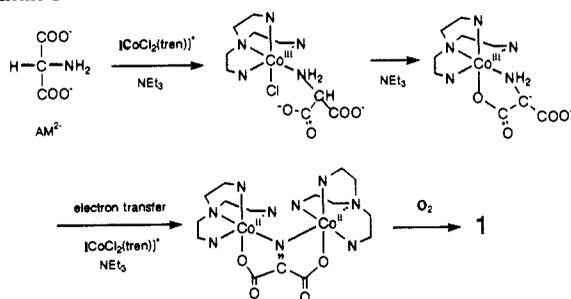
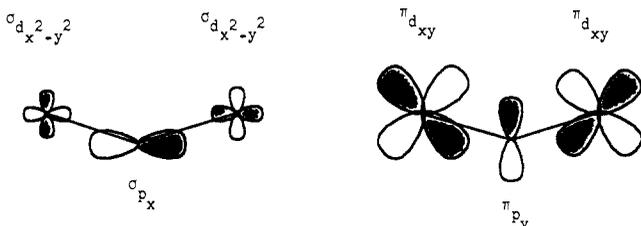


Scheme 1



of the two Co-N(imido) bonds and the widening of the Co(1)-N(9)-Co(2) angle (142.9 (3)°).



The polarogram¹⁰ of **1** in H₂O showed two 1e⁻ reduction waves corresponding to two quasireversible redox couples,¹¹ [Co(III),-Co(III)] ↔ [Co(III),Co(II)] and [Co(III),Co(II)] ↔ [Co(II),-Co(II)] ($E_{\text{exp}} = -0.05$ and -0.28 V vs SCE, respectively), and an additional irreversible¹¹ 2e⁻ reduction wave due to the reduction of the imido group at -0.91 V.¹² Similar reduction waves were also observed at $E_{\text{exp}} = -0.28$, -0.46 , and -1.07 V in a MeOH-DMF (1:1) solution. It is noteworthy that the Co(III)-Co(II) mixed valence state can be formed electrochemically in H₂O and in a MeOH-DMF (1:1) mixed solution.

The absorption spectrum of **1** in H₂O¹³ showed a large red shift from the typical spectrum of the Co(III)-N₃O chromophore of p-isomers in the tren system⁴ and was similar to that of t-isomers. The absorption spectra of Co(III)- α -imino acid complexes show a similar red shift by the deprotonation of the coordinated imino groups.^{8a,14} The weakness of the Co-N(imido) bonds reduces the ligand field of two Co(III) ions in complex **1**.

In the case of en and 3,2,3-*ter*³ used as polyamine ligands, α -diamine formation took place under N₂ via electron transfer accompanying the radical formation of AM²⁻.¹⁵ In contrast, as mentioned above, α -diamine formation was not observed when tren was used as an amine component. The structure of the tren moiety in complex **1** exhibits distortion toward the tertiary amino group, and this makes it difficult for the primary amino groups to attack the imine carbon. However, the isolation of the complex **1** having the imidomalonato provides strong evidence that the oxidation of AM²⁻ to the imidomalonato intermediate is performed through electron transfer to the two cobalt(III) ions and α -diamine formation should be performed with the aid of two metal centers. It is assumed that, in the tren system under air, an intermediate, [Co(II)₂(μ -imidomalonato)(tren)₂]⁺, is oxidized by air to afford **1**. The proposed mechanism for the formation of **1** was represented in Scheme 1.

The reaction temperature is important for the formation of complex **1**, since p-[Co(glycinato)(tren)]²⁺ was obtained instead of **1** when the reaction mixture was refluxed. The geometry of the glycinato complex is consistent with **1**.

In summary, a binuclear Co(III) complex **1** containing a novel μ_2 -imido ligand has been prepared and characterized and it represents the existence of an imine intermediate and a binuclear pathway for α -diamine formation between AM²⁻ and Co(III)-polyamine complexes.

Acknowledgment. We thank Drs. Mitsunobu Sato, Morio Yashiro, and Katsuki Ishida for their helpful discussions. T.K. also thanks Drs. H. Masuda and K. Kitaura (Institute for Molecular Science) for their helpful advice for EHMO calculations and Dr. M. Shionoya and Prof. E. Kimura (IMS) for the accommodation of electrochemical measurements. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan (No. 63470035, 6312002, and 01612002) and Grants from the Mitsubishi Foundation and by the Iwatani Naoji Foundation's research grant.

Supplementary Material Available: Listing of positional and thermal parameters for the title compound (4 pages); table of observed and calculated structure factors for the title compound (32 pages). Ordering information is given on any current masthead page.

Intercalation of Bis(ethylenedithio)tetrathiafulvalene (ET) into Iron Oxichloride: A Highly Conducting Low-Dimensional System

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Efforts to prepare new organic conducting materials have focused primarily on the preparation of new organic donors or modification of existing donors.² In our laboratory, we have been exploring an alternative approach to the synthesis of low-dimensional conductors that involves the use of layered materials as macroanionic electron acceptors and as matrices to enforce a particular structural arrangement upon an array of electron donor molecules. The synthetic method we have utilized is the intercalation³ of planar electron donors such as aromatic hydrocarbons,⁴ TTF,⁵ TSF,⁶ and related molecules⁷ into the van der Waals gap

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of layered transition-metal hosts such as FeOCl. Structural studies of these materials⁷ have shown that intercalation proceeds with formation of stacks of intercalant-derived cation radicals and that in some cases overlap of adjacent guest molecules within the FeOCl layers is sufficient to form a band within the interlayer region.⁶ However, complete electron transfer from the guest molecules to the host has thus far prevented the onset of metallic conduction within the guest stacks. Herein, we report the preparation and preliminary characterization of a new intercalation compound, FeOCl(ET)_{1/4}, where ET = bis(ethylenedithio)tetrathiafulvalene. Structural and electronic studies show that the material contains stacks that are partially oxidized, resulting in high electrical conductivity due to the intercalated electron donors.

The intercalate was prepared by treating FeOCl with an equimolar amount of a 0.01 M solution of ET in anhydrous dimethoxyethane (DME) for 21 days at 85 °C under N₂, followed by filtration and washing with DME. Absence of the characteristic interlayer reflection for FeOCl at $d = 7.92$ Å was used to confirm complete intercalation.⁸ Chemical ionization mass spectrometry revealed peaks at $m/z = 385$ and 193, assigned as (ET)H⁺ and (ET)H²⁺ or (ET)H₂²⁺. Elemental analyses are consistent with the stoichiometry FeOCl(ET)_{1/4}.⁹

The powder X-ray diffraction pattern of the intercalate was indexed with use of a body-centered unit cell with lattice parameters $a = 3.783$ (5) Å, $b = 3.307$ (4) Å, and $c = 44.76$ (1) Å. A strong low-angle reflection at $d = 22.18$ Å along with 22 00l reflections was observed in the X-ray powder diffraction profile of an oriented film of the intercalate, giving an interlayer distance of 22.35 (3) Å. The FeOCl interlayer spacing thus expands by 14.43 Å upon intercalation of ET. Given the dimensions of ET (15.9 × 7.1 Å), several orientations of intercalated ET molecules are possible based on these data alone. In order to determine the orientation of the intercalated ET molecules, a Fourier synthesis of the structure factors $F(l)$ derived from the intensities of 00l reflections was used to compute projections of the electron density of the intercalate along the interlayer axis. Atomic positions (0,0,z) could then be refined from the projection. The structure factors derived from the intensities of 00l reflections were initially phased considering the scattering of the FeOCl layers only. The resulting electron density map could be fit with the ET molecules canted at ca. 15° from the perpendicular (i.e., long axis of ET parallel to c) with respect to the FeOCl layers. Rephasing the data, including the contribution of the guest molecules, and a subsequent Fourier synthesis of the electron density gave the projection shown in Figure 1a.¹⁰ The structural model proposed for FeOCl(ET)_{1/4} is represented schematically in Figure 1b, along with the observed and calculated atomic distances relative to the origin (chosen as the midpoint of the interlayer separation). This orientation is similar to that in the (ET)₂X conducting salts,¹¹ such as (ET)₂BrO₄¹² and (ET)₂ReO₄,¹³ in which the ET molecules are canted

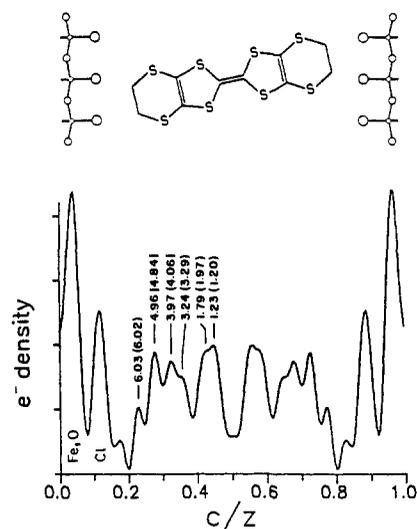


Figure 1. (a, bottom) Projection of the electron density of FeOCl(ET)_{1/4} along the c -axis. Numbers are distances in Å from the origin (taken as the midpoint of the interlayer separation). Numbers in parentheses are the corresponding distances in the ET molecule. (b, top) Illustration of the orientation of ET within the van der Waals region of FeOCl as deduced from the electron density projection: Fe = small circles, O = medium circles, Cl = large circles.

at an angle of ca. 10° from the perpendicular with respect to the anion sheets.

The FTIR spectrum of FeOCl(ET)_{1/4}¹⁴ shows strong absorptions corresponding to bands observed in the neutral ET molecule. In addition, two new strong bands at 1344 and 881 cm⁻¹ are observed in FeOCl(ET)_{1/4}; these are very likely of vibronic origin, since bands of nearly identical shape are observed in the organic conductor α -(ET)₂I₃.¹⁵ The IR data thus indicate that the ET molecules are partially oxidized within the FeOCl layers. The broad continuous absorptions observed in the 4000–2000-cm⁻¹ region of the spectrum are typical of highly conducting organic metals, resulting from electronic excitations of conduction electrons,¹⁶ and are consistent with partially oxidized guest layers.

Because single-crystal specimens of FeOCl(ET)_{1/4} are not yet available, conductivity measurements were performed on powders pressed at ca. 2 kbar. The temperature-dependent resistivity behavior of FeOCl(ET)_{1/4} shows semiconducting behavior with an apparent band gap of 0.216 eV and a room temperature conductivity of 0.26 (Ω·cm)⁻¹. The room temperature conductivity of FeOCl(ET)_{1/4} is by far the highest yet observed for a molecular intercalate of FeOCl, representing an increase in conductivity of 10⁶ over that of pristine FeOCl ($\sigma_{RT} = 10^{-7}$ Ω⁻¹·cm⁻¹),¹⁷ and is even higher than that of FeOCl intercalated with the known conductor polypyrrole.¹⁸ The observed conductivity does not necessarily reflect the intrinsic conductivity of the sample, since the pressed powder conductivity of a specimen is typically less than the single-crystal conductivity by a factor of ca. 10².^{18,19} These effects are expected to be particularly important in the FeOCl intercalates due to the intrinsic anisotropy of these materials, resulting in semiconducting behavior at grain boundaries. Given these effects, the exceptionally high conductivity of

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(10) Inclusion of the guest species into the model changed the signs of only two phases; thus, the assumption that the signs of the phases are determined predominantly by the FeOCl layers appears to be valid. Because 00l reflections could not be observed in oriented films of FeOCl(ET)_{1/4} below about $d = 1.016$ Å, the density projections are not fully resolved; the error in atomic positions is ca. 0.06 Å.

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FeOCl(ET)_{1/4} compared to other FeOCl intercalates, the FTIR data indicating the presence of vibronic bands due to partially oxidized ET molecules, and the broad electronic transitions in the near-IR, it is likely that the guest ET stacks are indeed responsible for the high conductivity of this material. Herber et al.²⁰ have found that typically only 10–13% of Fe³⁺ in FeOCl can be reduced to Fe²⁺ upon intercalation, which is consistent with the observation of partially oxidized guest stacks in FeOCl(ET)_{1/4}. Thus, in FeOCl(ET)_{1/4} only about half of the ET molecules can be oxidized, suggesting that the increased conductivity relative to other FeOCl intercalates is due to the partially oxidized array of ET molecules.

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Supplementary Material Available: A listing of observed intensities of 00l lines and calculated structure factors for FeOCl(ET)_{1/4} (1 page). Ordering information is given on any current masthead page.

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Site-Specific Cleavage of Duplex DNA with a λ Repressor–Staphylococcal Nuclease Hybrid

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The development of reagents capable of selective cleavage of large double-stranded DNA would greatly facilitate the manipulation and mapping of genomic DNA. Several such strategies have been reported including D-loop formation to deliver a semisynthetic nuclease to double-helical DNA,¹ and the use of triple-helix formation² or DNA-binding proteins³ to deliver oxidative cleaving agents to the target sequences. We report here the design and synthesis of a λ repressor–staphylococcal nuclease hybrid protein⁴ capable of efficient hydrolysis of both linear and supercoiled duplex DNA. The repressor domain of the hybrid nuclease binds specifically to its recognition sequence, λ operator O_R1 or O_L1, and delivers the nuclease activity to DNA sequences adjacent to the repressor binding site. Upon addition of Ca²⁺, the nuclease selectively hydrolyzes both DNA strands at the target region.

Staphylococcal nuclease⁵ was coupled to a truncated λ repressor^{6,7} lacking the C-terminal domain (Figure 1). A unique cysteine (Ser 32 to Cys 32) was introduced into the cysteine-free N-terminal domain (residues 1–102) via site-directed mutagenesis.⁸ The mutant cysteine is located in the loop region between α -helices

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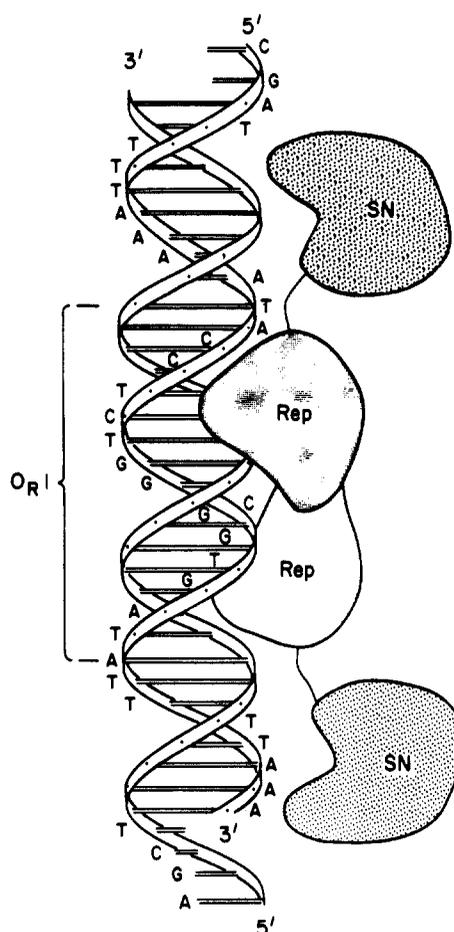


Figure 1. Scheme showing the binding of the hybrid protein to B-form DNA. The two DNA strands, 35 and 37 nucleotides, were chemically synthesized with restriction sites *Cla*I and *Hind*III at the termini. Repressor binds to the 17-base-pair O_R1 as a dimer and delivers two nuclease molecules to the two d(TA₄) target sites.

1 and 2 and has been previously shown not to appreciably alter the binding properties of the repressor.¹⁰

A water-soluble tether, methylbis[3-[3-(2-pyridylthio)propionamido]propyl]amine (**1**),¹¹ was used to cross-link staphylococcal nuclease to the repressor. This flexible cross-linker was designed to allow the hybrid protein to bind substrate and hydrolyze both strands of the duplex target. The construction of the hybrid protein involved two consecutive disulfide exchange reactions. Monomeric repressor¹³ was reacted with a 50-fold excess of the cross-linking agent (**1**) in water (pH adjusted to 7.0 with HCl). The derivatized repressor was purified by cation-exchange chromatography¹⁴ and subsequently reacted at pH 8.5 with 1 equiv of reduced K84C staphylococcal nuclease which contains a single surface cysteine.¹⁵ The reaction was complete within 1 h at room temperature, and the resulting hybrid protein was purified by cation-exchange chromatography.¹⁴

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(14) Purification was performed on a Pharmacia FPLC Mono S column (HR 5/5), by elution with 50 mM HEPES (pH 6.8), 2 mM EGTA, and a linear gradient of 50–600 mM NaCl. K84C staphylococcal nuclease, repressor derivatized with the tether, and the hybrid protein eluted at 370 mM, 300 mM, and 430 mM NaCl, respectively.

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