alpha$  radiation, graphite monochromator,  $\lambda = 0.7107$  Å), were collected in the range  $4^\circ < 2\theta < 50^\circ$ , corrected for absorption<sup>9</sup> and averaged ( $R_{av} = 3.0\%$ ) to yield 3438 independent reflections. Full-matrix least-squares refinement (all Cu, S, and O atoms with anisotropic temperature factors, H-atom positions calculated with idealized  $sp^3$  geometries, and C-H distances of 1.0 Å, with 293 variable parameters) yielded  $R(F) = 14.9\%$ ,  $R_w(F) = 10.2\%$  and GOF = 2.54. The stacks of BEDO-TTF donor molecules are linked by short ( $< 3.6$  Å) S-S contacts.
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**Figure 3.** (a, top) Dispersion relations of the highest three occupied bands calculated for a donor-molecule layer of  $\beta_m$ -(BEDO-TTF) $_3$ Cu $_2$ (NCS) $_3$ . The dashed line refers to the Fermi level;  $\Gamma = (0, 0)$ ,  $X = (a^*/2, 0)$ ,  $Z = (0, c^*/2)$ , and  $M = (a^*/2, c^*/2)$ . (b, bottom) Fermi surface associated with the highest occupied band of  $\beta_m$ -(BEDO-TTF) $_3$ Cu $_2$ (NCS) $_3$  in an extended zone scheme, where the parallelogram represents a primitive cell in reciprocal space.

is also the case for  $\beta_m$ -(BEDO-TTF) $_3$ Cu $_2$ (NCS) $_3$ , then crystals varying from single domain to those with a high density of stacking faults would produce varying intensities for the  $(h, k, l \pm 1/3)$  satellite reflections.

**Superconducting Transition.** Superconductivity in the crystals was detected by use of rf penetration depth measurements<sup>13</sup> carried out to temperatures as low as 0.58 K. In this method, superconductivity is detected by an increase in the resonant frequency ( $\sim 580$  kHz) of an rf coil in an inductance–capacitance circuit caused by the exclusion of the field in the test sample due to the occurrence of diamagnetic shielding currents. This is an ac shielding experiment and not a Meissner effect measurement, but the increasing resonant frequency relative to that of the empty coil is an approximate measure of the ac susceptibility and, therefore, indicates the existence of volume superconductivity. A plot of the resonant frequency versus temperature is illustrated in Figure 2. This figure shows a change in the resonant frequency of  $\sim 2.7$  kHz below  $\sim 1$  K for a sample of mass  $\sim 750$   $\mu\text{g}$ . The large change in frequency relative to the mass indicates that the sample itself rather than some minor impurity is the source of the superconducting signal. The tail of the superconducting transition begins near 1.2 K, but an extrapolation of the nearly linear portion of the transition curve gives  $T_c = 1.06 \pm 0.02$  K for the onset temperature of the bulk of the sample.

**Band Electronic Structure.** The electronic structure of  $\beta_m$ -(BEDO-TTF) $_3$ Cu $_2$ (NCS) $_3$  was examined by performing tight-binding band calculations<sup>14</sup> on its donor-molecule layer. Figure 3a shows the dispersion relations of the three highest occupied bands, which are largely represented by the HOMO of BEDO-TTF. As in the case of BEDT-TTF, the HOMO of BEDO-TTF is mainly concentrated on the central TTF moiety. The donor-molecule layer of  $\beta_m$ -(BEDT-TTF) $_3$ Cu $_2$ (NCS) $_3$  has three molecules per unit cell. With the formal oxidation (BEDO-TTF) $_3^+$ ,

therefore, the highest occupied band of Figure 3a is half-filled. The Fermi surface associated with this band is shown in Figure 3b, which consists of ellipse-like hole pockets centered at  $X$  and its equivalent points. Thus  $\beta_m$ -(BEDO-TTF) $_3$ Cu $_2$ (NCS) $_3$  is predicted to be a two-dimensional metal. Although  $\beta_m$ -(BEDO-TTF) $_3$ Cu $_2$ (NCS) $_3$  is a 3:1 salt, its electronic structure has a characteristic feature found in almost all superconducting 2:1 salts, viz., a half-filled band leading to a closed Fermi surface.<sup>1a</sup> The donor-layer packing pattern of this salt is quite similar to that of (BEDO-TTF) $_2X$  ( $X^- = \text{AuBr}_2^-, \text{ClO}_4^-$ ).<sup>7</sup> The donor molecules make short C–H $\cdots$ O contacts not only within each donor stack, but also between adjacent donor stacks. Due to slight differences in the interstack donor-donor overlap,  $\beta_m$ -(BEDO-TTF) $_3$ Cu $_2$ (NCS) $_3$  has a two-dimensional Fermi surface, but the (BEDO-TTF) $_2X$  ( $X^- = \text{AuBr}_2^-, \text{ClO}_4^-$ ) salts have one-dimensional Fermi surfaces.<sup>7</sup>

In summary, we have found the first organic superconductor based on an oxygen-containing donor molecule. This result opens up a completely new avenue in the search for organic superconductors with ever increasing transition temperatures.

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**Supplementary Material Available:** Tables of crystal structure data collection and refinement parameters (Table S1) and final atom positional parameters (Table S2) for  $\beta_m$ -(BEDO-TTF) $_3$ Cu $_2$ (NCS) $_3$  (3 pages). Ordering information is given on any current masthead page.

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Chemistry and Materials Science  
 Divisions  
 Argonne National Laboratory  
 Argonne, Illinois 60439

Mark A. Beno\*  
 Hau H. Wang\*  
 Aravinda M. Kini  
 K. Douglas Carlson\*  
 Urs Geiser\*  
 W. K. Kwok  
 James E. Thompson  
 Jack M. Williams\*

Department of Chemistry  
 North Carolina State University  
 Raleigh, North Carolina 27695-8204

Jingqing Ren  
 Myung-Hwan Whangbo\*

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### Synthesis and Structural Characterization of $[\text{cis}-(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2)(\text{neo-Pe})\text{PtGa}(\text{neo-Pe})_2]$ (Cy = $\text{C-C}_6\text{H}_{11}$ ; neo-Pe = $\text{CH}_2\text{C}(\text{CH}_3)_3$ )

We have been interested in the synthesis of organotransition-metal–group III<sup>1</sup> complexes to serve as precursors for the deposition of intermetallic films<sup>2</sup> of specified composition using organometallic chemical vapor deposition (OMCVD).<sup>3</sup> Mixed-metal complexes such as dichloro(tetracarbonylcobalt)gallium(III) tetrahydrofuranate<sup>4</sup> or platinumbis(dimethylglyoximate)bis(dimethylgallium)<sup>5</sup> have given depositions of CoGa or PtGa $_2$ <sup>6</sup> that are crystalline and highly reflective. However, these contain trace contaminations of heteroatoms derived from the ligands. On the

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