

Figure 2. Absorption spectra of O_2 and CO adducts of the Fe^{II} -(bipyridine-porphyrin) complex with *N*-methylimidazole in DMF at 25 °C.

complex shows peaks at 430 and 520 nm. The oxygen atoms of this oxygenated complex were easily replaced by carbon monoxide, as shown in Figure 2. When oxygen gas was passed through the solution containing CO complex again, its visible spectrum is almost the same as that of the oxygenated complex, indicating the formation of the O_2 complex. This property is very similar to 7,7-anthracene cyclophane heme, which was prepared by us already.^{3,7} The visible spectra of the O_2 and CO adducts are very broad. Probably, the cause of broadened peaks would come from the small cavity and the influence of lone-pair electrons. Thus, it seems that the O_2 or CO adducts of one species are formed in solution.

The $\nu(C=O)$ stretching band of the CO complex in the presence of 1 M *N*-methylimidazole was measured by using a Fourier transform infrared spectrometer, and its value in cyclohexane is 2044 cm^{-1} . We do not have any explanation for this higher frequency.¹¹

The striking result is the extreme stability of the oxygenated complex at room temperature. Though there is a possibility that the lone-pair electrons of coordinated dioxygen atoms interact with those on the nitrogen atoms of the bipyridine moiety, the oxygenated species are very stable ($T_{1/2} > 6\text{ h}$). In order to confirm the effect of lone-pair electrons, the $Fe(III)$ complex of biphenyl-porphyrin was reduced under the same conditions as in the case of (bipyridine-porphyrin)- Fe complex, and the oxygen gas was passed through the solutions of the $Fe(II)$ complex of biphenyl-porphyrin. However, the oxygenated complex was not formed, and its $Fe(II)$ complex was oxidized directly as shown in Figure 3. In addition, measurements of $\nu(C=O)$ stretching band of (biphenyl-porphyrin)- Fe^{II} -CO complex in cyclohexane were performed, but results were not gained due to the instability of its complex.

Though it was reported that the oxygenated complex is stabilized by hydrogen bonds between imidazole and dioxygen atoms,¹² these results suggest that the stability of the oxygenated

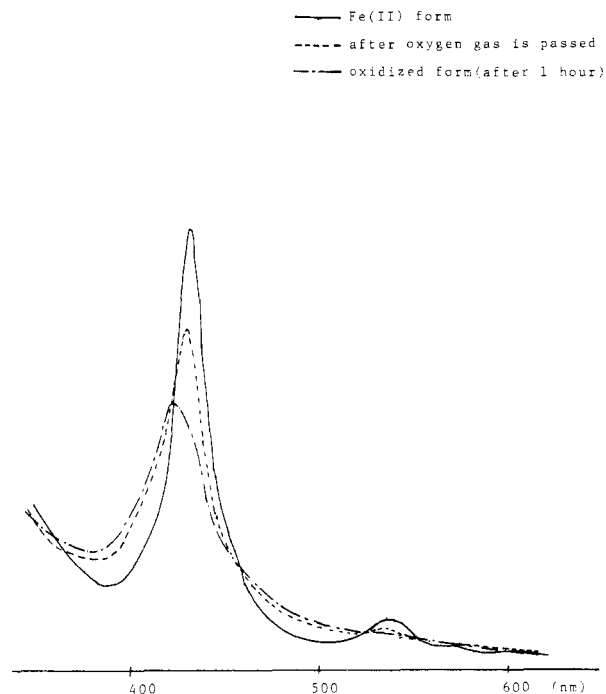


Figure 3. Absorption spectra of Fe complex of biphenyl-porphyrin with *N*-methylimidazole in DMF at 25 °C.

complex is also affected by the lone-pair electrons on the nitrogen atoms.

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Magnetic Susceptibility as a Probe of the Solid-Discotic Phase Transition in Binuclear Copper(II) *n*-Alkanoates

Sir:

The distinctive physical properties of thermotropic mesogens (i.e. compounds that exhibit liquid crystalline behavior above a given temperature) are usually characterized by using methods such as hot-stage optical microscopy, differential scanning calorimetry, or X-ray diffraction.¹ Recent progress in the synthesis of mesogenic compounds includes the preparation of square-planar transition-metal complexes with various patterns of alkyl chain peripheral substitution. Upon heating, these give rise to nematic, smectic, or discotic mesophases, depending on chain length and core symmetry.²⁻²⁰ As yet, little attention has been paid, however,

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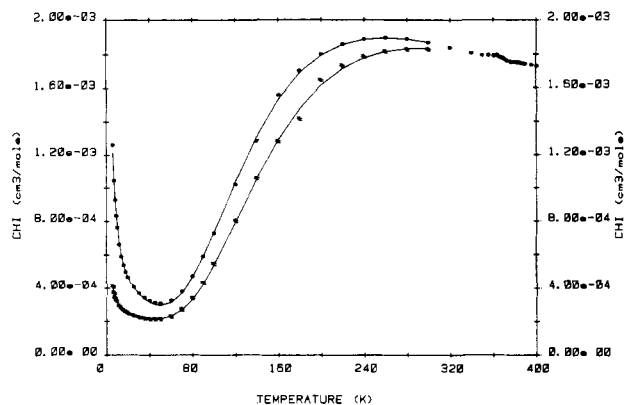


Figure 1. Plot of the molar magnetic susceptibility of copper(II) dodecanoate vs. temperature: upper curve, crystalline and discotic phases; lower curve, quenched phase (see text). Experimental points and theoretical curves obtained with best-fit values of the parameters (Table I) are shown.

to the magnetic properties of such complexes in their crystalline and mesomorphic states. In this report, we describe the utility of high-sensitivity magnetic susceptibility measurements (Squid) to probe the structural rearrangements of the higher homologues of binuclear copper(II) acetate upon their transition from the crystalline phase to the discotic mesophase.

The solid-state structures of anhydrous copper(II) *n*-alkanoates show discrete dimeric units analogous to that of copper(II) acetate.²¹ The binuclear cores, surrounded by four alkyl chains pointing away from the Cu–Cu axis, are linked to one another by apical Cu–O bonds, giving a polymeric chain lattice.^{22–25} The solid-state magnetic susceptibility of these compounds reflects intradimer, but not interdimer, exchange interaction between copper atoms;²⁶ these can be described by the Heisenberg–Dirac–Van Vleck spin Hamiltonian, $\hat{H} = -2J \hat{S}_1 \cdot \hat{S}_2$, which yields the Bleaney–Bowers equation.²⁷ Recent work from this labo-

Table I. Magnetic Susceptibility Parameters of Copper(II) Alkanoates in Their Crystalline, Discotic, and Quenched Phases^a

compd	phase	<i>g</i>	$-2J$, cm ⁻¹	<i>P</i> , %
copper(II) dodecanoate	crystalline (<i>T</i> < 380 K)	2.17	293	0.7
	discotic (<i>T</i> > 380 K)	2.16	313	0.7
	quenched	2.25	327	0.4
	quenched and aged	2.19	300	0.5
copper(II) octadecanoate	crystalline (<i>T</i> < 390 K)	2.05	278	0.3
	quenched	2.16	312	0.9
Cu ₂ [O ₂ CCH ₂ CH(C ₉ H ₁₉) ₂] ₄	crystalline (<i>T</i> < 348 K)	2.12	306	0.0
	discotic (<i>T</i> > 348 K)	2.15	333	0.0

^a Values of *g*, $-2J$, and *P* were obtained by fitting the data to the modified Bleaney–Bowers equation: $\chi^{\text{cor}} = (2Ng^2\beta^2/3kT)[1 + 1/3 \exp(-2J/kT)]^{-1} (1 - P) + (PNg^2\beta^2/2kT) + 2N\alpha$, where *P* is the mole fraction of paramagnetic impurity. The quantity minimized in the least-squares fitting process was $[\chi^{\text{cor}}(\text{exptl}) - \chi^{\text{cor}}(\text{calcd})]^2$. Estimated uncertainty in the *g* and $-2J$ values is about 1%.

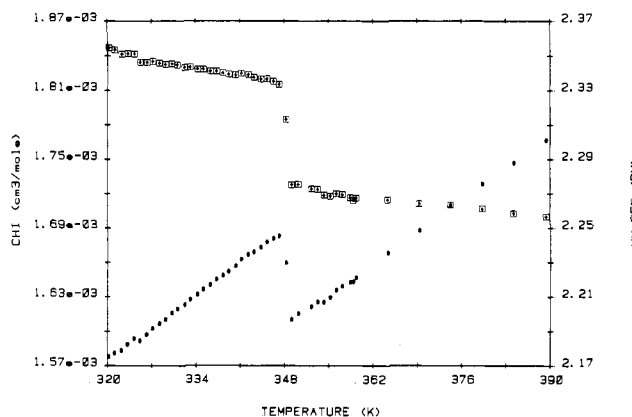
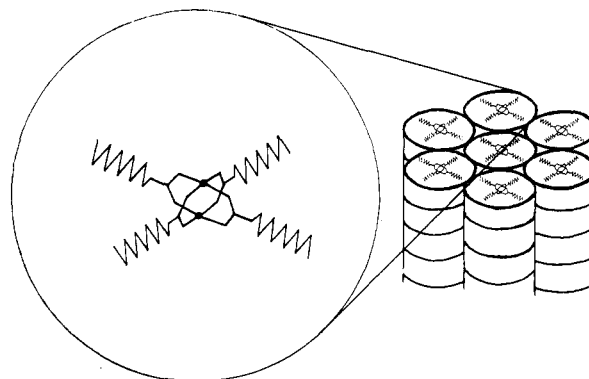


Figure 2. Detailed plots of the molar magnetic susceptibility (squares) and of the magnetic moment per binuclear unit (dots) vs. temperature for Cu₂[O₂CCH₂CH(C₉H₁₉)₂]₄ about the phase transition.

ratory²⁸ has shown that upon being heated above 380 K, copper(II) dodecanoate gives a discotic mesophase characterized by an hexagonal columnar lattice with a repeat distance of about 20 Å; each column is made of stacked binuclear units with a period of about 4.7 Å.



The magnetic susceptibility of copper(II) dodecanoate was measured from 6 to 400 K. A plot of χ_M vs. *T* over this temperature range (which includes the phase transition) is shown in Figure 1. Fitting the data below 380 K to the Bleaney–Bowers equation (modified to account for a small amount of paramagnetic

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impurities) yielded the parameters listed in Table I. The value $2J = -293 \text{ cm}^{-1}$ 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 ($2J = -313 \text{ cm}^{-1}$) 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 $(n\text{-C}_9\text{H}_{19})_2\text{CHCH}_2\text{CO}_2\text{H}$.²⁹ In all three cases, a decrease of $(6-9) \times 10^{-5}$ cgsu for χ_M and an increase of $20-30 \text{ cm}^{-1}$ 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 paramagnetic¹⁰ or diamagnetic³⁰ mesogens has already been noted, but it remains to be explored in a systematic fashion.

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Registry No. $\text{Cu}_2[\text{O}_2\text{CCH}_2\text{CH}(\text{C}_9\text{H}_{19})_2]_4$, 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 we reported the preparation, structure, and physical properties of three new manganese(III) complexes with such ligands, including an interesting trinuclear mixed-valence $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_2$ 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 $\sim 0^\circ\text{C}$ 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 ($\sim 45^\circ\text{C}$) DMF/THF to give analytically pure black prisms of $(\text{NMe}_4)_3[\text{Mn}_2(\text{Im})(\text{edt})_4]$ (**1**) in $\sim 40\%$ 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 $(\text{NEt}_4)[\text{Mn}(\text{edt})_2(\text{HIm})]$ (**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 $94.78-109.11 (21)^\circ$ and $86.60-88.87 (11)^\circ$, 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 $a = 17.965 (5) \text{ \AA}$, $b = 16.094 (4) \text{ \AA}$, $c = 14.789 (3) \text{ \AA}$, 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 diffractors of X-rays.

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