impurities) yielded the parameters listed in Table I. The value $2J = -293$ cm^{-1} obtained for the singlet–triplet separation is in agreement with previous determinations.[27]

The high-temperature part of the curve shows a slight drop of the susceptibility near the transition temperature of 380 K, indicating a decrease of the paramagnetism (ca. 6×10^{-5} cgsu) as the sample goes from the crystal to the discotic mesophase. Experimental points above the transition temperature also obey a Bleaney–Bowers relationship. Interestingly, the value found for the singlet–triplet separation is significantly higher in the discotic region ($2J = -313$ cm^{-1}) than in the crystal region (Table I), and this change is reversible as the temperature is decreased below 380 K. On the other hand, inclusion of an interdimer exchange term in the spin Hamiltonian leads to a less satisfactory agreement between the theoretical curve and the experimental points above 380 K. These observations suggest that a reversible rearrangement, which retains the binuclear structure of the complex, occurs at the transition temperature. Possible structural changes that would lead to a more efficient overlap of the copper magnetic orbitals within a dimer include the following: shortening of the metal–metal distance, alignment of the copper atoms along the column axis, and/or breaking of the apical Cu–O bonds. Infrared and EXAFS experiments are planned to probe further the structural changes of the dimer upon the phase transition, and they will be reported later.

Entirely similar behavior was observed with copper(II) octadecanoate, as well as with the copper(II) complex of the substituted carboxylic acid $(n\text{-}C_9H_{19})_2CHCH_2CO_2H$.[29] In all three cases, a decrease of $(6-9) \times 10^{-5}$ cgsu for χ_M and an increase of 20–30 cm^{-1} for $-2J$ were observed upon the transition from the crystalline solid to the discotic mesophase (Table I). The presence of eight, rather than four, peripheral alkyl chains in the latter complex lowers the transition temperature to 348 K, thus extending the range of accessible temperatures in the discotic region (Figure 2).

In additional experiments, the binuclear complex was heated in the discotic region for 30 min, then quickly immersed in liquid nitrogen for 5 min, and finally equilibrated at room temperature. The magnetic susceptibility of the quenched samples (Figure 1) showed Bleaney–Bowers behavior with a value of the singlet–triplet separation different from that of the normal crystalline phase, but close to that of the high-temperature discotic phase (Table I). Aging the quenched sample for a few weeks restored the $-2J$ value of the crystalline phase. Thus, it appears that the discotic structure can be trapped at room temperature, as a metastable phase however.

In summary, magnetic susceptibility provides a highly sensitive probe of the reversible phase transitions which occur upon heating binuclear copper(II) *n*-alkanoates. Its potential utility for the study of other paramagnetic[10] or diamagnetic[30] mesogens has already been noted, but it remains to be explored in a systematic fashion.

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Registry No. $Cu_2[O_2CCH_2CH(C_9H_{19})_2]_4$, 99280-68-9; copper(II) dodecanoate, 27811-42-3; copper(II) octadecanoate, 29720-62-5.

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Manganese(III) Thiolate Chemistry: New Structural Types, Including the First Mixed-Valence Metal Thiolate

Sir:

Several metallobiomolecules are now known to contain tightly bound manganese(III).[1-4] In no system has a manganese(III) porphyrin been detected, suggesting that ligation to the metal is by amino acid side-chain functions. To better understand these metallo sites, it is important to prepare model manganese(III) complexes with biologically relevant ligands like thiolate (RS^-) and imidazole. In this paper are reported the preparation, structure, and physical properties of three new manganese(III) complexes with such ligands, including an interesting trinuclear mixed-valence $Mn^{II}Mn^{III}_2$ species.

All manipulations were performed by using standard inert-atmosphere techniques and distilled solvents. An ethanolic reaction solution containing $MnCl_2$, Na_2edt, (edt^{2-} is ethane-1,2-dithiolate), NaIm (Im^- is imidazolate), and NMe_4Cl, in a 1:2:4:4 ratio,[5] was cooled to ~0 °C and oxidized by successive addition of small portions of air until generation of a deep green color and precipitation of a green powder could no longer be observed. At this point anaerobic conditions were reestablished, and the solid was filtered and recrystallized from warm (~45 °C) DMF/THF to give analytically pure black prisms of $(NMe_4)_3[Mn_2(Im)(edt)_4]$ (**1**) in ~40% overall yield. Recrystallization can also be effected from warm MeCN to yield crystals of the bis(acetonitrile) solvate.

The structure of **1** was determined;[6,7] the anion is shown in Figure 1. Two five-coordinate Mn(III) atoms are bridged by an imidazolate group in a symmetric fashion, both Mn–N distances being 2.197 (8) Å. Two terminal edt^{2-} ligands occupy the other four coordination sites at each metal center. The resulting Mn geometries are best described as square pyramidal, as found for the monomer $(NEt_4)[Mn(edt)_2(HIm)]$ (**2**).[8] In the anion of **1**, the imidazolate nitrogens occupy apical positions, and the overall symmetry closely approximates C_{2v}, although no elements are crystallographically imposed. N–Mn–S and S–Mn–S angles are in the range 94.78–109.11 (21)° and 86.60–88.87 (11)°, respectively, and Mn-S distances are in the range 2.318–2.357 (3) Å. Mn(1) and Mn(2) are 6.487 Å apart and almost coplanar with the imidazolate ring, deviations being 0.126 and 0.027 Å, respectively. Discrete structurally characterized imidazolate-bridged metal complexes are relatively uncommon at the present time, with most current examples being in Cu(II) chemistry where they have been synthesized as models for bovine (Cu, Zn) superoxide dismutase metallo sites.[9] Within Mn chemistry, both

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[5] Na_2edt and NaIm were generated in situ by addition of equimolar $edtH_2$ and HIm to 3 equiv of NaOEt, prepared by dissolution of Na metal in EtOH.

[6] All crystal structures were solved, with data collected at ca. −160 °C, by using standard direct methods and Fourier techniques. Refinement was by full-matrix least-squares techniques. Local programs were employed.

[7] Complex (**1**)·2MeCN crystallizes in the orthorhombic space group $Pna2_1$ with $a = 17.965$ (5) Å, $b = 16.094$ (4) Å, $c = 14.789$ (3) Å, and $Z = 4$. A total of 2322 unique data with $F > 2.33\sigma(F)$ were refined to $R = 4.58$ and $R_w = 4.40$. Crystals obtained from DMF/THF proved to be poor diffracters of X-rays.

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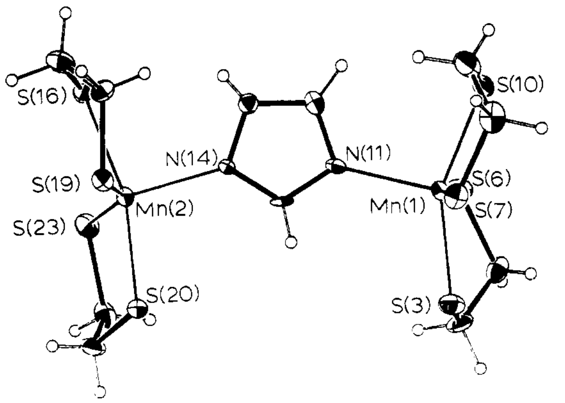

Figure 1. ORTEP projection of the anion of **1** showing the heavy-atom-labeling scheme. In this and subsequent figures, non-hydrogen atoms are depicted as 50% probability ellipsoids; hydrogen atoms are depicted as spheres of arbitrary size. Carbon atoms are numbered consecutively between sulfurs and nitrogens; thus, one ligand is S(3)–C(4)–C(5)–S(6). The carbon attached to both imidazolate N atoms is C(15).

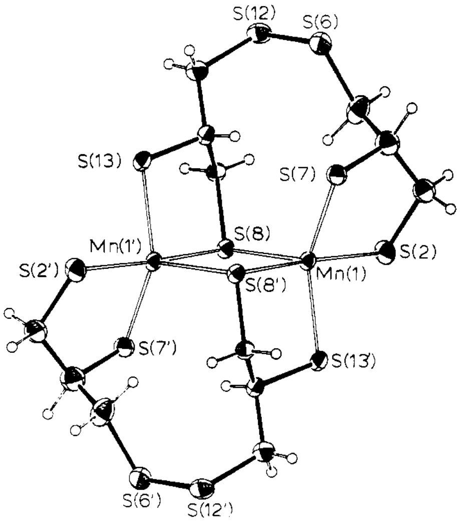

Figure 2. ORTEP projection of the anion of **3**. Carbon atoms are numbered as described in Figure 1.

structurally characterized species are polymeric.[10]

An ethanolic reaction mixture containing $MnCl_2$, Na_3ptt, and $(PhCH_2NEt_3)Br$ in a 1:2:4 ratio (ptt^{3-} is propane-1,2,3-trithiolate) was treated with air as described for **1**. A green coloration was again obtained, followed by precipitation of a green powder. Recrystallization of the filtered solid from DMF/ether gave black crystals of $(PhCH_2NEt_3)_2[Mn_2(SCH_2CH(S)CH_2SSCH_2CH(S)CH_2S)_2]$ (**3**) in ~40% yield in analytical purity. The structure of the anion is shown in Figure 2.[6,11] The anion in **3** possesses C_i symmetry with the center of inversion crystallographically imposed. Two adjacent thiolate sulfur atoms from each of the four (initially) ptt^{3-} ligands have behaved like edt^{2-} groups and assembled a Mn_2S_8 unit identical with that in $(NEt_4)_2[Mn_2(edt)_4]$ (**4**).[12,13] The other four trithiolate sulfur atoms have been oxidized to form interligand disulfide bonds S(6)–S(12) and S(6')–S(12'). Since these distances (2.0413 (16) Å) are as expected for a single covalent bond, the anion in **3** can be described as a Mn(III) dimer containing two bridging tetradentate, binucleating, tetrathiolate ligands, $C_6H_{10}S_6^{4-}$. As in the anion of **4**, Mn geometries are approximately trigonal bipyramidal.[12,13] Comparison of other structural parameters among the anions of **3** and **4** shows near congruency of the portions common to both molecules. The major difference is the Mn··Mn length in **3** (3.598 (2) Å), which is slightly longer than that in **4** (3.543 (2) Å), presumably due to decreased flexibility in the ligands of the former. As a result, the bridging Mn–S distances in **3** (2.3530 (12) and 2.6546 (12) Å) are also slightly longer than in **4** (2.341 (2) and 2.606 (2) Å), most noticeably for the longer, weaker interactions.

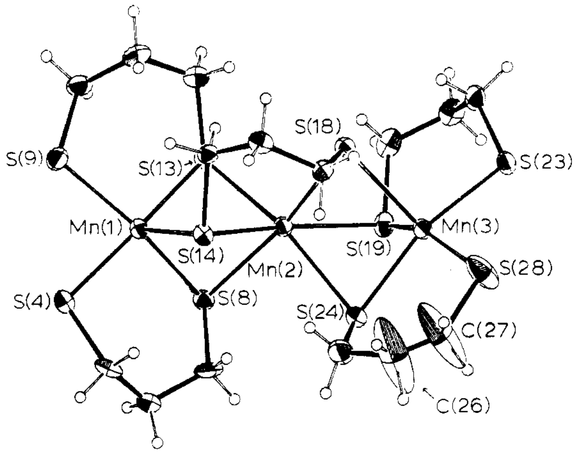

Figure 3. ORTEP projection of the anion of mixed-valence trimer **5**. Carbon atoms are numbered as described in Figure 1. The high thermal parameters of carbon atoms C(26) and C(27) may be due to two disorder positions, but these were not resolved.

An ethanolic reaction solution containing $MnCl_2$, Na_2pdt, and $(PPh_4)Br$ in a 1:2:1 ratio (pdt^{2-} is propane-1,3-dithiolate) was oxidized with air, as for **1** and **3**, to give a dark green coloration and a microcrystalline green precipitate. Recrystallization of the filtered material from DMF/ether at ~25 °C[14] yields black prisms of $(PPh_4)_2[Mn_3(pdt)_5]$ (**5**), in ~40% yield and analytical purity. The structure of the anion of **5** is shown in Figure 3.[6,15] The three Mn atoms are approximately linear (Mn(1)–Mn(2)–Mn(3) = 169.7 (1)°). The molecule possesses idealized C_2 symmetry, with the twofold axis passing through Mn(2) and C(16), but not crystallographically imposed. The overall charge on the anion requires one Mn(II) and two Mn(III) atoms. The central manganese, Mn(2), is readily assigned as the Mn(II) atom. It possesses distorted octahedral geometry, with each of its six thiolate sulfur ligands bridging to terminal Mn(III) atoms. The latter are five-coordinate with a geometry intermediate between the square-pyramidal and trigonal-bipyramidal extremes. Terminal Mn(III)–S bond distances (2.3152–2.3266 (26) Å) are similar to those in **1**–**4**, supporting the Mn(III) description. Mn(II)–S distances are much longer, as expected, in the range 2.5542–2.6770 (26) Å. Mn(1)··Mn(2) and Mn(2)··Mn(3) distances are 3.123 (3) and 3.101 (3) Å, respectively. Two unique features of **5** are as follows: (i) the six-coordinate Mn(II)-thiolate unit, since Mn(II) in a thiolate environment has hitherto displayed tetrahedral coordination;[13,16] (ii) **5** is the first example of a mixed-valence homoleptic metal thiolate.

Solid-state magnetic studies have been performed on powdered samples of **1**–**5** in the temperature range 2–300 K. The data for monomer **2** are the most straightforward and are fully consistent with an isolated high-spin d^4 Mn(III) center. Thus, the effective

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(10) (a) $[Mn^{III}(Im)(TPP)]_n$ (TPP = *meso*-tetraphenylporphinato): Landrum, J. T.; Hatano, K.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1980**, *102*, 6729. (b) Lehnert, R.; Seel, F. *Z. Anorg. Allg. Chem.* **1980**, *464*, 187.

(11) Suitable crystals were grown by vapor diffusion of ether into a DMF solution. Complex **3** crystallizes in monoclinic space group $P2_1/c$ with a = 11.540 (2) Å, b = 12.115 (2) Å, c = 17.478 (4) Å, β = 101.78 (1)°, and Z = 2. A total of 2651 unique data with $F > 3\sigma(F)$ were refined to R = 3.59 and R_w = 3.94.

(12) Christou, G.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1983**, 558.

(13) Costa, T.; Dorfman, J. R.; Hagen, K. S.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 4091.

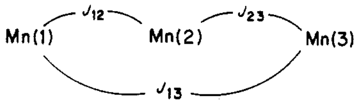
(14) Higher temperatures should be avoided as this may cause ligand oxidation, concomitant reduction of the Mn(III), and loss of the deep green color.

(15) Complex **5** crystallizes in the triclinic space group $P\bar{1}$ with a = 14.385 (6) Å, b = 23.734 (11) Å, c = 9.881 (3) Å, α = 100.39 (2)°, β = 93.25 (2)°, γ = 107.53 (2)°, and Z = 2. A total of 5844 unique reflections with $F > 3\sigma(F)$ were refined to R = 6.41 and R_w = 6.06.

(16) Swenson, D.; Baenziger, N. C.; Coucouvanis, D. *J. Am. Chem. Soc.* **1978**, *100*, 1932.

magnetic moment at 300 K is 4.97 μ_B in agreement with the spin-only value (4.90 μ_B). A sharp decrease in the moment below approximately 15 K is indicative of zero field splitting, and a value of 5.71 cm^{-1} has been obtained by least-squares fitting of the data. Dimers **1**, **3**, and **4** all possess moments per Mn at 300 K (4.51, 3.95, and 3.97 μ_B, respectively) that are below spin-only values and that decrease to near-zero values with decreasing temperature. Antiferromagnetic coupling of two high-spin d^4 Mn(III) centers to yield singlet ground states is thus indicated, and satisfactory least-squares fits to the data have been obtained, assuming an isotropic exchange interaction with a spin Hamiltonian $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$ and $S_1 = S_2 = 2$. Values of the exchange parameter J are −1.9, −18.7, and −18.7 cm^{-1}, respectively. The behaviors of **3** and **4** are thus very similar, as expected from their similar structures; the slight difference in their Mn··Mn distances is obviously not reflected to a noticeable degree in their magnetic properties.

Trimer **5** has a moment of 6.75 μ_B at 300 K decreasing to ~3.9 μ_B below ~25 K, corresponding to a spin quartet ($S = {}^3/_2$) ground state. The data were fit to the magnetic susceptibility equation derived with two exchange parameters, defined by



Satisfactory fits have been obtained, however, by taking $J_{13} = 0$ with $S_1 = S_3 = 2$ and $S_2 = {}^5/_2$, yielding a value of $J_{12} = J_{23} = -18.3$ cm^{-1}. Allowing J_{13} to vary leads to only very small values of this parameter, and has an almost insignificant effect on the quality of the fit or the value of J_{12}.

The combined magnetic data thus demonstrate that complexes **1**–**5** all contain high-spin metal centers, which, with the exception of Mn(2) in **5**, are in the +3 oxidation level. In addition, **1**, **3**, **4**, and **5** are antiferromagnetically coupled with values of the exchange parameter J that are relatively small ($|J| < 20$ cm^{-1}).

The results described above serve to further emphasize the accessibility and stability of the Mn(III) oxidation level in a thiolate environment. The usual redox instability of Mn(III) to readily oxidizable thiolate functions is suppressed by use of dithiolate ligands. One important aspect of **5** in this respect has been to demonstrate that the stabilization of Mn(III) is not due to some unique property of the edt^{2-} ligand. Armed with this reassurance, conditions are now being sought to stabilize Mn(III) with other thiolates, including monothiolates, and with additional biologically relevant ligands.

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Supplementary Material Available: Listings of fractional atomic coordinates and isotropic thermal parameters for non-hydrogen atoms (4 pages). Ordering information is given on any current masthead page.

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Polymer–Pendant Ligand Chemistry. 1. Reactions of Organoarsonic Acids and Arsenic Acid with Catechol Ligands Bonded to Polystyrene–Divinylbenzene and Regeneration of the Ligand Site by a Simple Hydrolysis Procedure

Sir:

The use of polymer-supported pendant ligands for metal ion removal is a well-developed field.[1] More recent studies have focused on specific reactions of these polymer-bonded ligands and include separations of biological substrates,[2a] protein fractionation,[2b] racemate separations,[2c] and transport of cations through membranes.[2d] Interestingly, very few of the reported methods incorporate a chemical reaction that forms discrete covalent metal–heteroatom bonds with loss of a small molecule such as water for the metal ion removal step; but rather, they usually entail an ion exchange or binding phenomena for reaction to occur.[3]

Additionally, an important area concerning processing of complex matrices such as synthetic fuels and petroleum crudes, for the removal and recovery of trace organometallic compound contaminants, has received little or no attention in this field[4] due to the lack of molecular characterization of these carbon–metal-bonded compounds in these sources. Thus, it is evident from an environmental and economic standpoint, that new and innovative methods for removal and recovery of trace organometallic compounds as well as inorganic anions from the above-mentioned matrices would be useful.

In this communication, we wish to report a novel method for reactions of organoarsonic acids and arsenic acid, known to be present in oil shale and its pyrolysis products,[5] with catechol ligands bonded to either 2% or 20% cross-linked methylated polystyrene–divinylbenzene (PS-DVB) resins.[6] A previous study with catechol-bonded ligands on PS-DVB resins dealt with their reactions with metal ions in aqueous solution and showed a selectivity toward Hg^{2+} ions.[7] As far as we have been able to determine, reactions of this polymer-supported ligand with organometallic compounds or inorganic anions have not been reported.

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(4) Flett, D. S.; Pearson, D. *Chem. Ind.* (*London*) **1975**, 639.

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(6) Synthesized by reaction of catechol with 2% or 20% chloromethylated polystyrene–divinylbenzene resins in the presence of stannic chloride to provide an 11% by weight (2%) and 6% by weight (20%) incorporation of catechol in the polymer. See: Warshawsky, A.; Kahana, N. *J. Am. Chem. Soc.* **1982**, *104*, 2663.

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