Figure 2 shows the dispersion relations of the two highest lying occupied bands of κ-(ET)$_2$Cu(NCS)$_2$, which we calculated for its room-temperature crystal structure by employing the tight-binding band scheme[15] based upon the extended Hückel method.[16] To better represent the interstack S···S interactions between adjacent donor molecules, double-ζ Slater-type orbitals were used for the s and p orbitals of carbon and sulfur as reported earlier.[15] The two bands of Figure 2 are derived mainly from the HOMO's of four ET molecules in each unit cell. The HOMO's of two ET molecules in each dimer interact to give the bonding and antibonding levels ψ_+ and ψ_-, respectively. The upper and lower bands of Figure 2 are represented largely by the ψ_- and ψ_+ orbitals, respectively. Since there are two (ET)$_2^+$ dimers per unit cell, the upper band becomes half-filled. This band is cut by the Fermi level, represented by the dashed line, in all three directions of the reciprocal space shown in Figure 2.

Also shown in Figure 2 is the Fermi surface associated with the half-filled band of κ-(ET)$_2$Cu(NCS)$_2$. The Fermi surface is shown in an extended Brillouin zone scheme, due to the folded nature of the two bands in Figure 2. The Fermi surface is closed and approximately circular, so that this salt is expected to be a 2D metal. This is consistent with our analysis of the HOMO interaction energies described above. In this 2D electronic structure, the new ambient-pressure superconductor κ-(ET)$_2$Cu(NCS)$_2$ is similar to the series of ambient-pressure superconductors β-(ET)$_2$X,[14,15,17] although the two classes of salts have widely *different* packing patterns of donor molecules.

(MT)$_2$Au(CN)$_2$ would be similar to κ-(ET)$_2$Cu(NCS)$_2$ in band electronic structure since the two salts have a nearly identical packing pattern of donor molecules and since the HOMO's of ET and MT are almost the same. When the temperature is lowered, however, (MT)$_2$Au(CN)$_2$ does not become a superconductor but undergoes a metal-to-semiconductor transition.[12] Therefore, κ-(ET)$_2$Cu(NCS)$_2$ must possess certain translational or librational modes of vibration critical for superconductivity. Recently, it has been suggested[18] that an important factor controlling the superconductivity of the β-(ET)$_2$X salts is the lattice softness associated with the intermolecular hydrogen···anion and hydrogen···hydrogen contacts. The same factor might also operate in κ-(ET)$_2$Cu(NCS)$_2$.

Conclusion. We have shown that the new ET-based superconducting salt κ-(ET)$_2$Cu(NCS)$_2$ can be prepared by at least three different synthetic routes. We have verified superconductivity at ambient pressure of this product in the region 9–10 K, with all three synthetic routes yielding crystals of comparable T_c. The route involving the use of (n-Bu$_4$N)SCN, however, yields crystals of the largest dimensions and highest diffraction quality. We have also shown that other, as yet unidentified, phases of the ET-Cu(SCN)$_2^-$ system are produced and that the ESR line widths at room temperature can be employed to select the superconducting κ-phase materials. We have found that the ET derivatives of the Ag(SCN)$_2^-$ and Au(SCN)$_2^-$ anions yield nonsuperconducting phases, different from the κ-phase at least in the case of the Ag(SCN)$_2^-$ salt. The electronic band structure of κ-(ET)$_2$Cu(NCS)$_2$ indicates that this is a 2D metal, similar to the superconducting β-(ET)$_2$X materials. Thus, an entirely new organic material (the κ-phase) has been found to be superconducting at a T_c exceeding, for the first time, the highest T_c of the elements (9 K in Nb). Because the structure of the κ-phase is different from that of the β-(ET)$_2$X superconductors, there is now considerable promise for deriving new and extended structure–property relationships and obtaining even higher T_c's.

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Note Added in Proof. Gärtner[19] et al. confirm a T_c of 10.2 K at ambient pressure in (BEDT-TTF)$_2$Cu(NCS)$_2$. They also report a room-temperature ESR line width of ~26 G for the superconducting phase which is substantially different from that we observe of 60–70 G.

Supplementary Material Available: Tables of crystal structure data collection and refinement parameters (Table X1), final atom positional parameters and anisotropic temperature factors (Table X2), and HOMO interaction energies (Table X3) and a figure showing the superconducting transitions as measured by rf penetration and four-probe resistance (Figure X1) for κ-(ET)$_2$Cu(NCS)$_2$ (5 pages). Ordering information is given on any current masthead page.

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Isolation of a Bis-Oxo-Bridged Mn^{III}Mn^{IV} Intermediate by Regulated Air Oxidation. Synthesis, Structure, and Properties of [Mn$_2$O$_2$(tren)$_2$](CF$_3$SO$_3$)$_3$

Sir:

Manganese is known to participate in a variety of biological reactions related to the metabolism and evolution of molecular oxygen. Evidence for this conclusion derives from the fact that manganese is required for activity in enzymes such as pseudocatalase,[1] superoxide dismutase,[2] and the oxygen-evolving complex in photosystem II (PSII).[3] For the S$_2$ state in PSII, the multiline signal in the EPR spectrum[4] and the short Mn···Mn distance (2.70 Å, as indicated by X-ray absorption spectroscopy[5]) are both

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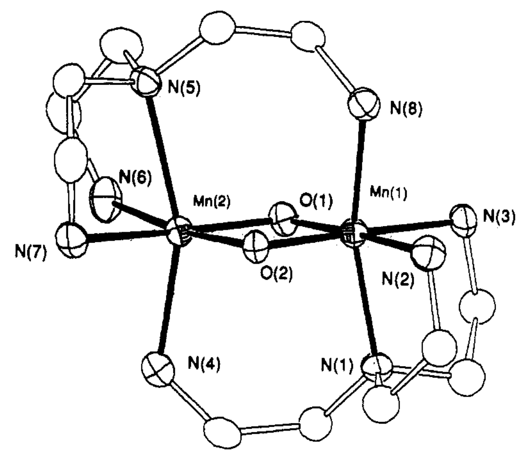

Figure 1. Structure of the bis(μ-oxo)bis(2,2′,2″-triaminoethylamine)dimanganese(III,IV) cation, showing the 50% probability thermal ellipsoids and atom-labeling scheme. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg) are as follows: Mn(1)–O(1), 1.774 (4); Mn(1)–O(2), 1.773 (4); Mn(2)–O(1), 1.847 (4); Mn(2)–O(2), 1.852 (4); Mn(1)–N(1), 2.092 (6); Mn(1)–N(2), 2.096 (5); Mn(1)–N(3), 2.098 (5); Mn(1)–N(8), 2.007 (5); Mn(2)–N(4), 2.207 (7); Mn(2)–N(5), 2.344 (5); Mn(2)–N(6), 2.125 (5); Mn(2)–N(7), 2.101 (5); O(1)–Mn(1)–O(2), 86.8 (2); O(1)–Mn(2)–O(2), 82.5 (2); Mn(1)–O(1)–Mn(2), 95.4 (2); Mn(1)–O(2)–Mn(2), 95.3 (2); Mn(1)···Mn(2), 2.679 (1) [Mn(1) = Mn(IV), Mn(2) = Mn(III); see text].

consistent with, minimally, a binuclear formulation for the manganese center. These physical properties are modeled reasonably well by the mixed-valence species $[L_2MnO_2MnL_2]^{3+}$ (L = bpy (**1**), phen (**2**)).[5-9] Both **1** and **2** have been characterized by single-crystal X-ray diffraction techniques,[10,11] and only in the former can the Mn(III) and Mn(IV) ions be clearly distinguished.[10] Mixed-valence complexes containing manganese atoms bridged by two oxo groups and one acetate group have recently been reported.[12] Considering the number of iron[13] and chromium[14] binuclear oxo- and hydroxo-bridged species that have been characterized, relatively few binuclear manganese complexes of this type are known. The extent to which variation of terminal ligands around a $[Mn_2O_2]^{3+}$ core will alter chemical, electrochemical, magnetic, and spectroscopic properties remains an important issue. Herein are reported the synthesis, structure, and properties of a novel, class II[15] mixed-valence binuclear complex with aliphatic amine capping ligands, $[Mn_2O_2(tren)_2](CF_3SO_3)_3$ (**3**).

Mixed-valence compounds **1** and **2** have been prepared by oxidation of Mn(II) precursors using either persulfate[8b] or permanganate.[7] Exposure of a colorless mixture of 1.40 g of $Mn(CF_3SO_3)_2{\cdot}x MeCN$,[16] 0.64 g (4.4 mmol) of tren, and 70 mL of CH_3CN to the air results in a green solution initially, which gradually changes to brown over an extended period of time. In contrast, **1** and **2** are relatively air-stable in CH_3CN solution. When air oxidation in the tren system is terminated after 2.0 h, compound **3** can be isolated by evaporation of CH_3CN followed by recrystallization of the residue from 10 mL of EtOH. This procedure afforded 0.77 g (38% yield) of **3**·EtOH as a dark green analytically pure crystalline solid.[17] Crystals suitable for X-ray diffraction measurements[18] were obtained by slow cooling of an EtOH solution of **3**. Efforts to characterize both the Mn(II) precursor to **3** and the brown species obtained by air oxidation of **3** are underway.

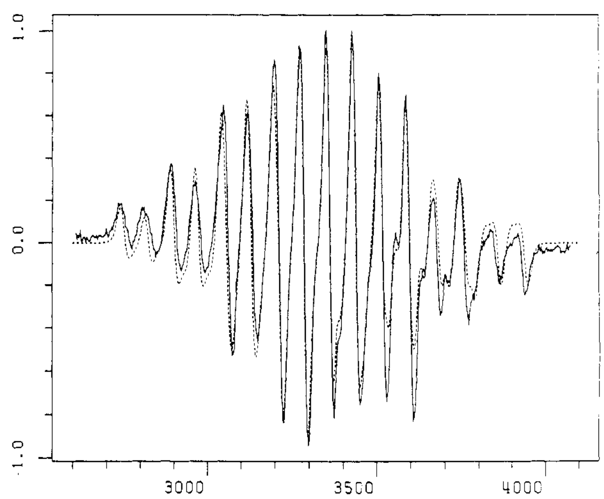

Figure 2. X-Band EPR spectrum of $[Mn_2O_2(tren)_2]^{3+}$ in EtOH/MeOH (5/1) at 6 K with the following instrument settings: microwave power, 10 mW; modulation amplitude, 5 G; modulation frequency, 100 kHz. Solid line = observed data; dashed line = theoretical fit for an anisotropic model using parameters given in the text.

The structure of **3**, shown in Figure 1, consists of a planar bis(μ-oxo)dimanganese core with capping tren ligands. One ethylamine chain from each tren spans the binuclear core. Larger Mn–N–C, and N–C–C angles for the bridging arms than for the terminal ones[19] indicate a certain degree of strain.[20] As was the case for the bpy dimer (**1**), the Mn(III) and Mn(IV) ions in the solid-state structure of **3** are clearly distinguishable. Shorter Mn–oxo bond distances for Mn(1) compared to Mn(2) indicate that the former is the Mn(IV) ion. The average Mn(III)–oxo and Mn(IV)–oxo bond distances for **3** are in good agreement with those for the bpy dimer, **1**. The Mn···Mn separation in **3** (2.679 Å) is 0.037 Å smaller than the corresponding distance in **1** (2.716 Å), perhaps in part due to the bridging ethylenediamine groups. The difference between Mn(III) and Mn(IV) ions is even more evident upon inspection of the Mn–N distances. The average Mn(2)–N bond cis to the μ-oxo groups (2.276 Å) is 0.163 Å longer than the average trans distance (2.113 Å), consistent with an axial distortion as predicted by the Jahn–Teller theorem for a high-spin d^4 ion.[21] In contrast, the average Mn(1)–N distance cis to the

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(9) Abbreviations used: PSII, photosystem II; EPR, electron paramagnetic resonance; IR, infrared; bpy, 2,2′-bipyridine; phen, 1,10-phenanthroline; tren, 2,2′,2″-triaminotriethylamine; TACN, 1,4,7-triazacyclononane.

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(17) Anal. Calcd for $C_{17}H_{42}F_9Mn_2N_8O_{12}S_3$: C, 22.01; H, 4.56; N, 12.08; S, 10.37. Found: C, 21.70; H, 4.47; N, 11.99; S, 9.99.

(18) X-ray analysis (125 K): **3**·EtOH crystallizes in the monoclinic system, space group $P2_1/n$, with a = 12.251 (4) Å, b = 15.698 (5) Å, c = 18.739 (4) Å, β = 99.66 (2)°, V = 3552.7 Å^3, ρ_{calcd} = 1.734 g cm^{-3}, and Z = 4. With use of 3988 unique reflections out to 2θ = 50° (Mo Kα radiation) on a single-crystal X-ray diffractometer, the structure was solved by direct methods and refined with anisotropic thermal parameters (with the exception of three methylene carbon atoms), to an R index of 0.053. Atomic positional and thermal parameters are provided as supplementary material. Full details will be reported elsewhere.

(19) For example, Mn(2)–N(5)–C_t = 106.7, 105.5°, Mn(2)–N(5)–C_b = 115.8°, N(5)–C_t–C_t = 110.4, 109.8°, and N(5)–C_b–C_b = 115.2°, where t = terminal and b = bridging.

(20) For an example of a complex of tren containing an uncoordinated ethylamine chain see: Zehnder, von Margareta; Thewalt, U.; Fallab, S. *Helv. Chim. Acta.* **1979**, *62*, 2099–2108.

μ-oxo groups (2.050 Å) is 0.047 Å shorter than the average trans distance (2.097 Å). This elongation trans to the μ-oxo groups for the Mn(IV) ion is often observed for oxo-bridged species,[22] including **1**. Unlike the situation for **1** and **3**, mixed-valence complexes **2** and $[(\mathrm{TACN})\mathrm{Mn}(\mu\text{-O})_2(\mu\text{-OAc})\mathrm{Mn}(\mathrm{TACN})]^{3+}$ (**4**)[12a] do not have distinguishable Mn(III) and Mn(IV) ions.

Cyclic voltammetry of **3** reveals a quasi-reversible redox wave with $E_a = 0.87$ V, $E_c = 0.79$ V, and $E_{1/2} = 0.83$ V (vs Ag/Ag$^+$), corresponding to the III, IV/IV,IV couple and a wave at $E_a = 0.15$ V, $E_c = -0.02$ V, and $E_{1/2} = 0.085$ V, due to the III,IV/III,III couple.[23] The former couple for **1**, and **2**, lies at significantly higher values: $E_{1/2} = 1.25$ and 1.26 V, respectively.[7] The EPR spectrum of **3**, displayed in Figure 2, bears a remarkable resemblance to that for a recently reported species suspected of being a peroxy-bridged $\mathrm{Mn^{II}Mn^{III}}$ complex.[24] Preliminary simulations for the 16-line pattern in Figure 2 yielded spectral parameters $A_1 = 150 \times 10^{-4}$ cm^{-1} and $A_2 = 78 \times 10^{-4}$ cm^{-1}, in good agreement with hyperfine values derived for **1**, **2**, and **4**.[6,12a] Anisotropy is indicated by splitting in the high-field region of the spectrum; thus, an improvement in the simulation resulted by using parameters $g_{x,y} = 1.961$, $g_z = 1.953$, $A_{1x} = A_{1y} = 150 \times 10^{-4}$ cm^{-1}, $A_{1z} = 128 \times 10^{-4}$ cm^{-1}, and $A_{2x} = A_{2y} = A_{2z} = 69 \times 10^{-4}$ cm^{-1}. Magnetic susceptibility measurements on a powdered sample of **3** were fit to the expression for χ_M vs T derived from the isotropic spin-exchange Hamiltonian,[25] $H' = -2JS_1S_2$, with $S_1 = 2$, $S_2 = {}^3/_2$, $g = 1.958$, and $J = -146$ cm^{-1}.[26] Antiferromagnetic interactions of this magnitude between Mn(III) and Mn(IV) ions were also observed for **1** (−150 cm^{-1})[6] and **2** (−134 cm^{-1},[6] −148 cm^{-1} [11]). An IR absorption band at 694 cm^{-1} for a CH_3CN solution of **3** can be tentatively assigned to a vibration of the Mn_2O_2 core. IR spectra of **1** and **2**[7] display analogous bands at 688 and 686 cm^{-1}, respectively. The electronic absorption spectrum of **3** in CH_3CN[27] is similar to that of **1**, with the exception of a broad band at 800 nm that is observed for **1** but not for **3**. This near-IR absorption in **1** has been assigned to an intervalence transition.[7]

In conclusion, the second example of a complex containing a $[\mathrm{Mn^{III}}(\mu\text{-O})_2\mathrm{Mn^{IV}}]^{3+}$ core for which the Mn(III) and Mn(IV) ions can be clearly distinguished in the solid state has been discovered. The principal differences between $[\mathrm{Mn_2O_2(tren)_2}]^{3+}$ (**3**) and the bpy or phen dimers (**1**, **2**) are (i) the III,IV/IV,IV redox couple is shifted to a lower potential by 0.42 V for **3** compared to **1**, (ii) compound **3** has a greater reactivity toward dioxygen and/or water, and (iii) an absorption band in the near-IR region for **1** is not present in the same position for **3**. Further model studies of the sort presented here will be directed toward an understanding of the role of manganese in the oxygen-evolving complex of photosystem II and manganese aggregation chemistry in general.

Acknowledgment. We thank Jean-Luc Zimmermann for the simulation of the EPR spectrum. This work was supported by Grant No. GM382751-01 from the National Institutes of General Medical Sciences.

Supplementary Material Available: A table of atomic positional and thermal parameters for **3**·EtOH (2 pages). Ordering information is given on any current masthead page.

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[27] Electronic spectrum in CH_3CN [λ, nm (ϵ, M^{-1} cm^{-1})]: 380 (1170), 428 sh, 526 sh, 548 (440), 590 sh, 638 sh, 680 (570).

Synthesis and Structures of $[(C_6H_5)_4P]_2[M(CO)_4Te_4]$ (M = Cr, W), Containing a Polytelluride Ligand Derived from a Soluble Zintl Anion

Sir:

The chemistry of compounds containing inorganic chalcogenide ligands has recently been reviewed by several authors,[1–3] and notable by their absence are rings containing tellurium atoms. The ligand chemistry of the polysulfides[1,3] is reasonably well developed, and there have been several polyselenides reported.[4–6] However the ligand chemistry of tellurium in general has received little study, and the only metal polytellurides have been obtained through extraction of alloys containing Zintl phases.[7,8] We report here the first examples of polytelluride rings chelating to transition metals.

The primary synthetic approach to metal polysulfides and polyselenides is usually to dissolve H_2S (or H_2Se) in aqueous base to generate polysulfide solutions, which are then reacted with appropriate metal compounds, usually a metal–oxo or metal sulfide compound. Often the initial product is a tetrathiometalate.[9] However this is not a convenient route to tellurides because of the instability of H_2Te. In addition, solutions containing tellurides are extremely air sensitive and generally unstable. We have found, however, that extraction of the Zintl phases, such as K_2Te_3 or K_2Te_4, into basic solvents like DMF affords a convenient method of generating solutions containing polytellurides suitable for reaction with transition-metal complexes.[10] This is similar to the approach used to generate several new organotellurium compounds.[11–13]

The synthesis of $[(C_6H_5)_4P]_2[M(CO)_4Te_4]$ (M = Cr (Ia) and W (Ib)) is carried out by typically reacting 0.200 g (0.340 mmol) of K_2Te_4 with 1 equiv of the appropriate metal carbonyl in 10 mL

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