equilibrium $K^{II}_{O_2}$. The correlation lines have slopes that are entirely different from that previously observed in toluene. This is to be related to the fact that in the first case we are dealing with the replacement of a PhCN molecule by dioxygen as discussed before rather than with an addition of dioxygen on a five-coordinated iron(II) complex as is the case in toluene.

Experimental Section

The instrumentation and procedures for cyclic voltammetry and thin-layer spectroelectrochemistry were the same as already described. The oxygen partial pressure was adjusted to the desired value by means of a gas distributor containing ball-flow meters, one for oxygen and the other for argon.

The synthesis and characterization of the porphyrins investigated in this work have been described previously with the exception of the e-(C11Im)(C12)-CT compound: e-(C12)$_2$-CT,[11c] a-(C12)$_2$-CT,[36b] e-(diC3py)(C12)-CT,[36a] a-(diC3py)(C12)-CT,[36b] a-(diC4py)(C12)-CT,[36b] a-(C11Im)(C12)CT.[36b] The e-(C11Im)(C12)-CT porphyrin was prepared along the lines of the same procedure as the e-(diC3py)(C12)-CT compound.[36a] Its characteristics are as follows. Anal. Calcd for C$_{70}$H$_{73}$N$_6$O$_8$: C, 79.14; H, 6.93; N, 7.91. Found: C, 78.94; H, 7.20; N,

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8.00. ^{1}H NMR (ppm): 8.78 (d, 8 × H$_{pyr}$); 8.08 (d, 4 × H$_6$ Ph); 7.8–7.3 (m, 12 × H Ph); 6.32, 5.91, 4.95 (3 × H Im); 3.9 (b, 8 × OCH$_2$); 2.81 (b, CH); 1.32 to −1.72 (32 × methylene); −2.54 (s, 2 × NH).

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Neutral Spin-Delocalized Mixed-Valence Mn^{I}Mn^{II} Dimers Bridged by Alkoxide, Imidazolate, or Malonodinitrile Anions

Renate Gross and Wolfgang Kaim*†

The complexes [(η^5-C$_5$H$_4$CH$_3$)(CO)$_2$Mn]$_2$(μ-L), L = *t*-BuO$^-$, AdO$^-$, imidazolate, *t*-BuC(CN)$_2^-$, HC(CN)$_2^-$, were produced from Mn^I precursor complexes by oxidation with O$_2$ (air) or PbO$_2$ in aprotic media and were characterized by EPR as spin-delocalized Mn^{I}Mn^{II} systems. Stability and extent of formation of these dimers depend on the σ-donor strength of the anionic bridging ligands and correlate with their basicity, the alkoxides being the strongest and the malonodinitrile anions the weakest bases. A comparison of the mixed-valence dimers with corresponding mononuclear low-spin Mn^{II} complexes (η^5-C$_5$H$_4$CH$_3$)(CO)$_2$(L)Mn reveals similar g values and halving of the ^{55}Mn coupling constants, except for the alkoxide-bridged dimers, which exhibit some metal–metal interaction. Intervalence (IT) transitions of the imidazolate and malonodinitrile anion bridged Mn^{I}Mn^{II} dimers in toluene solution are remarkably similar to the IT features measured for corresponding Ru^{II}Ru^{III} ammine complexes in aqueous solutions. The significance of the spectroscopic results with regard to photosynthetic O$_2$-evolving manganese centers is briefly discussed.

Introduction

The vast majority of mixed-valence complexes with metal centers in d^5/d^6 configurations involve the group 8 metals, especially ruthenium,[1] in their +II/+III oxidation states.[2] The paramount position of ruthenium ammine fragments in this chemistry is due to their kinetic stability in *both* oxidation states[1,3] and to the conveniently accessible redox potential range in which these complexes are available.[1] Considering these criteria, we have set out to search for organometallic systems with similar properties but which contain metals in lower oxidation states.[4] The kinetic stability and redox potential requirements for a ruthenium ammine related chemistry seem to be met by the (η^5-C$_5$R$_5$)(CO)$_2$Mn(L) complexes (R = H, Me); ruthenium(II,III) systems are connected to manganese(I,II) by a diagonal relationship in the periodic table. Complexes with the substitutionally very inert[5] fragment (η^5-C$_5$R$_5$)(CO)$_2$Mn undergo reversible one-electron oxidation over a potential range of more than 2 V;[4b,6] some stable oxidized species were characterized recently as low-spin manganese(II) complexes.[4b]

Mixed-valence complexes of manganese are currently attracting considerable attention[7] because such species were observed by EPR

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during irradiation of the O_2-producing enzymatic centers in photosynthetic membranes of chloroplasts.[8] Several $Mn^{II}Mn^{III}$ and $Mn^{III}Mn^{IV}$ model compounds have been reported[7] and used to assign tentatively the oxidation state of the S_2 intermediate of the oxygen-evolving complex. However, it has been pointed out that great care has to be exercised in relating the magnitudes of the ^{55}Mn ($I = {}^5/_2$) hyperfine splittings with the metal oxidation states.[7d]

Mixed-valence Mn^IMn^{II} systems were reported as electrogenerated cations, viz., $[(\eta^5\text{-}C_5H_5)(NO)Mn(\mu\text{-}SR)]_2^{+}$[9] and $\{(\mu\text{-}CH_2)[(\eta^5\text{-}C_5H_5)(CO)_2Mn]_2\}^+$;[10] however, it was only recently that a neutral Mn^IMn^{II} intermediate, $(CO)_3Mn(\mu\text{-}SPh)_3Mn(CO)_3$, had been characterized at -40 °C by McDonald.[7e] Neutral mixed-valence complexes are of special interest because the absence of change trapping in nonpolar solvents should lead to a high degree of delocalization (class IIIA[11a]), even at considerable metal–metal distances.[1]

We can now present EPR and electron spectroscopic evidence for neutral Mn^IMn^{II} complexes that, though highly labile, are formed at ambient temperatures during oxidative processes involving $Cp'(CO)_2Mn$ fragments ($Cp' = \eta^5\text{-}C_5H_4CH_3$) and bridging alkoxide (1), imidazolate (2), and malonodinitrile anions (3).
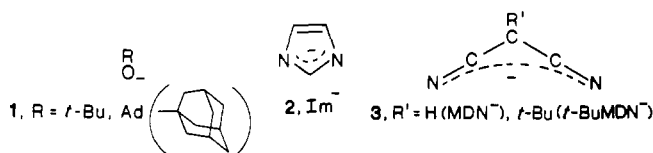
Alkoxide-type ions[12] and imidazolate (Im)[13] are rather common bridging ligands that are also ubiquitous in biological environments (e.g. deprotonated histidine and tyrosine), and a number of recent studies have dealt with the ability of these anionic ligands to bring about electronic and magnetic interactions between two coordinated metal fragments.[13,14] The third kind of anionic ligands used,

Scheme I

Cp'(CO)₂Mn(THF)
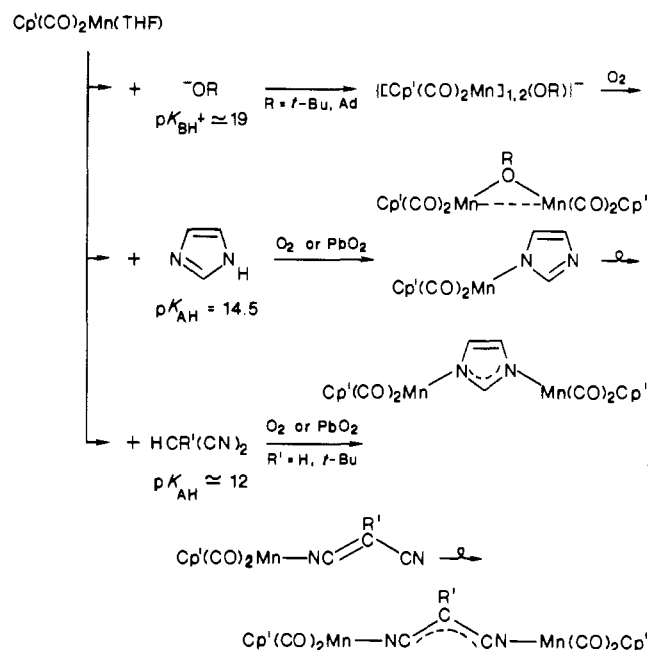
the deprotonated malonodinitriles (3), were successfully applied in $Ru^{II}Ru^{III}$ mixed-valence chemistry by Krentzien and Taube and were shown to effect strong interaction between the bridged metal centers.[15]

The anions 1–3 can be classified in two ways with regard to their function as bridges between metal centers of different valency. First, the metal–metal distance d_{M-M} is an important factor in determining the extent of interaction in mixed-valence complexes;[1] a rough estimate of d_{M-M} gives 330 pm (1), 620 pm (2), and 800 pm (3) if $d_{M-\text{ligand}} \approx 200$ pm.[16] A second essential ligand property, especially for the coordination of weak electrophiles, is the σ-donor strength, as measured by pK_{BH^+}, the pK_a value of the acid conjugate to the base B;[17] the reported values are $pK_{BH^+} = 19.2$ (**1**, R = t-Bu),[18] 14.5 (**2**),[19] 11.2 (**3**, R' = H),[20] and 13.1 (**3**, R' = t-Bu).[21]

Experimental Section

Instrumentation. EPR: Varian E9, X-band (9.5 GHz), 0.31 T magnetic field strength. Calibration and g value determination were accomplished by use of the double-cavity technique with the perylene radical anion in dimethoxyethane as reference.[22] EPR data are corrected for second-order effects;[11b] low-temperature spectra (-150 °C) in toluene glass could not be interpreted[4d] because of extensive overlapping of lines. Computer simulation of isotropic spectra was accomplished with use of available programs.[23a] IR: JASCO A-100; solution spectra in THF. UV/vis/near-IR: Pye-Unicam SP 1800 and Perkin-Elmer Lambda 9.

Preparations. Mixed-valence alkoxide complexes were obtained by the following procedure: KOR (R = t-Bu or adamantyl, Ad) and the photogenerated solvate $Cp'(CO)_2(THF)Mn$[23b] were reacted in equimolar ratio in THF solution to slowly yield a fine orange-red and highly airsensitive suspension. Infrared spectroscopy showed two pairs of CO

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Table I. EPR and IT Absorption Data of $Cp'(CO)_2(L)Mn$ and $[Cp'(CO)_2Mn]_2(\mu\text{-}L)$ Complexes[a,b]

	mononuclear complex		binuclear complex		
L	a_{Mn}	g	a_{Mn}	g	ν_{IT} $(\Delta\nu_{1/2})$
^-O-t-Bu	6.4	2.027	2.65	2.059	9640 (3500)
^-OAd	6.4	2.027	2.70	2.058	9800 (3500)
$^-Im^c$	6.1	2.035	3.05	2.035	7000 (>6000)[c]
					7270 ($\sim$10 000)[d]
$^-CH(CN)_2$	5.9	2.037	3.1	2.039	8180 (2500)[c]
					7810[d]
^-C-t-Bu(CN)_2$	5.25	2.021	2.70	2.017	8940 ($\sim$2500)[c,e]
					8550 (2120)[d]

[a] Coupling constants a_{55Mn} in mT (=10 G); absorption energies ν_{IT} and band half-widths $\Delta\nu_{1/2}$ in cm^{-1}. [b] In THF solution, except where noted. [c] In toluene solution. [d] Data for corresponding $Ru^{II}Ru^{III}$ ammine complexes in aqueous solution.[2d,15]

stretching bands, indicative of one species with ν_{CO} = 1855 and 1770 cm^{-1} (slowly decreasing, mononuclear anionic complex) and another species with ν_{CO} = 1890 and 1805 cm^{-1} (binuclear anionic complex). The values given are those of the t-BuO complexes; with AdO systems the frequencies ν_{CO} are still lower by about 10 cm^{-1}. Attempts to further characterize these compounds were unsuccessful due to their poor solubility and highly pyrophoric nature in the solid state. Careful oxidation of the THF suspension with PbO_2 or by admittance of air results in the formation of mixed-valence species as evident from EPR and electronic spectroscopy; IR monitoring shows a decrease of the bands noted above and the appearance of new CO stretching bands at 1895, 1845, and 1825 cm^{-1}. The region above 1900 cm^{-1} is dominated by the bands from $Cp'(CO)_3Mn$ that always accompany the formation of the mixed-valence complexes described here.

Imidazolate complexes were obtained from $Cp'(CO)_2(ImH)Mn^{4b}$ by oxidative deprotonation with O_2 or PbO_2 in THF or toluene solution (cf. Scheme I), with metal fragment acquisition by the first formed mononuclear manganese(II) complex $Cp'(CO)_2(Im)Mn$ producing appreciable amounts of the imidazolate-bridged mixed-valence dimer. Whereas the CO stretching frequencies ν_{CO} = 1910 and 1830 cm^{-1} (in toluene) show little change on oxidative deprotonation, the formation of the mixed-valence dimer is accompanied by a very broad IT absorption band with a maximum around 1400 nm.

Paramagnetic malonodinitrile complexes were formed by oxidative deprotonation with O_2 or PbO_2 of yellow diamagnetic precursor complexes, which were formed from $Cp'(CO)_2(THF)Mn$ and malonodinitrile (MDNH) or *tert*-butylmalonodinitrile (t-Bu-MDNH)[24] and which were characterized by IR: $Cp'(CO)_2(MDNH)Mn$ ν_{CN} = 2260 cm^{-1}, ν_{CO} = 1925, 1870 cm^{-1}; $Cp'(CO)_2(t$-BuMDNH)Mn$ ν_{CN} = 2240 cm^{-1}, ν_{CO} = 1930, 1870 cm^{-1}. EPR and electronic spectroscopy (Figures 3 and 4) show that oxidative deprotonation yields primarily mononuclear manganese(II) complexes with intense ligand-to-metal charge-transfer (LMCT) bands[4b,d] at 676 nm (MDN complex) and 835 nm (t-BuMDN complex); stretching frequencies were found in the IR spectra at ν_{CN} = 2190 cm^{-1} and ν_{CO} = 1945, 1890 cm^{-1} for the MDN system and at ν_{CN} = 2165 cm^{-1} and ν_{CO} = 1945, 1885 cm^{-1} for the t-BuMDN system. The additional formation of mixed-valence dimers is evident from both EPR and electronic spectroscopy (cf. Figures 3 and 4).

Results

Organometallic mixed-valence $Mn^I Mn^{II}$ dimers were produced via the routes summarized in Scheme I. The alkoxide-bridged species were obtained by careful oxidation of the substitution products from photogenerated $Cp'(CO)_2(THF)Mn$ with potassium salts of very basic[17,18] alcohols; the vibrational data (cf. Experimental Section) suggest that these poorly soluble and highly pyrophoric precursors can be formulated as anionic mono- and binuclear complexes $\{[Cp'(CO)_2Mn]_{1,2}(OR)\}^-$ since related compounds such as $[(\eta^5\text{-}C_5Me_5)(CO)_2(t\text{-}BuS)Mn]^-$ and $[(\eta^5\text{-}C_5H_5)(CO)_2(PhSe)Mn]^-$ display similarly low (<1900 cm^{-1}) CO stretching frequencies.[25a] Oxidation is accompanied by the

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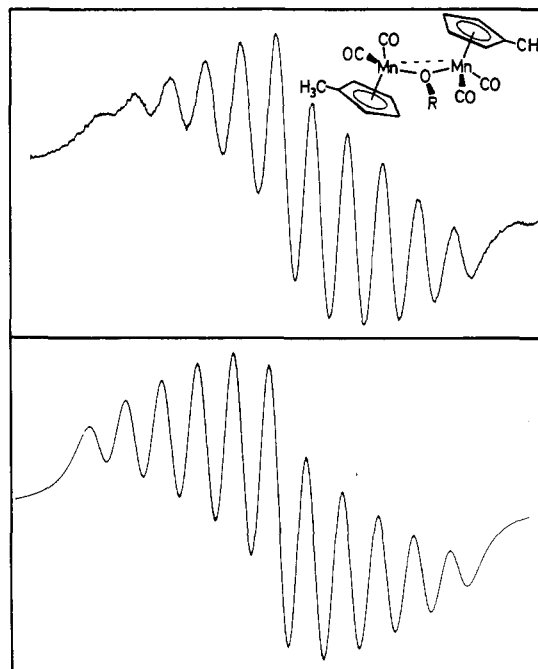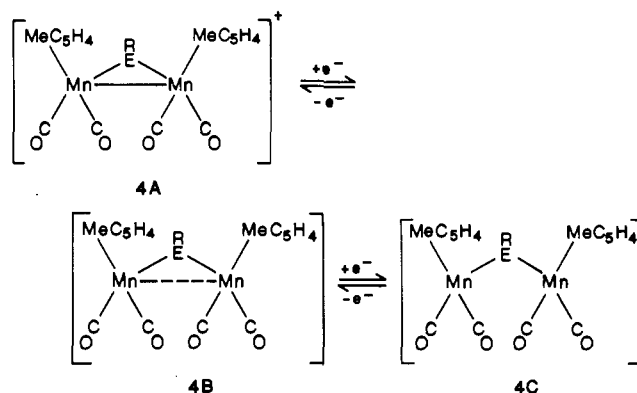

Figure 1. EPR spectrum of $[Cp'(CO)_2Mn]_2(\mu\text{-}OAd)$ in THF at room temperature (top) with computer simulation (bottom) (line width for simulation 2.0 mT). Note the line broadening at low field.

disappearance of the low-energy CO stretching bands and by the formation of new IR bands at higher energies; the thus formed neutral, hydrocarbon-soluble, mixed-valence species are recognized by characteristic EPR spectra (Figure 1) and by the presence of intervalence (IT) electronic transitions in the near-infrared region of the spectrum (Table I).

The EPR signal consists of 11 lines in the intensity ratio 1:2:3:4:5:6:5:4:3:2:1 and can thus be simulated by assuming full equivalency of the two ^{55}Mn nuclei ($I = ^5/_2$) with respect to the coupling with one unpaired electron. Furthermore, the isotropic coupling constant a_{55Mn} is only about half as large as in comparable mononuclear Mn^{II} complexes[4b,d] and closer to values reported for other $Mn^I Mn^{II}$ species;[7e,9,10] mononuclear compounds $Cp'(CO)_2(RO)Mn$ are observed during dissociative processes of the mixed-valence systems or after oxidation of the anions $[Cp'(CO)_2(RO)Mn]^-$ formed with less basic[17] alkoxides or aryloxides. Although the alkoxide-bridged mixed-valence complexes $[Cp'(CO)_2Mn]_2(\mu\text{-}OR)$, R = t-Bu, Ad, can be obtained in high concentrations and can be kept for several days at ambient temperatures in solution, we were unable to isolate these compounds because of the notorious lability of $Cp'(CO)_2(L)Mn$ complexes;[26] one final decomposition product is $Cp'(CO)_3Mn$, accompanied by brown precipitate. The use of $(\eta^5\text{-}C_5Me_5)(CO)_2(THF)Mn$ starting material did not lead to any detectable binuclear paramagnetic complexes, presumably because of steric congestion in the arrangement **4B**.

(26) Gross, R.; Kaim, W. *J. Organomet. Chem.* **1985**, *292*, C21.
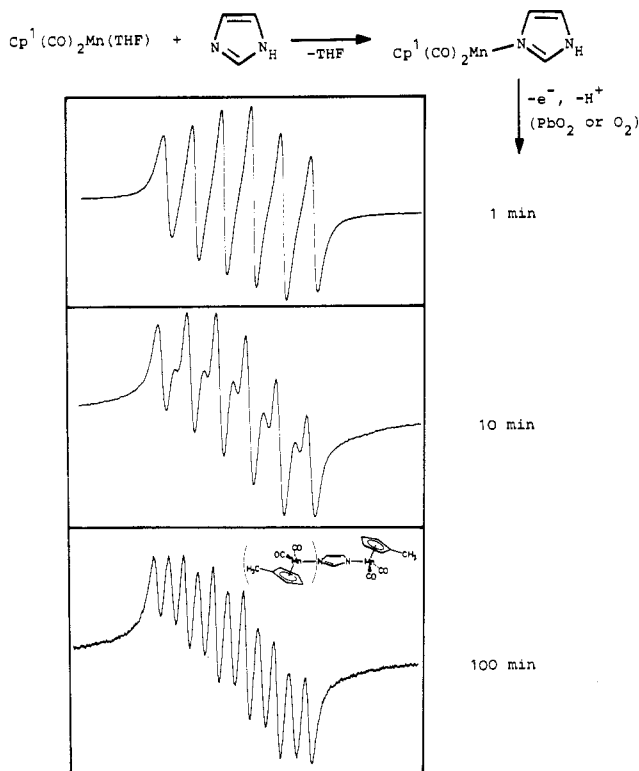
Figure 2. Formation of the mixed-valence dimer [Cp'(CO)$_2$Mn]$_2$(μ-Im) from the corresponding Mn^{II} monomer as evident from EPR spectra at room temperature in toluene solution.

Paramagnetic imidazolate and malonodinitrile anion complexes were obtained as mixtures of mononuclear Mn^{II} complexes and binuclear Mn^{I}Mn^{II} compounds via oxidative deprotonation of neutral mononuclear Mn^I precursors by aerial oxygen or lead dioxide (Scheme I). Neither the coordination of the second organometallic fragment nor the concomitant formation of Cp'(CO)$_3$Mn or the maximal ratio of Mn^{I}Mn^{II} to Mn^{II} product could be significantly influenced e.g. by addition of excess metal fragment. For determination of that maximal ratio, one has to consider the different sums of relative EPR intensities for both species; while this sum is only 6 for the 6 equivalent components of the mononuclear complex, it amounts to a total of 36 for the 11 components of a binuclear arrangement (cf. preceding paragraph). Accordingly, an equimolar mixture would exhibit the 1:2:3:4:5:6:5:4:3:2:1 intensity ratio for the binuclear system in relation to a 6:6:6:6:6:6 intensity pattern of the mononuclear species.

For the imidazolate system (Figure 2), the symmetrical 11-line pattern arises because g(dimer) = g(monomer) and because $2a_{Mn}$(dimer) = a_{Mn}(monomer); however, the observed intensity ratios indicate that considerable amounts of Mn^{II} complex remain. The bottom spectrum in Figure 2 illustrates the maximum ratio obtained between Mn^{I}Mn^{II} and Mn^{II} complexes, showing overlap of every other line of the Mn^{I}Mn^{II} 11-line pattern with a Mn^{II} sextet; it can be fairly well reproduced by assuming a molar ratio of $\sim$3:1 between the dimer and the monomer as shown by the "stick-diagram" calculation (1) or by computer simulation.

intensity ratio

1:2:3:4:5:6:5:4:3:2:1	Σ = 36	Mn^{I}Mn^{II} dimer
2 : 2 : 2 : 2 : 2 : 2	Σ = 12	Mn^{II} monomer
3:2:5:4:7:6:7:4:5:2:3		3:1 mixture (Figure 2C)

$$(1)$$

A small line width of ca. 0.7 mT and a slight difference in g values allow a clear distinction between the six-line spectrum of Cp'(CO)$_2$(t-BuMDN)Mn and the 11-line pattern of spin-delocalized [Cp'(CO)$_2$Mn]$_2$(μ-t-BuMDN) (Figure 3). This time, the obtainable ratio of dimer to monomer can be calculated from the intensity ratio of 1:7 between the two separate outermost high-field lines of both species; as with computer simulations, one
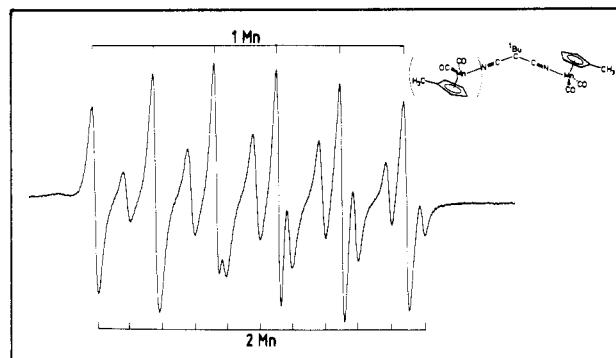

Figure 3. EPR spectrum of a 55:45 mixture of Cp'(CO)$_2$(t-BuMDN)Mn (6-line spectrum) and of [Cp'(CO)$_2$Mn]$_2$(μ-t-BuMDN) (11-line spectrum) at room temperature in THF.
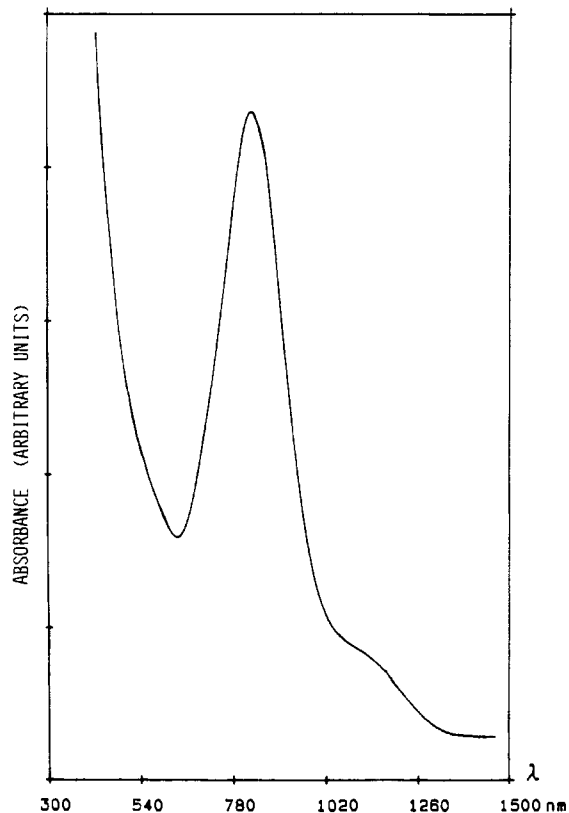
Figure 4. Electronic absorption spectrum of the mixture [Cp'-(CO)$_2$Mn]$_{1,2}$(t-BuMDN) in toluene (cf. Figure 3), showing the LMCT transition of the monomer at 835 nm and the IT band of the mixed-valence dimer as a shoulder at 1120 nm.

arrives at a 1:1.2 molar ratio in favor of the mononuclear complex. In no instance could we detect superhyperfine coupling from ^{1}H or ^{14}N nuclei, in agreement with calculated spin densities.[4b,d]

Formation of the mixed-valence species as evident from EPR spectra is accompanied by new absorption bands in the near-infrared region that are not present in solutions of the mononuclear complexes[4b,d] or of the final decomposition products; hence, they are assigned to the expected intervalence transitions (IT). The IT bands of the Mn^{I}Mn^{II} complexes with the ligands **2** and **3** are remarkably similar to the spectral features displayed by corresponding Ru^{II}Ru^{III} ammine compounds.[2d,15] The imidazolate system exhibits a very broad band with an absorption maximum at 1400 nm while the malonodinitrile anion bridged species have much more narrow IT bands, partly obscured by intense LMCT (d(Mn^{II}) $\leftarrow$ ($^-$CR(CN)$_2$)) bands[4b,d] in the visible region of the spectrum (Figure 4).

Discussion

The determining factor for the formation of mixed-valence dimers [Cp'(CO)$_2$Mn]$_2$(μ-L) is the σ-donor strength of the anionic

bridging ligands μ-L. Whereas the strong bases AdO$^-$ and t-BuO$^-$ (pK_{BH^+} = 19.2)[18] can form mixed-valence dimers as the only paramagnetic products, the less basic imidazolate (pK_{BH^+} = 14.5)[19] and malonodinitrile anions (pK_{BH^+} = 11–13)[20,21] yield only mixtures of binuclear Mn^{I}Mn^{II} and the remaining mononuclear Mn^{II} compounds, the maximal ratios being 3:1 for the imidazolate system (Figure 2) and 1:1.2 for the *tert*-butylmalonodinitrile complexes (Figure 3). Mixed-valence dimer formation was not observed when benzimidazolate (pK_{BH^+} = 12),[17] phenolates (pK_{BH^+} = 10), and most other alkoxides were used;[17] apparently, additional coordination of a neutral Mn^I fragment to a neutral Mn^{II} system Cp′(CO)$_2$(L)Mn requires considerable ligand basicity despite the gain in delocalization energy. The notorious kinetic lability of complexes with Cp′(CO)$_2$Mn fragments[4c,26] has made it possible to obtain the Mn^{I}Mn^{II} dimers via intermolecular exchange processes according to Scheme I; however, this propensity of the organometallic fragment is also responsible for the failure to isolate the dimeric species because of facile degradation processes (steady-state situation).

Nevertheless, the EPR results clearly allow the characterization of Mn^{I}Mn^{II} dimers as neutral spin-delocalized species even in those cases where the metal centers are separated by ca. 800 pm (ligands 3). It is assumed that the organometallic Mn fragments are always N-coordinated in the complexes of malonodinitrile anions since the *tert*-butyl substituent would not permit C-coordination and since the high affinity of Cp′(CO)$_2$Mn fragments for N(cyano) coordination has been demonstrated recently by us;[26] the presence of negative charge density at these N centers is illustrated by the resonance structures **5A** and **5C**.
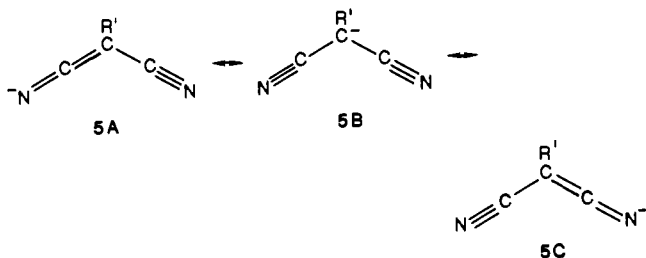
The observed delocalization on the EPR time scale of approximately 10^{-7} s supports the notion that the absence of charge trapping in aprotic, nonpolar solvents may permit such delocalization even if only small electronic interaction energies are involved.[1] Low-spin manganese(II) complexes with strong σ-donor ligands are particularly suitable for EPR studies because a relatively large gap between the doublet ground state and higher excited states results in slow spin-lattice relaxation and good conditions for observation of EPR signals at room temperature; further advantages of the isotope ^{55}Mn (100% natural abundance) are the characteristic nuclear spin of $^5/_2$ and the high magnetic moment.

The ^{55}Mn coupling constants of the mononuclear complexes show a decrease in the order alkoxides > imdazolate > malonodinitrile anion > *tert*-butylmalonodinitrile anion complexes (Table I), indicating slowly increasing delocalization of spin into the ligand π system;[4b,d] in agreement with this interpretation, the LMCT transition (2) is shifted considerably from ν_{LMCT} > 25 000 cm^{-1} for the alkoxide and imidazolate complexes to 14 800 and 11 980 cm^{-1} for the MDN and *t*-BuMDN species, respectively.

$$[Cp′(CO)_2Mn^{II}]^+(L)^- \xrightarrow[\text{LMCT}]{h\nu} {}^*[Cp′(CO)_2Mn^I](L^•) \quad (2)$$
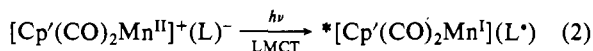
Spin-delocalized mixed-valence dimers should exhibit half the metal isotope coupling constant of corresponding mononuclear systems, thereby leaving the total spectral width unchanged.[8g,14a,27] This rule is fairly well obeyed by the imidazolate and malonodinitrile anion complexes; however, a conspicuous discrepancy must be noted for the alkoxide species, where a^{55}_{Mn} = 2.7 mT of the

dimers is significantly smaller than half of the coupling constant $a^{55}_{Mn}/2$ = 3.2 mT of the mononuclear complexes (Table I). In addition to that difference, the alkoxide-bridged dimers are distinguished by unusually high[4b,d] isotropic g values whereas the other pairs of mono- and binuclear $S = {}^1/_2$ complexes have very similar g values as would be anticipated.[28]

The special spectroscopic behavior of the alkoxide-bridged dimers must be traced back to the steric situation **4**: Sterically demanding alkoxides[12b] such as AdO$^-$ or t-BuO$^-$ may induce not only bond distortions but also weak metal–metal interactions within an arrangement (**4B**) so that the estimated[16] metal–metal distances of 280–350 pm for RO-bridged dimers[12,14] overlap with the bonding range of Mn–Mn-bonded organometallic complexes;[29] even a small extent of metal–metal interaction should then lead to a reduction of the metal isotope coupling.[30]

This interpretation is supported by X–ray crystallographic results for the complexes **4A** and **4C** with ER = SEt[25c] and TePh,[25b] which clearly indicate the presence of a Mn–Mn single bond in the cations **4A** and no bonding interaction in the anions **4C**; the neutral species should then adopt the intermediate position **4B**. There is, of course, less steric repulsion in the complexes **4** with the higher homologues E of oxgyen and in the related neutral dimers [Cp(CO)$_2$Mn]$_2$(μ-E′R) with group 15 elements E′ = P, As, Sb,[31] which are isoelectronic with the cationic group 16 complexes **4A**. The fact that the neutral group 15 element species[31] and the cationic thiolate complexes **4A**[25c] have one valence electron less than the neutral alkoxide-bridged dimers is evident from their rather high (>1900 cm^{-1}) CO stretching frequencies.[25c,31]

The dissociative lability of the complexes with first-row-element donor atoms O and N precluded satisfactory electrochemical measurements; the stability constants $K = 10^{E_1-E_2/59 \text{ mV}}$, which can be calculated for thiolate-bridged Mn^{I}Mn^{II} systems, range from 10^5 for (CO)$_3$Mn(μ-SPh)$_3$Mn(CO)$_3$[7e] to 10$^{6.5}$ for **4** (ER = SPh)[25c] to 10^{12} for [(η^5-C$_5$H$_5$)(NO)Mn(η-SR)]$_2$$^+$.[9]

A characteristic spectroscopic feature of class II and IIIA mixed-valence complexes is the IT transition which often occurs at rather low energies;[1] such a transition was also observed after irradiation of the photosynthetic O$_2$-evolving complex.[8g] The result that the IT absorption of the alkoxide-bridged species occurs at lower energies than that of the triply thiophenolato bridged compound (CO)$_3$Mn(μ-SPh)$_3$Mn(CO)$_3$[7e] may again by attributed to the closer metal–metal distance in the former systems; μ-hydroxy-bridged Ru^{II}Ru^{III} dimers were reported to have ν_{IT} ≈ 16 000 cm^{-1}.[2e] However, the most remarkable result from electronic spectroscopy is that the position and the width of the IT bands measured in toluene for Mn^{I}Mn^{II} complexes with the ligands **2** and **3** are virtually identical with the data obtained for corresponding Ru^{II}Ru^{III} ammine species in aqueous solution (Table I).[2d,15] We cannot, as yet, offer an explanation for this intriguing correspondence; however, this result does not only emphasize once more[32,33] the crucial role of the bridging ligand in determining the spectroscopic properties of mixed-valence compounds, it also constitutes excellent support for the validity and usefulness of the concept of diagonal relationship between Ru and Mn compounds

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that was mentioned in the Introduction and has been exploited by us[4] and others.[34]

Summary

This study adds further examples to the rapidly growing number of organometallic mixed-valence complexes.[2b,35] The combination of "hard" ligands which are commonly used with more "inorganic" metal fragments[12–15] and the weakly electrophilic organometallic fragments $[Cp(CO)_2Mn]^{0/+}$ [4,26] results in an unsatisfactory situation as concerns coordinative stability; we shall try to overcome this problem by using either more electrophilic metal fragments or even more basic bridging ligands. Nevertheless, it has been possible with some ligand systems to change from $Ru^{II}Ru^{III}$ ammine to organometallic Mn^IMn^{II} systems without affecting the position and shape of the IT transition but with having the valuable opportunity for convenient EPR studies of the spin distribution.[33b]

One reason to use small biochemically relevant O and N ligands in this study despite the preparative difficulties was to answer the question whether further spectroscopic knowledge can be gathered with regard to mixed-valence manganese species such as the ones observed during irradiation of photosynthetic O_2-evolving complexes in chloroplast membranes.[8] There are mixed-valence Mn^IMn^{II} complexes with one,[25c] two,[9] or three[7e] thiolate bridges, and other approaches have included the use of sulfur ligands to stabilize higher-valent manganese as mixed-valence species[7f] or in the presence of μ-imidazolate[7f,13g,h] or μ-OR ligands;[14e] however,

EXAFS studies of enzymatic material have strongly suggested that the first coordination shell around the Mn centers contains only light donor atoms such as O or N and that the manganese atoms are in close contact, possibly bridged by O.[36] Although the photosynthetic processes do not involve manganese in the +I oxidation state or in organometallic form[8] and model systems involving higher valent Mn and oxo ligands[7c] are certainly more realistic (oxygen is *used* and not *produced* in our system), the application of the alkoxide/oxide analogy[37] may stimulate further investigation and speculation on the nature of the photosynthetically active manganese centers.[8i]

A final comment should be made on the relation between ^{55}Mn coupling constants and oxidation-state assignments. The isotropic values a^{55}_{Mn} of organometallic low-spin Mn^{II} and Mn^IMn^{II} (doubled value) range from 5.4 mT (alkoxide-bridged dimers) to 6.1 mT (imidazolate-bridged dimer and monomer) and 6.4 mT (alkoxide-coordinated monomers) to 6.6 and 7.2 mT for thiolate- and methylene-bridged dimers,[7e,9,10] thus illustrating again[7d] the difficulty of determining metal oxidation states[8g] from EPR hyperfine values only.

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Preparation and Structural Studies of Methylmercury Compounds Containing Amino-Deprotonated Adenine

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Reaction of CH_3HgOH with adenine (HAd) in water–ethanol mixtures yielded 2:1 and 3:1 compounds. Substitution of the imidazole proton and one of the amino protons in $[(CH_3Hg)_2(Ad-H)]\cdot EtOH$ was deduced from the IR spectra. Crystals of $[(CH_3Hg)_3(Ad-2H)]\cdot^1/_2H_2O$ are monoclinic, $C2/c$, with a = 20.809 (7) Å, b = 7.263 (1) Å, c = 18.788 (1) Å, β = 104.91 (4)°, and Z = 8. The structure was refined on 1104 nonzero Mo Kα reflections to R = 0.050. The imidazole proton and both of the amino protons have been substituted by linearly coordinated CH_3Hg^+ groups in this compound. Reaction of CH_3HgOH and CH_3HgX (X = NO_3^-, ClO_4^-) led to isolation of compounds of the type $[(CH_3Hg)_4(Ad-2H)]X$. Crystals of $[(CH_3Hg)_4(Ad-2H)]NO_3$ are monoclinic, $P2_1/c$, with a = 14.458 (5) Å, b = 7.478 (1) Å, c = 20.174 (5) Å, β = 126.34 (2)°, and Z = 4. The structure was refined on 1502 nonzero Cu Kα reflections to R = 0.053. This compound contains NO_3^- anions and $[(CH_3Hg)_4(Ad-2H)]^+$ cations, in which three CH_3Hg^+ groups occupy the same sites as in the above compound, whereas the fourth CH_3Hg^+ group is bound to N3. The infrared spectra of these compounds and of their C8-deuteriated derivatives were compared with those of CH_3HgAd, and diagnostic regions were identified to characterize each type of bonding. The ^1H and ^{13}C NMR results are discussed.

Introduction

As part of our continuing research on the binding of the CH_3Hg^+ cation with DNA bases, a series of adenine complexes (Chart I) have been structurally characterized in this laboratory.[1–6]

They invariably showed that metal complexation first occurred with N9 by substitution of the labile acidic H9 proton. Extra CH_3Hg^+ groups could be introduced into the ring without proton displacement. They were found to bind first to N7 and then to

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