have carried out similar CV studies on the carboxylate-bridged compounds in order to investigate the degree of electronic coupling between the two dinuclear centers. A summary of the electrochemical data is given in Table I together with comparative data for related bridged mononuclear complexes.

Using the electrochemical data for reversible oxidations of linked mononuclear complexes of the formula $[(NH_3)_5M]_2(\mu\text{-}L)^{4+/5+/6+}$, where M = Ru and Os and L = N_2, pyrazine, and other bidentate donor ligands, Taube and co-workers[7] have determined values of K_c (conproportionation equilibrium constant) for the equilibrium reaction 2. The greater the magnitude of K_c, the greater the degree of charge delocalization in the mixed-valence state and the greater the electronic coupling of the two redox centers.

$$[M\text{–}L\text{–}M]^{4+} + [M\text{–}L\text{–}M]^{6+} \overset{K_c}{\rightleftharpoons} 2[M\text{–}L\text{–}M]^{5+} \qquad (2)$$

For the dicarboxylate-linked dinuclear systems we observed two successive one-electron-oxidation processes,[8] the first of which is reversible and the second essentially irreversible.[9] By analogy with Taube's work, we define a conproportionation equilibrium constant K_c for the mixed valence state of the linked quadruply bonded compounds in eq 3.

$$[M_2\sim\sim\sim M_2] + [M_2\sim\sim\sim M_2]^{2+} \overset{K_c}{\rightleftharpoons} 2[M_2\sim\sim\sim M_2]^{1+} \qquad (3)$$

As seen in Table I, the electronic coupling in the carboxylate-bridged tetranuclear compounds is greater for M = W than for M = Mo and directly parallels the trend in Taube's pentaamine system where coupling for the third-row element Os is greater than for the second-row element Ru. As expected, the shorter perpendicular link (oxalate) exhibits greater electronic coupling than the longer perfluorophenyl dicarboxylate bridge, and their magnitudes are similar to those obtained for pyrazine and 1,4-dicyanobenzene bridged pentaamine systems, respectively.

The K_c values for the parallel-linked systems are similar for both the 1,8-anthracenedicarboxylate bridged species and the saturated 9,10-dihydro-1,8-anthracenedicarboxylate bridged species. Thus the electron transfer is probably occurring directly between the metals of the subunits rather than through the carboxylate bridge, and in any event the contribution to these K_c values from direct $M_2\cdots M_2$ electron delocalization in the mixed-valence state is likely to be small compared to contributions arising from electrostatic factors.[10]

The preliminary results reported here indicate that strong electronic coupling between covalently linked M–M multiple bonds is possible and that this coupling should be tunable by choice of metal (e.g., Mo versus Rh), the covalent link, and the orientation of the M_2 axes. This is encouraging with respect to achieving electronic communication along one-dimensional polymer chains of either type I or II.[11]

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[8] The one-electron nature of the redox couples was established by comparing the magnitude of the current flow with that measured for equimolar concentrations of the corresponding $M_2(O_2C\text{-}t\text{-}Bu)_4$ compound under identical CV conditions.

[9] For well-separated redox couples (i.e., >250 mV), the ratio of the anodic peak current to the cathodic peak current for the first couple was found to be unity. For successive redox couples separated by <250 mV, such criteria could not be applied.

[10] For a discussion of factors influencing the relative stability of mixed-valence species, see: Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 114–119. We thank Professor Taube for bringing this matter to our attention.

[11] We gratefully acknowledge the National Science Foundation for a postdoctoral fellowship for R.H.C.

Detection of EPR Spectra in $S = 2$ States of Trivalent Manganese Complexes

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The presence of trivalent manganese is implicated in a number of redox-active metalloenzymes, including the photosynthetic oxygen-evolving complex,[2] superoxide dismutase,[3] pseudocatalase,[4] and ribonucleotide reductase.[5] Considerable effort has been focused on the synthesis and characterization of inorganic complexes as structural models for these biological metal centers.[6] However, EPR spectroscopy has rarely been applied to study the electronic structure of trivalent manganese complexes. This is perhaps a result of a prevalent assumption that the non-Kramers spin states of such systems would be EPR silent, as a result of either large zero-field splittings or fast spin relaxation processes. Although a few EPR studies of trivalent manganese impurity ions in solid-state systems have been reported,[7] these have relied largely on indirect detection methods or very high observation frequencies.

In this communication, we present X-band EPR spectra of $S = 2$ spin states of three trivalent manganese complexes, including the mononuclear manganese(III) tris(acetylacetonate) and tris(picolinate) coordination complexes and the weakly antiferromagnetically exchange coupled binuclear complex $Mn_2^{III,III}O(O_2CCH_3)_2(HB(pz)_3)_2$ ($HB(pz)_3$ = hydrotris(1-pyrazolyl)borate).[8] In all cases, stronger signals were obtained with a geometry in which the microwave magnetic field was polarized parallel to the applied magnetic field, in contrast to the conventional EPR method in which the microwave field is polarized perpendicular to the applied field. The parallel microwave polarization induces magnetic dipole transitions with the selection rule $\Delta m = 0$, which can become partially allowed in spin systems with $S > {}^1/_2$ when zero-field Hamiltonian terms mix the Zeeman basis states. The zero-field interaction $D[S_z^2 - {}^1/_3S(S + 1)] - E(S_x^2 - S_y^2)$ splits the levels of an $S = 2$ spin system into two doublets, one comprised of linear combinations of the $m_s = |\pm 2\rangle$ states and the other of the $m_s = |\pm 1\rangle$ states, and a singlet corresponding to the $m_s = |0\rangle$ state.[9] EPR transitions may be observed between the levels of

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[1] (a) Department of Physics. (b) Department of Chemistry. (c) Chemical Biodynamics Division, Lawrence Berkeley Laboratory, University of California, Berkeley. (d) Present address: Department of Chemistry, Emory University, Atlanta, GA.

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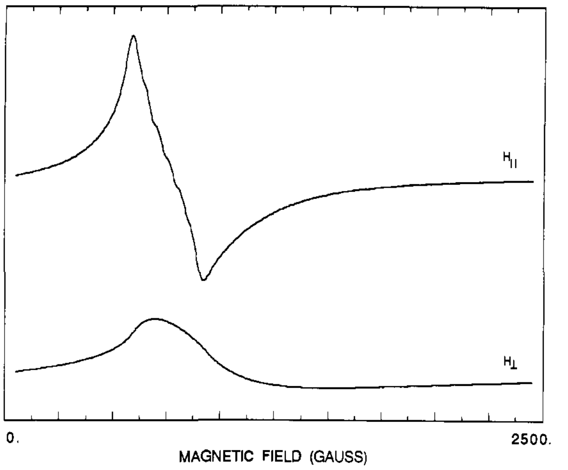

Figure 1. X-band EPR spectra of manganese(III) tris(acetylacetonate) in butyronitrile/propionitrile: upper trace, parallel polarization; lower trace, perpendicular polarization. Spectrometer conditions: microwave frequency, 9.20 GHz (parallel polarization), 9.34 GHz (perpendicular polarization); microwave power, 2 mW; field modulation amplitude, 20 G; modulation frequency, 100 kHz; temperature, 12 K.

the $|\pm 2\rangle$ non-Kramers doublet if the splitting between the levels at zero field, $3E^2/D$, does not exceed the microwave frequency. In principle, EPR transitions may also be allowed within the $|\pm 1\rangle$ non-Kramers doublet and between the levels of this doublet and the $|0\rangle$ level, but these splittings are generally larger than the X-band microwave quantum for zero-field parameters typical of Mn(III) species and for standard laboratory fields.

The X-band EPR spectra[10] of a frozen solution of manganese(III) tris(acetylacetonate) in a mixture of butyronitrile and propionitrile are shown in Figure 1. A low-field feature centered at an effective g value of 8.7 is present in the parallel polarization, and a broader feature at slightly higher field appears in the perpendicular polarization. The field positions of the signals are consistent with transitions within the $|\pm 2\rangle$ non-Kramers doublet, and the line shapes are consistent with the different orientation dependence for the two selection rules. Partially resolved hyperfine structure with a spacing of 55 G appears in the parallel polarization signal. Since the parallel polarization response is dominated by molecular orientations with the spin z axis close to the direction of the applied magnetic field, the observed hyperfine splitting corresponds approximately to A_z. The observed hyperfine spacing is close to the value of A_z determined for Mn(III) impurity ions in TiO_2.[7a] Since the magnitude of the isotropic part of the Mn(III) hyperfine interaction is expected to be intermediate between those of Mn(II) and Mn(IV),[11] the observed spacing indicates that a high degree of anisotropy may be present in the hyperfine tensors of Mn(III) complexes.

The X-band EPR spectra of a frozen solution of manganese(III) tris(picolinate)[12] in acetonitrile are shown in Figure 2. The parallel polarization signal consists of a trough with a minimum at an effective g value of 10, and the perpendicular polarization signal appears as a broader trough at higher field. The field positions are again consistent with transitions within the $|\pm 2\rangle$ non-Kramers doublet, and the line shapes are similar to those observed for $S = 2$ Fe(II) complexes.[13] Such line shapes appear in field-modulated first-derivative EPR spectra when the width of the resonance is sufficiently large relative to its field position.

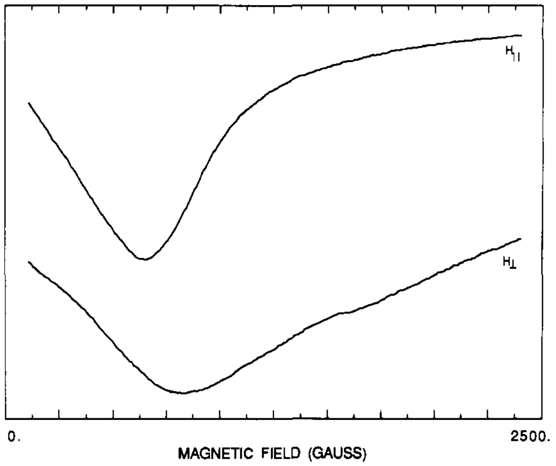

Figure 2. X-band EPR spectra of manganese(III) tris(picolinate) in acetonitrile: upper trace, parallel polarization; lower trace, perpendicular polarization. Spectrometer conditions: as in Figure 1, except microwave power, 20 mW; temperature, 7 K.

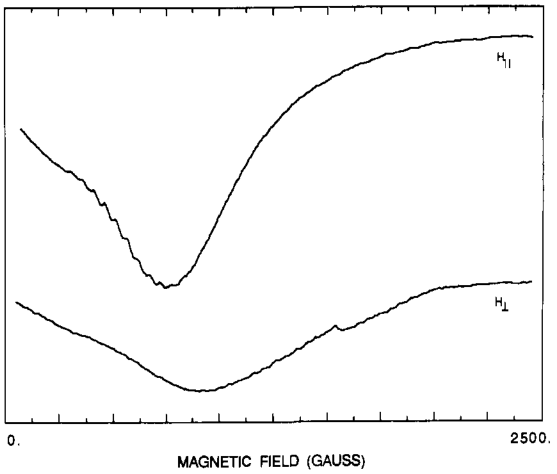

Figure 3. X-band EPR spectra of $Mn_2^{III,III}O(O_2CCH_3)_2(HB(pz)_3)_2$ ($HB(pz)_3$ = hydrotris(1-pyrazolyl)borate) in butyronitrile/propionitrile: upper trace, parallel polarization; lower trace, perpendicular polarization. Spectrometer conditions: as in Figure 1, except temperature, 4.2 K. A small signal due to an Fe(III) impurity is present at an effective g of 4.3 in the perpendicular polarization.

Figure 3 shows the spectra of the binuclear complex $Mn_2^{III,III}O(O_2CCH_3)_2(HB(pz)_3)_2$ in a mixture of butyronitrile and propionitrile. Magnetic susceptibility measurements on this complex[8] indicate a weak antiferromagnetic exchange coupling of approximately 0.5 cm^{-1}, resulting in an $S = 0$ ground state with thermally accessible excited spin states at liquid helium temperatures. The observed signals are consistent with a formal $S = 2$ state. A trough with a minimum at an effective g of 8.7 appears in the parallel polarization, and a weaker, broader trough appears at higher field in the perpendicular polarization. Partially resolved hyperfine structure with a spacing of 52 G is visible in the parallel polarization spectrum, and the presence of at least 10 lines is consistent with an exchange-coupled dimer as the origin of the signal. The absence of any signals corresponding to an $S = 1$ state may be explained by sufficiently large zero-field splitting parameters. This would lead to highly anisotropic and, therefore, very weak perpendicular polarization transitions between the $|0\rangle$ and $|+\rangle$ and the $|-\rangle$ and $|0\rangle$ levels of the $S = 1$ state and could also preclude the observation of a half-field X-band transition between the $|+\rangle$ and $|-\rangle$ levels in either the perpendicular or parallel polarization.

Care must be exercised in the assignment of low-field EPR features to Mn(III) species. Low-symmetry $S = {}^5/_2$ Mn(II)

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(10) EPR spectra were recorded on a Varian E-109 X-band spectrometer equipped with a modified V-4536 bimodal cavity and an Air Products Helitran cryogenic system. Solutions were prepared in dry solvents under nitrogen gas.

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species, which may be present as impurities in Mn(III) preparations, can also give rise to EPR features at low field. Since $S = 2$ Mn(III) signals are quite weak if present at all, a small amount of an Mn(II) impurity can easily interfere with the identification of an Mn(III) signal. The two species can be distinguished, however, because the $S = {}^5/_2$ system will in general produce a resonance near $g = 2$ in addition to any other features at low field. In preliminary preparations of the monomeric Mn(III) complexes described above, features near $g = 2$ were observed in addition to the low-field signals. Upon further purification, the amplitudes of the $g = 2$ signals decreased markedly relative to the low-field features. This result, together with the consistency of the field positions and line shapes of the low-field features with an $S = 2$ spin Hamiltonian, provides additional confirmation of the assignment of the signals to Mn(III). In the case of the binuclear complex, a small amount of an Mn(III,IV) impurity produced a multiline signal centered near $g = 2$ that also decreased in amplitude relative to the low-field features upon further purification. In light of these considerations, we call into question the validity of recent reports of the assignment of $g = 2$ EPR signals to trivalent manganese species.[14]

In conclusion, we have observed and interpreted X-band EPR spectra of complexes of trivalent manganese. This work provides examples of spectral features observable in the $S = 2$ state of Mn(III) complexes and demonstrates the utility of X-band EPR for studying these systems. Studies of a similar nature on biological manganese centers and related inorganic model complexes are in progress.

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Ptilomycalin A: A Novel Polycyclic Guanidine Alkaloid of Marine Origin

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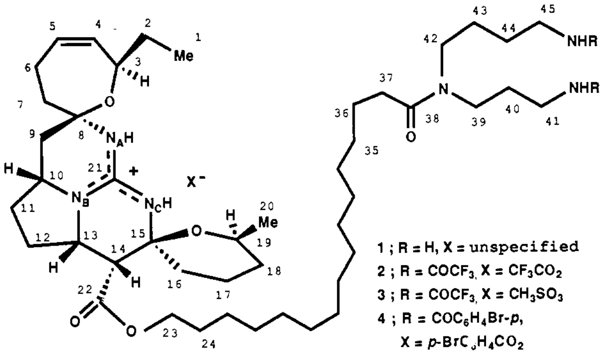
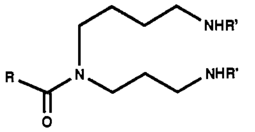
In the course of screening for novel bioactive agents from marine sponges, we have isolated from the Caribbean sponge *Ptilocaulis spiculifer*[1] and from a red *Hemimycale* sp. of the Red Sea the same antitumor, antiviral, and antifungal compound designated ptilomycalin A (**1**),[2] which possesses a unique polycyclic guanidine structure.

The molecular formula, $C_{49}H_{78}N_6O_7F_6$, of the bis(trifluoroacetyl) derivative **2**, an oil, $[\alpha]_D$ −15.8° (*c* 0.68, $CHCl_3$), was determined by HR-FAB mass spectrum (MH^+, *m/z* 977.5915 for $C_{49}H_{79}N_6O_7F_6$, Δ 1.0 mmu).

Right Half. The ^1H and ^{13}C NMR spectra (Bruker AM-500, $CDCl_3$)[3] of **2** suggested the presence of a spermidine moiety[4] as well as an aliphatic long chain (δ 1.25). A clue for the whole structure of the right half was obtained when **5** was isolated from both sponges as the bis(trifluoroacetyl) derivative **6**. Eventually, the structure of the right half (from position 23 to position 45) was established by reduction (excess $LiAlH_4$ in THF; 0 °C, 50 min) or methanolysis (2% MeONa in MeOH; reflux for 3 h) of **2** and by methanolysis (0.1% MeONa in MeOH, room temperature, 7 days) of the bis(*p*-bromobenzamide) **4**, which resulted in the isolation of the fragments **8** (after acetylation) and **7**, respectively.[5]



1 ; R = H, X = unspecified
2 ; R = $COCF_3$, X = CF_3CO_2
3 ; R = $COCF_3$, X = CH_3SO_3
4 ; R = COC_6H_4Br-*p*, X = *p*-$BrC_6H_4CO_2$



5 ; R = $CH_3(CH_2)_{14}$, R' = H
6 ; R = $CH_3(CH_2)_{14}$, R' = $COCF_3$
7 ; R = $HO(CH_2)_{15}$, R' = COC_6H_4Br-*p*
8 ; R = $AcO(CH_2)_{15}$, R' = $COCF_3$
9 ; R = CF_3, R' = $COCF_3$

Left Half. From the HOHAHA spectrum,[6] the protons could be classified into three spin-relaying groups: (i) CH_3-1 to CH_2-7, (ii) CH_2-9 to CH-14, and (iii) CH_2-16 to CH_3-20. Besides these proton signals, two D_2O-exchangeable signals appear at δ 10.22 and 9.87, which are ascribable to those of an ammonium or iminium group.[7] The fact that **2** is actually a salt was verified by the presence of one set of carbon signals ($CF_3CO_2^-$) [δ 116.8 (q, $J = 292$ Hz) and 162.7 (q, $J = 34$ Hz)] and also by the finding that shaking a $CDCl_3$ solution of **2** with an aqueous solution of sodium methanesulfonate resulted in the incorporation of 1 molar equiv of the methanesulfonate anion (**3**; detected by ^1H NMR spectrum; δ_{Me} 2.78) in the organic layer. Also, washing a $CDCl_3$ solution of **2** with 0.1 N NaOH brought about disappearance of the low-field NH signals, which reappeared slowly on standing. These properties suggested the presence of a strongly basic moiety in **2**.[8] When the ^{13}C NMR spectra ($CDCl_3$) were taken in the presence of 3 molar equiv of CD_3OD, the carbon signal at δ 149.09, which showed no correlation with protons in the COLOC[9] or

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(2) The freeze-dried animal (*P. spiculifer*) (15 g) was extracted with $CHCl_3$-MeOH (9:1), to give a brown oil (1.5 g), which was separated by chromatography (3×) on an NS-gel column (Nippon Seimitsu Kagaku 10503) eluted with MeOH-H_2O, affording **1** (30 mg), $[\alpha]_D$ −2.5° (*c* 0.7, $CHCl_3$).

(3) The NMR spectra were measured also in pyridine-d_5 by using 2–65 mg of **2**. The shifts ($CDCl_3$) described herein are those obtained for a 60 mM solution of **2**.

(4) Compound **2** exists in a mixture (3:1) of rotational isomers (at the amide linkage of C-38). This was confirmed by preparing **9**, which indicated that it also exists in a 3:1 mixture of isomers. The NMR properties of **9** parallel those of **2** with respect to the spermidine moiety.

(5) Many attempts to isolate the left half fragment were made in the reactions described herein. However, no trace of such a compound was obtained.

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(8) It is well-known that a solution of a strongly basic organic compound absorbs carbon dioxide from air, and the compound exists as a carbonate. (See, e.g.: Stecher, P. G., Ed. *The Merck Index*, 8th ed.; Merck & Co., Inc.: Rahway, NJ, 1968; p 510.)

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