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Investigations of Time-Dependent Delocalization and the Correlation of Carbonyl IR Shifts with $\Delta E_{1/2}$ Values for Hydrocarbon-Linked Class II and Class III Mixed-Valent Complexes

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Abstract: A series of fulvalenediyl-bridged dimanganese complexes has been studied by electrochemistry and by IR, optical, and ESR spectroscopic methods. The redox site is based on the Mn(I) moiety $(C_5H_4R)Mn(CO)_2PPh_3$ and variations thereof. Six dinuclear complexes are each oxidized in two one-electron steps with $E_{1/2}$ separations ($\Delta E_{1/2}$) of between 80 and 450 mV. Each of the monocations exhibits trapped valence by IR spectroscopy. Analysis of the carbonyl stretching frequencies of the mixed-valent systems allows calculation of a charge distribution parameter, $\Delta\rho$, that estimates the relative charges at the two redox sites and which correlates linearly with the $\Delta E_{1/2}$ values. This correlation extends to mixed-valent Cr(I)Cr(0) systems linked by a biphenyl bridge. The doubly linked system $[(Fulv)\{Mn(CO)_2\}_2(\mu\text{-dppm})]^-$, $\mathbf{1}^+$, displays trapped valence in its IR spectra, but delocalized valence in its ESR spectra, implying a time-dependent delocalization process.

Introduction

Continuing inquiries into the fashion in which metals interact through or across bridging ligands are driven by the need to understand metal−metal interactions in metalloproteins,[1] conducting metallopolymers,[2] and redox-triggered molecular switches,[3] to name just a few areas in which polymetallic redox systems find relevance.[4] Among organometallic complexes, the metal−(μ-ligand)−metal arrangement based on fulvalenediyl-type ligands has been most intensely studied owing to the full range of weak-to-strong metal/metal interactions possible in this molecular arrangement.[4,5] Among the factors identified as affecting the nature and magnitude of metal−metal interactions in *mixed-valent* complexes of this type are their physical state,[6] the identity of the solvent and counterion in the matrix,[7] the nature of any groups connecting the two cyclopentadienyl rings,[8,9] and the d-orbital electron count at the metal centers.[5a]

We communicated preliminary results[10] showing that one member of this set of complexes, namely the doubly bridged complex $(Fulv)[Mn(CO)_2]_2(\mu\text{-dppm})$, **1**, where Fulv = $[C_{10}H_8]^{2-}$ and dppm = bis(diphenylphosphino)methane,[11] when oxidized by a single electron, shares the characteristics of both a trapped-valent (Robin−Day Class II)[12] system and a fully delocalized (Class III) system and suggested that the time scale of the

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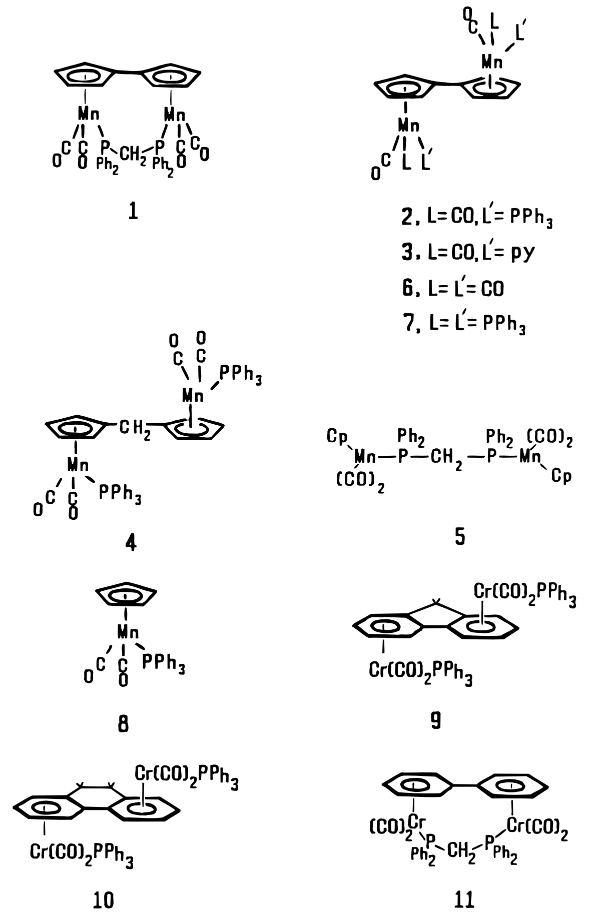
experimental observation may be the key to understanding the intramolecular electron-transfer behavior of $\mathbf{1}^+$. The arguments involved are reminiscent of those involving study of the Creutz−Taube ion $[\{(NH_3)_5Ru\}_2(\mu\text{-pyrazine})]^{5+}$,[13] now generally accepted as a delocalized system,[14] by a variety of physical methods.[15] There is sustained interest in dinuclear systems which are on the borderline of Class II and Class III behavior,[16−22] owing perhaps to their sensitivity to structural or environmental factors that might trigger intramolecular electron transfer, and the concomitant opportunities to incorporate those factors into molecular designs.[21]

Complex **1** has certain physical properties that improve prospects for a quantitative probe of its mixed-valent ion. Two of these, namely the $\Delta E_{1/2}$ values[23] involving oxidation of the two Mn(I) redox centers and the optical properties of the intervalence transfer (IT) band,[9a,24] are common to mixed-valent complexes in general. Additionally, however, hyperfine splittings from the two sets of Mn and P atoms afford information on *spin* trapping from ESR experiments, and the sensitive link of carbonyl stretching frequencies to metal oxidation states[25] ensures a probe of *charge* trapping from IR experiments. Given the short time scale of IR spectroscopy and its often definitive interpretations,[16,26] this physical method is arguably the most powerful for the diagnosis of trapped vs delocalized valence.[5a,8a,15b,16,27−31]

Chart 1



We now report details of electrochemical and spectroscopic studies of **1** and its oxidation products, $\mathbf{1}^+$ and $\mathbf{1}^{2+}$. Certain spectroscopic results are also included for the related complexes $\mathbf{2}^+$−$\mathbf{7}^+$, the electrochemistry of which has largely been previously described.[32] For reasons that will become apparent, we include newly obtained IR and near-IR spectra of the oxidation products of the dichromium complexes **9**−**11**. It is worth noting that complex **1** with its two *syn*-oriented d^6 metals is related directly to fulvalenediyl complexes in which the metals are confined to the same side of the hydrocarbon by a second bridging ligand,[33] among them bis[(fulvalenediyl)$M_2]^{n+}$ [M = Fe, $n = 0$ (**12**);[34] M = Co, $n = 2$ (**13**)[7a,35]] and **11**,[36] the latter included here even though the bridging hydrocarbon is a biphenyl group.

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The separation of $E_{1/2}$ potentials for successive one-electron processes has been routinely interpreted as being associated with the degree of metal−metal interactions in homodinuclear complexes,[2b,8a,23,37−45] larger $\Delta E_{1/2}$ values (or, equivalently, larger K_{comp} values)[46] arising from increased (largely electrostatic) M−M interactions.[47] The $\Delta E_{1/2}$ values of the *syn*-dimetal complexes mentioned above [450 mV for **1**,[10] 540 mV for **11**,[36] 590 mV for **12**,[34a] and 930 mV for (reductions of) **13**[17a]] are all higher than the value of ca. 350 mV typically viewed as the upper end for Class II systems.[39] Yet, from among them, the mixed-valent ion of **1** stands out as showing evidence of valence trapping. We therefore sought to learn more about $\mathbf{1}^+$ and about the relationship between "delocalization" and $\Delta E_{1/2}$ values by analysis of the shifts in ν_{CO} brought about by the successive one-electron oxidations of the dinuclear complexes shown which contain carbonyl groups. Employing the IR shifts to estimate the charge distribution between the two redox sites in eight mixed-valent systems, we find a linear correlation of a charge distribution parameter, $\Delta\rho$, with increasing $\Delta E_{1/2}$ values that is consistent with an electrostatic model for vibrationally trapped mixed-valent systems, including $\mathbf{1}^+$.

Experimental Section

All operations were conducted under an atmosphere of nitrogen using standard Schlenk or drybox conditions. Solvents were distilled from appropriate drying agents. Dichloromethane and 1,2-dichloroethane, when used for electrochemical or ESR experiments, were distilled from CaH_2 in vacuo and subjected to three cycles of freeze−pump−thaw to ensure the absence of oxygen. THF and 2-methyl-THF were similarly distilled from potassium. Ligands such as phosphines or pyridine were obtained from commercial sources and recrystallized or distilled before use. ESR spectra were obtained using a modified Varian E-4 spectrometer and NMR data were obtained at 250 mHz.

Compounds. Most of the complexes had been previously reported. Preparations followed the literature methods for **8**,[48] **1**, **2**, **4**, **5**,[49] **6**,[50] **9**, **10**,[51] and **11**.[52] Difficulty was encountered in obtaining **6** through the Karasch coupling of $CpMn(CO)_3$ when the recommended[50] diethyl ether was used as solvent. Substitution of THF in the procedure gave an 80% yield of pure (vacuum sublimed at 70 °C) **6**. Complexes **3** and **7** are apparently new. Both were prepared by photolysis of **6** in the presence of an excess of either pyridine (**3**) or PPh_3 (**7**). Neither complex was obtained in a pure state, judging from elemental analysis, but their identities were inferred from their electrochemical and IR properties. When 200 mg of **6** was UV-photolyzed for 35 min at 278 K in a mixture of 75 mL of toluene and 25 mL of pyridine, the originally yellow solution turned red and the IR bands of the starting material were replaced by a pair at lower energies. Removal of the solvent under vacuum gave a dark residue that was subjected to column chromatography on silica gel under nitrogen at 288 K. Hexanes and hexane/dichloromethane mixtures eluted several fractions of starting material or other unidentified species, and finally pure dichloromethane was used at 258 K to elute a red sample that gave an orange-red powder (78 mg, 31%) having electrochemical and IR data (Tables 1 and 2, respectively) consistent with the formulation (Fulv)$[Mn(CO)_2(py)]_2$, **3**. The complex **7** was prepared by similar photolysis of **6** (150 mg) with excess PPh_3 (5 g) in benzene (8 h, 280 K). Decrease of the IR bands of **6** and appearance of a broad band at 1821 cm^{-1} signaled the production of a substituted product. After stripping the solvent, the residue was eluted with hexanes and then 2:1 toluene/hexane, whereupon a dark red band was collected which appeared to be a mixture of the desired **7** and the less-fully substituted system (Fulv)$[Mn(CO)_2PPh_3]$-

Table 1. $E_{1/2}$ Potentials (Volt vs Ferrocene/Ferrocenium) in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$

compd	$E_{1/2}$ (1)[a]	$E_{1/2}$ (2)[b]	$\Delta E_{1/2}$[c] (mV)
(Fulv)$[Mn(CO)_2]_2(\mu$-dppm) (**1**)	−0.07	0.38	450
(Fulv)$[Mn(CO)_2PPh_3]_2$ (**2**)	0.19	0.40	210
(Fulv)$[Mn(CO)_2(py)]_2$ (**3**)	−0.20	0.06	260
(Dcm)[d]$[Mn(CO)_2PPh_3]_2$ (**4**)	0.19	0.27	80
$[CpMn(CO)_2]_2(\mu$-dppm) (**5**)	0.19	0.31	120
(Fulv)$[Mn(CO)_3]_2$ (**6**)	0.91	*e*	
(Fulv)$[Mn(CO)(PPh_3)_2]_2$ (**7**)	−0.64	−0.40	240
$CpMn(CO)_2(PPh_3)$ (**8**)	0.23		
(Fluor)$[Cr(CO)_2PPh_3]_2$ (**9**)	−0.21	0.06	270[f]
(Phen)$[Cr(CO)_2PPh_3]_2$ (**10**)	−0.28	−0.01	270[f]
(Biphenyl)$[Cr(CO)_2]_2(\mu$-dppm) (**11**)	−0.36	0.18	540[g]

[a] 0/1+ couple. [b] 1+/2+ couple. [c] $E_{1/2}(2) - E_{1/2}(1)$. [d] Dcm = dicyclopentadienyl methane; Fluor = fluorene; Phen = 9,10 dihydrophenanthrene. [e] Precipitation of oxidation product appeared to mask the second oxidation wave. [f] From ref 51. [g] From ref 36, potentials converted from SCE reference to ferrocene by subtraction of 0.46 V.

Table 2. IR Frequencies and Frequency Shifts (in cm^{-1}) for Compounds and Ions in CH_2Cl_2

compd	neutral	1+	2+	$\Delta\nu_{ox}$[a]	$\Delta\nu_{red}$[a]	$\Delta\rho$[a]
(Fulv)$[Mn(CO)_2]_2$-(μ-dppm) (**1**)	1861 1934	1888 1931 1952 2003	2025 2053 (2007)[b] (1990)[b]	50	18	0.29
(Fulv)$[Mn(CO)_2PPh_3]_2$ (**2**)	1861 1930 1959 2036	1878 1938	1972 2050	14	8	0.09
(Fulv)$[Mn(CO)_2(py)]_2$ (**3**)	1840 1907	1978 1919	1864 2055	28	12	0.16
(Dcm)$[Mn(CO)_2PPh_3]_2$ (**4**)	1860 1928 1959 2044	1866 1932	1967 2050	6	4	0.04
$[CpMn(CO)_2]_2(\mu$-dppm) (**5**)	1861 1928 1963 2041	1865 1935	1971 2047	6	7	0.05
(Fluor)$[Cr(CO)_2PPh_3]_2$ (**9**)	1822 1875 1895 1972	1853 1876	1894 1994	22	20	0.18
(Phen)$[Cr(CO)_2PPh_3]_2$ (**10**)	1824 1875 1894 1974	1850 1875	1902 1994	20	19	0.16
(Biphenyl)$[Cr(CO)_2]_2$-(μ-dppm) (**11**	1833 1895	1899 1963	1989 2015	52	68	0.50

[a] See eq 4. [b] Weak intensity band.

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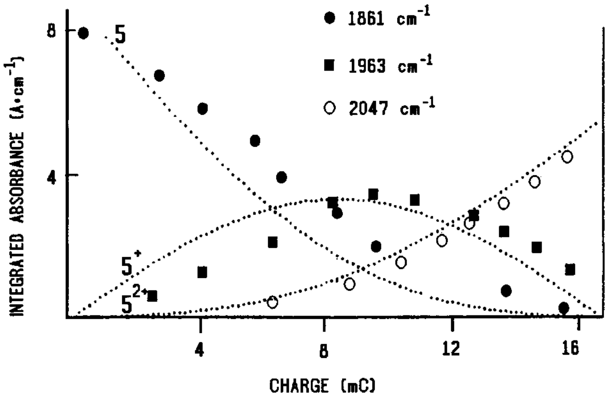

Figure 1. Plots of absorbance vs charge passed in an IRTTLE experiment in which 0.97 mM **5** is oxidized at 273 K in CH_2Cl_2/0.76 M $[NBu_4][PF_6]$ for selected IR bands arising from either neutral **5** (1861 cm^{-1}), $\mathbf{5}^+$ (1963 cm^{-1}), or $\mathbf{5}^{2+}$ (2047 cm^{-1}). The dotted lines are the calculated product distributions based on a value of $\Delta E_{1/2} = 121$ mV.

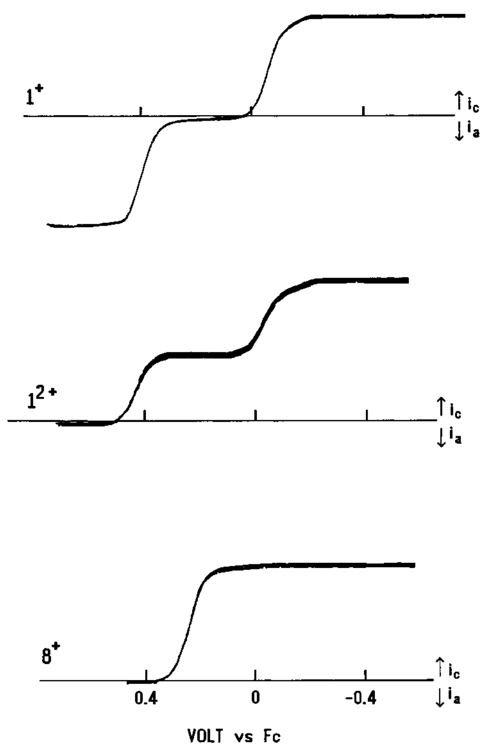

Figure 2. Voltammetric scans at the rotating Pt electrode for three isolated cationic complexes, all about 1 mM in CH_2Cl_2/0.1 M $[NBu_4]$-$[PF_6]$ at ambient temperatures, scan rate 5 mV/s. The sign of the currents (i.e., cathodic vs anodic) may be used to infer the relative concentrations of the oxidized and reduced species, respectively, for a particular redox pair.

$[Mn(CO)(PPh_3)_2]$.[53] When recrystallized from dicloromethane/pentane, this sample gave red crystals of a complex with a single CO band (1822 cm^{-1} in CH_2Cl_2) and very negative $E_{1/2}$ values (−0.64 and −0.40 V) that are consistent with the properties expected for the tetraphosphino-substituted **7** (^{1}H NMR in C_6D_6: equally intense singlets at 4.307 and 3.892 ppm). This sample was exceedingly air sensitive and satisfactory elemental analyses were not obtained. It decomposed in $CDCl_3$.

Oxidation products of 1: (i) $[(Fulv)\{Mn(CO)_2\}_2(\mu\text{-dppm})][BF_4]$, $[\mathbf{1}][BF_4]$: 66 mg of **1** and 16.5 mg of $Ag[BF_4]$ were combined in 80 mL of dichloromethane under low light conditions. The resulting deep purple solution was filtered and reduced in volume to 15 mL. Addition of 35 mL of pentane caused precipitation [30 mg (41%)] of a dark purple solid which gave satisfactory C,H analysis based on $C_{39}H_{30}BF_4Mn_2O_4P_2$. (ii) $[\mathbf{1}][BF_4]_2$: Oxidation of **1** with 2 equiv of $Ag[BF_4]$ in dichloromethane, filtration, and dilution with an equal volume of THF gave a thermally and photolytically sensitive dark purple precipitate that was vacuum-dried and stored at 253 K under nitrogen (73 mg, 68%). It was primarily characterized by its voltammetry, which showed two reduction waves at the expected $E_{1/2}$ values of 0.38 and −0.07 V (Table 1). No electrochemically active impurities were observed, and the steady-state currents of the voltammograms showed that >95% of the complex was present in its doubly oxidized form, i.e., as $\mathbf{1}^{2+}$ (see Figure 2).

Electrochemical and Spectroelectrochemical Procedures. Aspects of instrumentation and procedures for these methods have been previously described.[32] Potentials are reported vs the ferrocene/ferrocenium (Fc) couple and may be converted to the SCE by addition of 0.46 V for dichloromethane solutions. The supporting electrolyte was 0.1 M $[NBu_4][PF_6]$ unless otherwise noted. The IR spectroelectrochemical data were obtained with an IR-Transparent Thin-Layer Electrolysis (IRTTLE) cell operating in the transmission mode. The experimental procedure, which is similar to that described by Mann and co-workers,[54] has been detailed elsewhere.[32] A gold minigrid served as the working electrode in a cell having a volume of 80 μL (calibrated by coulometry with ferrocene/CH_3CN, 0.2 M $[NBu_4][PF_6]$). Since the working electrode potentials in a thin-layer arrangement in highly resistive media like CH_2Cl_2 electrolyte solutions may not be well defined, the progress of anodic oxidation processes was followed by coulometry as well as by spectroscopy. Bands were assigned to the mono- and dications of test compounds based on their intensity changes as a function of the number of equivalents of charge passed. A typical result is shown in Figure 1. Each IR spectrum was simulated using an in-house program employing Lorentzian line shapes for the absorption bands.

Electronic Spectra. The optical and near-IR spectra of the compounds and ions were recorded with a Cary 14 spectrometer for the spectral range 2500−750 nm and a Perkin-Elmer Lambda 6 spectrometer for wavelengths below 750 nm. The oxidized forms of the complexes in this study were photolabile when exposed to visible light between 500 and 700 nm, bleaching to insoluble brown decomposition products, so their solutions had to be photoprotected in the Cary 14 spectrometer, which has its monochromator after the sample chamber. Very effective filtering of the Cary source light was achieved by inserting seven blue and three red plastic transparency sheets between the source and the sample. Spectra recorded as a function of wavelength were digitized using a Summagraphics platen and then re-plotted vs energy.

Results and Discussion

Oxidative Electrochemical Properties. Potentials for the oxidation of the seven dinuclear Mn complexes and three dinuclear Cr complexes referred to in this paper are collected in Table 1. Each redox couple is a fully reversible process, in both the Nernstian and chemical senses, on the voltammetric time scale, and decomposition of the various ions was rarely encountered. Such instances will be specifically mentioned. Full electrochemical characterizations of all complexes except **1**, **3**, and **7** have been previously reported[32] and are consistent with the simple electron-transfer sequences of either eq 1 or 2:

$$\mathrm{Mn(I)Mn(I)} \overset{-e^-}{\rightleftharpoons} [\mathrm{Mn(I)Mn(II)}]^+ \overset{-e^-}{\rightleftharpoons} [\mathrm{Mn(II)Mn(II)}]^{2+} \tag{1}$$

$$\mathrm{Cr(0)Cr(0)} \overset{-e^-}{\rightleftharpoons} [\mathrm{Cr(0)Cr(I)}]^+ \overset{-e^-}{\rightleftharpoons} [\mathrm{Cr(I)Cr(I)}]^{2+} \tag{2}$$

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(53) IR spectroelectrochemistry was performed on this mixture. The component suspected as being the trisubsituted complex had IR absorptions at 1821, 1854, and 1920 cm^{-1}. When oxidized to the apparent monocation ($E_{1/2}$ ca. −0.4 V vs Fc), the 1821 cm^{-1} band shifted to 1914 cm^{-1}, whereas the other pair increased by only about 20 cm^{-1}.

(54) Bullock, J. P.; Boyd, D. C.; Mann, K. R. *Inorg. Chem.* **1987**, *26*, 3084. Original cell design in: Heineman, W. R.; Burnett, J. N.; Murray, R. W. *Anal. Chem.* **1968**, *40*, 1974.

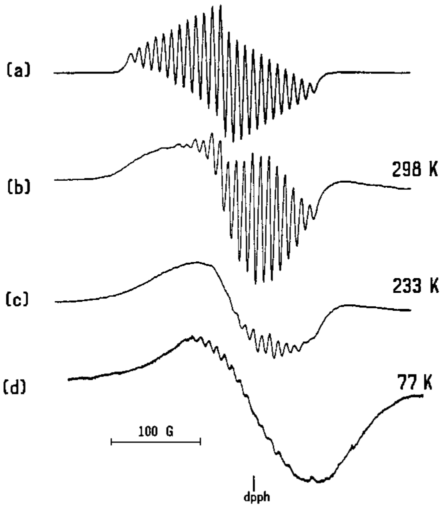

Figure 3. ESR spectra of $\mathbf{1}^+$: (a) simulated isotropic spectrum based on $g = 2.045$, two spins of 5/2, $\langle a \rangle = 17.1 \times 10^{-4}$ cm^{-1}, and two spins of $^1/_2$, $\langle a \rangle = 8.6 \times 10^{-4}$ cm^{-1}; (b) room temperature fluid spectrum of 0.5 mM **1**[BF$_4$] in CH$_2$Cl$_2$; (c) reduced temperature fluid spectrum of the same solution as in part b; and (d) anisotropic spectrum at 77 K of 0.3 mM **1**[BF$_4$] in a 1:1 glass of CH$_2$Cl$_2$:C$_2$H$_4$Cl$_2$.

I. Oxidation of 1 and Properties of $\mathbf{1}^+$. A. Electrochemistry. Given the centrality of **1** and its oxidation products to this study, some details of the anodic behavior of this complex are warranted. The rather large separation of the two one-electron oxidations of **1** ($\Delta E_{1/2} = 450$ mV) is suggestive of a strong interaction, if not delocalization, between metal centers.[39,44]

Bulk electrolysis of millimolar solutions of **1** in CH$_2$Cl$_2$ at an applied potential of 0.2 V gave a purple solution of the monocation $\mathbf{1}^+$ and subsequent oxidation at $E_{\text{appl}} = 0.6$ V gave the red-purple dication $\mathbf{1}^{2+}$. Solutions of the monocation were used for optical and ESR spectroscopies to characterize the mixed-valent species (vide infra). Oxidation of **1** with either 1 or 2 equiv of Ag[BF$_4$] in dichloromethane enabled isolation of tetrafluoroborate salts of both the mono- and dications. Although a satisfactory elemental analysis of **1**[BF$_4$]$_2$ was not obtained, steady-state voltammetry showed no evidence of electroactive impurities (see Figure 2, where the voltammetric scans of the three oxidized complexes $\mathbf{8}^+$, $\mathbf{1}^+$, and $\mathbf{1}^{2+}$ are compared; note that the steady-state currents for $\mathbf{1}^{2+}$ are entirely cathodic, consistent with the virtual absence of either **1** or $\mathbf{1}^+$ in the sample).

B. ESR Spectroscopy of $\mathbf{1}^+$. ESR spectra of this ion were recorded under a variety of conditions involving different solvents and temperatures. The complex tended to form apparent microcrystals when its solutions were cooled, giving broad spectra characteristic of paramagnetic powders. Randomly oriented anisotropic spectra were obtained, however, using frozen solutions of a 1:1 mixture of CH$_2$Cl$_2$:1,2-C$_2$H$_4$Cl$_2$, which gives an ESR-quality glass at 77 K. Although hyperfine features are manifest [Figure 3d], they are not well resolved over the whole envelope of the spectrum. More interpretable results were obtained with ambient temperature fluid solutions, although broadening of the low-field hyperfine components still restricts good resolution to the high-field side [Figure 3b]. This situation did not qualitatively change over a temperature range of 230–310 K.

A simulation using a single line width [Figure 3a] allowed assignment of the spectrum ($\langle g \rangle = 2.0245$) as arising from hyperfine interactions with two equivalent spins of $^1/_2$ (^{31}P), $\langle a \rangle_{\text{P}} = 8.6 \times 10^{-4}$ cm^{-1}, and two equivalent spins of $^5/_2$ (^{55}Mn), $\langle a \rangle_{\text{Mn}} = 17.1 \times 10^{-4}$ cm^{-1}. Of primary importance is the implication that the two metals have *identical spin densities*, diagnostic of delocalized mixed valence. As a point of reference, the mononuclear Mn(II) complex [CpMn(CO)$_2$PPh$_3$]$^+$, $\mathbf{8}^+$, has average *g*- and *A*(Mn)-values respectively of 2.075 and about 45×10^{-4} cm^{-1}.[55]

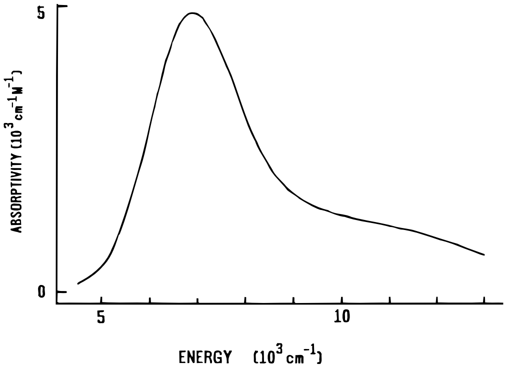

Figure 4. Near-IR spectrum of 0.2 mM **1**[BF$_4$] in CH$_2$Cl$_2$ at room temperature.

C. Optical Spectra of $\mathbf{1}^+$. The mixed-valent monocation has an intense absorption band in the near-IR at 1440 nm ($\epsilon = 5130$ M^{-1} cm^{-1}) with a broad low shoulder at somewhat higher energy (Figure 4). The high intensity band is assigned to the mixed-valent intervalence transition (IT). Measurements in three solvents varying considerably in solvent dielectric parameter,[7a] namely CH$_2$Cl$_2$, CH$_3$CN, and CH$_3$NO$_2$, showed no variation in band energy, consistent with a delocalized (Class III) system. There was likewise no spectral dependence on ionic strength up to electrolyte concentrations of 0.1 M in [NBu$_4$][PF$_6$], and no shift in absorbance for the solid salt (as a Nujol mull). Since the bandwidth, $\Delta\nu_{1/2}$ (2.5×10^3 cm^{-1}), was much less than predicted (4.0×10^3 cm^{-1}) for a valence-trapped (Class II) system (eq 3),[24] the commonly used optical diagnostics[7a,9] are in agreement with an assignment of a delocalized mixed-valence system for $\mathbf{1}^+$.

$$\Delta\nu_{1/2} = (2310\nu_{\text{max}})^{1/2}\ \text{cm}^{-1} \qquad (3)$$

where ν_{max} is taken at the center of the band.

The optical data recorded for various ions in this study are collected in Tables 3 (visible to near-IR range) and 4 (characteristics of absorptions assigned as IT bands). A discussion of the optical data of the other dinuclear systems is deferred until later in the paper. The dication $\mathbf{1}^{2+}$ lacked near-IR bands but had an intense absorption in the visible (512 nm) that is likely a ligand-to-metal charge transfer (LMCT) transition.

D. IR Spectra of $\mathbf{1}^+$ and $\mathbf{1}^{2+}$. Given the ESR and IT data, both of which supported a delocalized model for $\mathbf{1}^+$, we expected its carbonyl-region IR spectrum to consist of two bands at frequencies intermediate between those of the Mn(I)/Mn(I) neutral complex (1861 and 1934 cm^{-1}) and those of a fully oxidized, Mn(II)/Mn(II), system (the mononuclear Mn(II) system [CpMn(CO)$_2$PPh$_3$]$^+$ has 1966 and 2048 cm^{-1} in similar media).[32] The doubly bridged bimetallic chromium complex [(biphenyl){Cr(CO)$_2$}$_2$(dppm)]$^+$, $\mathbf{11}^+$, showed just such behavior (i.e., two bands were observed at frequencies appropriate for a Cr(0.5)Cr(0.5) complex).[36]

Instead, the spectrum of $\mathbf{1}^+$ consists of *four* intense ν_{CO} features (Figure 5) typical of *trapped-valent* systems in which

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(55) Pike, R. D.; Rieger, A. L.; Rieger, P. H. *J. Chem. Soc., Faraday Trans.* **1989**, *85*, 391.

Table 3. Absorptions in the Near-IR to Visible Regions for Ions in CH_2Cl_2

ion	bands in 10^{-3} cm^{-1} (ϵ in M^{-1} cm^{-1})
$[(Fulv)\{Mn(CO)_2\}_2(dppm)]^+$, **1**$^+$	6.94 (5130); ≈10^a (1000); 18.3 (780)
1^{2+}	11.7^b (720); 19.5 (8300)
$[(Fulv)\{Mn(CO)_2PPh_3\}_2]^+$, **2**$^+$	4.88 (1400); 8.33 (300); 20.0 (2000)
$[\{CpMn(CO)_2\}_2(dppm)]^+$, **5**$^+$	6.33 (120); 11.1^a (35); 18.4 (400)
$[CpMn(CO)_2PPh_3]^+$, **8**$^+$	5.71 (100); 17.7 (420)
$[(biphenyl)\{Cr(CO)_2\}_2(dppm)]^+$, **11**$^+$	6.56 (2110); 10.5 (sh, 400); 15.7 (1240)

Table 4. Characteristics of Intervalence Bands for Mixed-Valent Cations in CH_2Cl_2

			bandwidth (cm^{-1})	
mixed-valent ion	energy (cm^{-1})	ϵ^a	expt	theory for Class II^b
$[(Fulv)\{Mn(CO)_2\}_2(dppm)]^+$, **1**$^+$	6.94×10^3	5130	2.5×10^3	4.0×10^3
$[(Fulv)\{Mn(CO)_2PPh_3\}_2]^+$, **2**$^+$	4.88×10^3	710	4.1×10^3	3.3×10^3
$[\{CpMn(CO)_2\}_2(dppm)]^+$, **5**$^+$	6.33×10^3	150	4.9×10^3	3.9×10^3
$[(biphenyl)\{Cr(CO)_2\}_2(dppm)]^+$, **11**$^+$	6.56×10^3	2110	$2.9_5 \times 10^3$	3.9×10^3

[a] Units of M^{-1} cm^{-1}. [b] From eq 3.

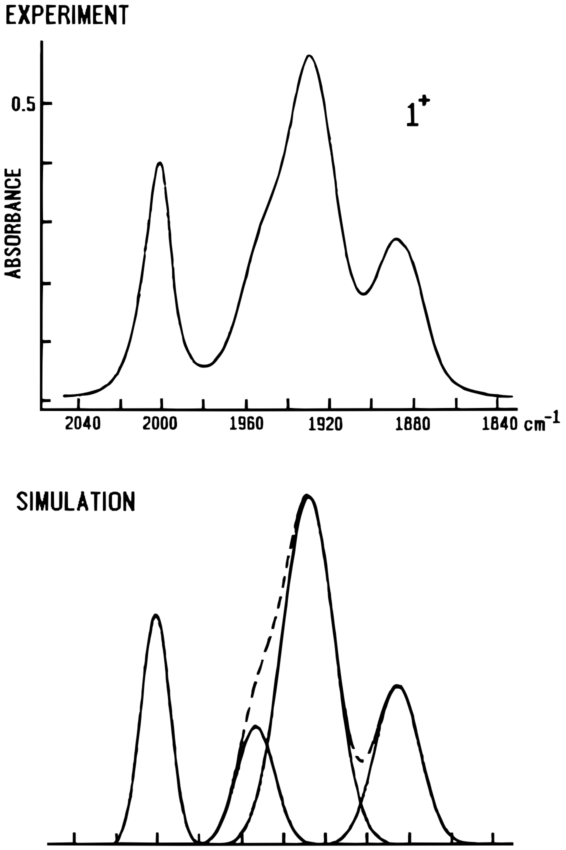

Figure 5. Experimental (top) IR spectrum of **1**$^+$ from the IRTTLE cell oxidation of 2.8 mM **1** in CH_2Cl_2/$[NBu_4][PF_6]$ at 273 K. The simulated spectrum (bottom) is based on four energies listed in Table 2; the addition of the central components is depicted as the dashed line.

overlap of the ν_{sym} feature of the reduced M − CO fragment with the ν_{asym} feature of the oxidized M − CO fragment gives an incompletely resolved center absorption envelope.[56] Spectral simulation allowed deconvolution of the central branch (Figure 5, bottom) and assignment of the four frequencies as 1888, 1931, 1952, and 2003 cm^{-1}. The lower intensity of the 1952 cm^{-1} band as compared to the 1931 cm^{-1} band favors its assignment as ν_{asym} [Mn(II)], since spectral intensities usually decrease as the oxidation state increases in M − CO moieties.[51,57] This spectrum remained unchanged through many variations in conditions chosen to probe for valence de-trapping.[58] Of particular note among these attempts is one that probes the possibility that ion-pairing (with $[PF_6]$ or $[BF_4]$) may be responsible for the valence trapping. The monocation was prepared as the $[Ni(S_2C_2(CF_3)_2)_2]^-$ salt by treatment of **1** with an equimolar quantity of the strong one-electron oxidant[59] $Ni(S_2C_2(CF_3)_2)_2$. Since the large, square-planar Ni(III) counteranion is expected to have a different ion-pairing tendency toward **1**$^+$ compared to the other anions employed, the lack of change in spectra in either dichloromethane or in the solid state can be taken to eliminate cation−anion interactions as being responsible for the trapped-valent IR behavior of the mixed-valent species.

It is appropriate at this point to comment on the IR spectra of the Mn(II)/Mn(II) dication **1**$^{2+}$. Two bands of almost equal intensity are observed at energies >100 cm^{-1} higher than **1**, in that sense consistent with expectations of a full unit increase in metal oxidation state, but two points are unusual: the closer spacing of the two bands (only 28 cm^{-1} difference compared, e.g., to the 82 cm^{-1} difference in **8**$^+$) and the presence of two lower intensity features at 1990 and 2007 cm^{-1} (see spectral simulation, Figure 6, bottom). Various control experiments established to our satisfaction that the two minor features do not arise from impurities. We are at present unable to account for these aspects of the spectrum of **1**$^{2+}$ except to point out that they might be expected to arise from vibronic coupling of the four carbonyl ligands. It is possible that the molecular structure of the dication allows this through formation of a weak metal−metal bond, continuing the lowering of the Mn−Mn distance as the oxidation state of the complex increases (d_{Mn-Mn} decreases by 0.52 Å to 4.07 Å in going from **1** to **1**$^+$).[10]

II. Weakly Coupled Mixed-Valent Dimanganese Systems. Four dimanganese complexes studied had $\Delta E_{1/2}$ values of 260 mV or less, typical of less strongly coupled dimetallic systems: the two fulvalendiyl complexes **2** (210 mV) and **3** (260 mV), a system in which a CH_2 group interrupts the two Cp rings (**4**, 80 mV) and one in which the dppm ligand is the only bridge between the two metals (**5**, 120 mV). IR spectra were obtained for both the monocations and dications of all four

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(56) Overlap of central components in mixed-valent complexes having multiple carbonyls on each metal is common: see refs 32, 36, 51, and the following: (a) Geiger, W. E.; Van Order, Jr.; Pierce, D. T.; Bitterwolf, T. E.; Rheingold, A. L.; Chasteen, N. D. *Organometallics* **1991**, *10*, 2403. (b) Merkert, J. W.; Geiger, W. E.; Paddon-Row: M. N.; Oliver, A. M.; Rheingold, A. L. *Organometallics* **1992**, *11*, 4109.

(57) Bullock, J. P.; Mann, K. R. *Inorg. Chem.* **1989**, *28*, 4006.

(58) Virtually identical spectra were obtained over a temperature range of 202−295 K in CH_2Cl_2, and at ambient temperature with changes in solvent (CH_3CN), supporting electrolyte ($[PF_6]^-$ or $[ClO_4]^-$ as counterions), ionic strength (ca. 10^{-3} to 10^{-1}), and physical state (Nujol mulls).

(59) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

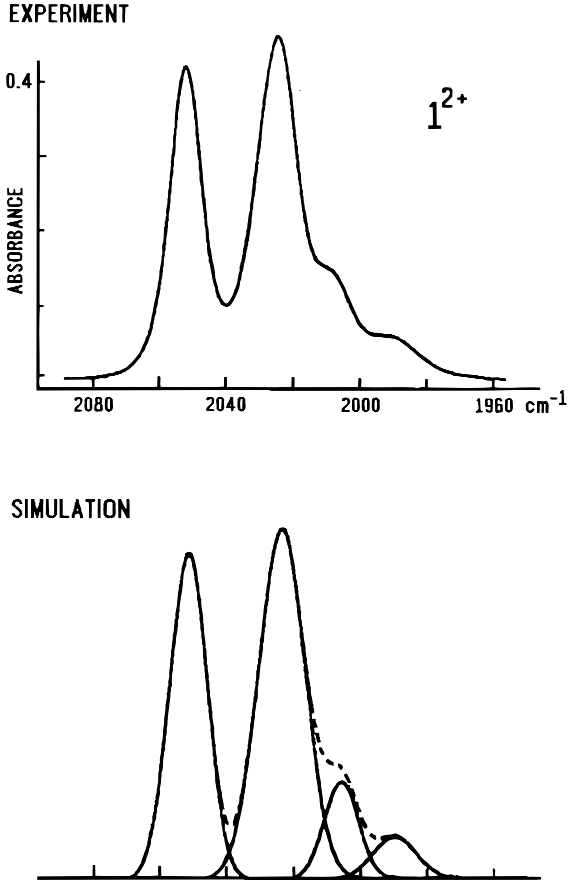

Figure 6. Experimental and simulated IR spectra of $\mathbf{1}^{2+}$ obtained in the same experiment described in the caption of Figure 5 after exhaustive double oxidation of 2.8 mM **1**.

complexes, and optical spectra were recorded for the monocations of **2** and **5**. In each instance, the spectral evidence favors the expected result of trapped valence in the mixed-valent ions.

A. Optical Spectra of 2^+ and 5^+. Because the visible-range spectra of these two mixed-valent ions each has a single absorption (543 nm for $\mathbf{5}^+$, a shoulder at ca. 525 nm for $\mathbf{2}^+$) at a position similar to that of the mononuclear Mn(II) system $\mathbf{8}^+$ (565 nm), these visible-region bands are assigned to a LMCT transition involving a localized Mn(II) valence. Excitation into this band is most likely responsible for the photosensitivity observed for all the Mn cationic samples except $\mathbf{1}^+$. Exposure of the Mn(II) complexes to strong room light or to unfiltered spectral source light resulted in decomposition, as evidenced by decolorization of the generally purple solutions and the appearance of brown precipitates.

The near-IR absorptions of the two dimanganese systems $\mathbf{2}^+$ and $\mathbf{5}^+$ each had two features (Figure 7). It is important to note that 17-electron Mn(II) centers of the type found in $\mathbf{2}^+$ and $\mathbf{5}^+$ may have metal d $\Rightarrow$ d transitions in this energy range if the metal centers have approximate C_s symmetry.[60] This fact introduces some ambiguity into the assignments for $\mathbf{5}^+$, which has two transitions of approximately the same intensity as the d $\Rightarrow$ d transition of $\mathbf{8}^+$ (ϵ ca. 100). The breadth of the feature centered at ca. 10000 cm^{-1} leads us to assign this band as the IT transition of $\mathbf{5}^+$ (Table 4). It seems more certain that in $\mathbf{2}^+$ the IT band is the one centered at about 2050 nm, since the intensity of this transition ($\epsilon > 700$) is too high to be ascribed to a d $\Rightarrow$ d transition similar to that found in $\mathbf{8}^+$. The breadths

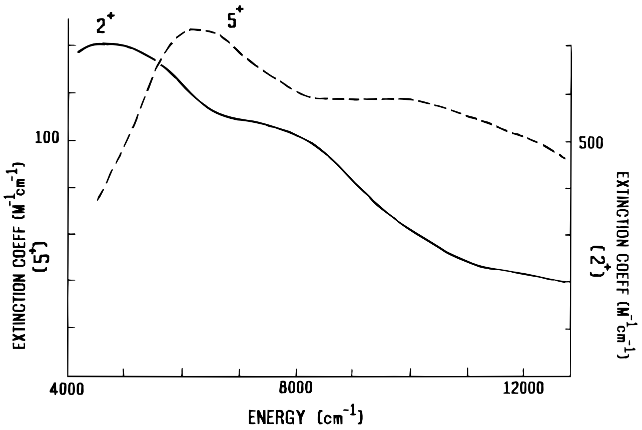

Figure 7. Electronic spectra in the near-IR range for two mixed-valent monocations obtained by bulk electrolysis in CH_2Cl_2/0.1 M [NBu_4][PF_6]. The concentrations of the precursors were 2.0 mM for **5** and 0.49 mM for **2**.

of the IT bands were consistent with formulation of the ions as Class II mixed-valent systems. As shown in Table 4, the bands were at least as wide as predicted by the Hush equation, eq 3, for Class II trapped-valent systems.

B. IR Spectra of Monocations and Dications of 2−5. The stepwise oxidation of these four complexes was followed through the monocation stage to the final dications by monitoring the charge passed in the IRTTLE cell. This is especially important in cases of weakly coupled metal centers in which the spectral shifts between oxidation states might be close to the spectral resolution. The assignment of particular features to the mono- or dications was based, therefore, on intensity vs charge data that were compared with theoretical expectations for a two-step oxidation process with the $\Delta E_{1/2}$ values measured by voltammetry (Table 1, Figure 1).

The pattern of four CO bands for the monocations and two CO bands for the dications is repeated in each case. In the potentially most weakly coupled systems, $\mathbf{4}^+$ and $\mathbf{5}^+$, the highest and lowest energy bands among the set of four absorptions were barely shifted from the energies expected for a fully oxidized Mn(II) site (for the high-energy band) and fully un-oxidized Mn(I) site. Whereas this observation is valuable in the qualitative sense in that it is consistent with trapped-valent monocations for $\mathbf{2}^+$−$\mathbf{5}^+$, further analysis enables a *quantitative* estimate of the charge distribution between the two metal centers. To this purpose, we follow the energy of the symmetric CO stretch for the three charged species and use eq 4 to express a “charge distribution parameter”, $\Delta\rho$, in terms of the spectral shifts. This parameter was introduced recently[22] in an attempt to use IR spectral shifts to calculate the actual ground-state charge distributions between two IR-active centers in mixed-valent systems.

$$\Delta\rho = (\Delta\nu_{\mathrm{ox}} + \Delta\nu_{\mathrm{red}})/2[\nu'(\mathrm{ox}) - \nu'(\mathrm{red})] \qquad (4)$$

where $\Delta\nu_{\mathrm{ox}} = \nu'(\mathrm{ox}) - \nu_{\mathrm{meas}}(\mathrm{ox})$, $\Delta\nu_{\mathrm{red}} = \nu_{\mathrm{meas}}(\mathrm{red}) - \nu'(\mathrm{red})$, and $\nu'(\mathrm{ox})$ and $\nu'(\mathrm{red})$ are the frequencies of the *fully oxidized and reduced*, respectively, redox centers. The parameters in eq 4 are presented graphically in Figure 8.

In this equation $\Delta\nu_{\mathrm{ox}}$ is the shift in ν_{CO} for the oxidized site in the mixed-valent complex from that of a fully oxidized Mn(II) moiety. Since the latter is available from the spectra of the dinuclear dications, $\Delta\nu_{\mathrm{ox}} = \nu_{\mathrm{CO}}(2+) - \nu_{\mathrm{CO}}(\mathrm{ox}, 1+)$; similarly, for the reduced site in the mixed-valent complex, $\Delta\nu_{\mathrm{CO}} = \nu_{\mathrm{CO}}$(red, 1+) $- \nu_{\mathrm{CO}}(0)$, where the number in parentheses refers to

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[60] Atwood, C. G.; Geiger, W. E. *J. Am. Chem. Soc.* **1994**, *116*, 10849.

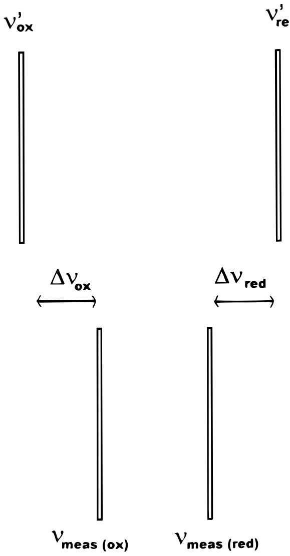

Figure 8. Schematic depiction of absorption energies of IR labels on the oxidized and reduced sites of a mixed-valent dinuclear complex. The symbols are defined as in eq 4 and the accompanying text.

the overall charge on the dinuclear complex. For the sake of simplicity we include only the symmetric stretching frequency in this analysis. Whereas the assignment of ν_{CO}(ox, 1+) is straightforward as the highest energy band in the spectrum of the monocation, that of ν_{CO}(red, 1+) is not as obvious owing to the relatively similar energies of the symmetric stretch of the reduced site and the asymmetric stretch of the oxidized site. Each mixed-valent spectrum was simulated (e.g., Figures 5 and 6) to get the exact energies of this overlapped pair, and the assignment of one band to ν_{CO}(red, 1+) was made on the assumption that its energy is lower than that of the asymmetric stretch of the oxidized side. This led to the intuitively satisfying result of similar values for $\Delta\nu_{ox}$ and $\Delta\nu_{red}$, whereas the opposite assignment gave values that were quite different. For example, in $\mathbf{5}^+$ the value of $\Delta\nu_{red}$ is 7 cm^{-1} under the former assignment, whereas it is 35 cm^{-1} under the latter, compared to a value of 6 cm^{-1} for $\Delta\nu_{ox}$ for this ion. Values of $\Delta\rho = 0.05$ to 0.29 are obtained for the five mixed-valent Mn_2 complexes (Table 2). The highest value, found in $\mathbf{1}^+$, may be interpreted in terms of an approximately 30:70 distribution of the positive charge between the two redox centers.

The larger values of $\Delta\rho$ also coincided with the larger values of $\Delta E_{1/2}$ deduced from electrochemical measurements. In an attempt to see if there is a systematic relationship between these two parameters, both of which are reputed to increase with the increasing strength of metal−metal interactions, we reevaluated three other dinuclear complexes (**9**−**11**) which have been diagnosed as either trapped- or delocalized-valent systems[36,51] based on their carbonyl IR properties. New IRTTLE-cell data were obtained for the dication of **11**, which had not previously been characterized by IR.[36] The doubly bridged mixed-valent ion $\mathbf{11}^+$ is intrinsically delocalized, thereby providing a test of eq 4. Confirming the efficacy of the charge distribution parameter, a value of $\Delta\rho = 0.50$ is found for $\mathbf{11}^+$, i.e., equal charges on the two metal centers.

A plot of $\Delta\rho$ vs $\Delta E_{1/2}$ for the eight mixed-valent systems investigated shows a clear correlation. If the single intrinsically delocalized system $\mathbf{11}^+$ is excluded from the analysis (Figure 9), a correlation coefficient of 0.984 is obtained with an intercept of 40 mV on the abscissa. The latter is close to the value expected for two electronically isolated metal centers,[61] although this level of agreement with theory is almost certainly fortuitous. Nevertheless, the correlation between the electrochemical potentials and IR shifts lends quantitative support to the often espoused view that larger $\Delta E_{1/2}$ values arise from more strongly coupled metal centers. This deduction must be applied with caution. The analyzed set of complexes certainly shares similarities in solvation and ion-pairing and, to some extent, changes in structure with electron count that tend toward constancy. A similar analysis applied recently to dicobalt−cyclophane mixed-valent complexes successfully reproduced charge distributions calculated by ab initio methods.[22] Application of the charge distribution parameter in eq 4 appears to be worthy of further testing. We note that a similar concept has been employed to estimate a “fractional charge” in the excited state of bipyridyl−metal complexes from a comparison of ground- and excited-state Raman frequencies.[62]

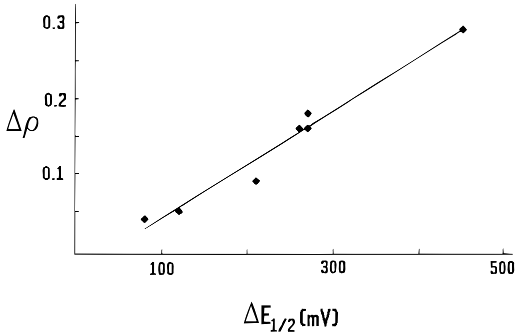

Figure 9. Plot of the charge distribution parameter, $\Delta\rho$, vs the measured separation in $E_{1/2}$ values for seven dinuclear complexes **1**−**5**, **9**, and **10** (data from Tables 1 and 2).

As this paper was being prepared, an important study appeared involving organic mixed-valent systems on the Class II/Class III borderline.[17c] That work revealed a linear relationship between the energies of electronic coupling in the mixed-valent ions (deduced from their electronic IT bands) and the $\Delta E_{1/2}$ values for coupled triarylamine redox centers. The Lambert/Noell paper[17c] gives references to attempts at correlation of $\Delta E_{1/2}$ with properties obtained from optical mixed-valent transitions; our data in the present paper establish, apparently for the first time, the correlation of $\Delta E_{1/2}$ with IR spectral properties.

Relevant to the diagnosis of possible delocalization in $\mathbf{1}^+$, it is most important to note that the IR properties of this ion are *quantitatively* consistent with all the Class II systems analyzed in Figure 9. That is, its IR shifts arise from a simple extrapolation of the *inductively shared* charge observed for less strongly interacting systems and strongly support its description as trapped valent on the vibrational time scale.

Although informative about the charge distributions, the present studies do not definitively answer the question of why the mixed-valent ion $\mathbf{11}^+$ is intrinsically delocalized, whereas $\mathbf{1}^+$ is not. The fact that the metal−metal distance is *smaller* in the latter (4.07 Å[10] vs 4.37 Å[36]) suggests that a direct through-space mechanism is not responsible for the delocalization of the former.

Conclusions

1. All members of the series of formal Mn(I)Mn(II) mixed-valent ions containing a single fulvalendiyl bridge ($\mathbf{2}^+$, $\mathbf{3}^+$, $\mathbf{7}^+$),

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(61) Ammar, F.; Saveant, J. M. *J. Electroanal. Chem.* **1973**, *47*, 215.

(62) Caspar, J. V.; Westmoreland, T. D.; Allen, G. H.; Bradley, P. G.; Meyer, T. J.; Woodruff, W. H. *J. Am. Chem. Soc.* **1984**, *106*, 3492. We thank a reviewer for bringing this article to our attention.

a dicyclopentadienylmethane bridge (**4**$^+$), or a dppm bridge (**5**$^+$) display trapped valent (Class II) behavior. Both optical (IT) spectroscopy and IR spectroscopy are consistent with this conclusion.

2. The doubly bridged complex **1**$^+$ is delocalized on the ESR time scale (ca. 10^{-8} s). Along with its larger value of $\Delta E_{1/2}$, this is strong evidence that the metal−metal interactions in **1**$^+$ are stronger than in any of the singly bridged complexes. On the vibrational time scale, however, **1**$^+$ is also valence trapped and so is designated as having between Class II and Class III behavior.

3. The carbonyl IR oxidative spectral shifts are analyzed in terms of a charge distribution parameter, $\Delta\rho$, which suggests that the overall ground-state positive charges are shared between metals in the monocations in the sequence **1**$^+$ > **9**$^+$ > **3**$^+$, **10**$^+$ > **2**$^+$ > **4**$^+$, **5**$^+$.

4. The charge distribution parameter correlates linearly with the separation in potentials of the successive one-electron oxidations, $\Delta E_{1/2}$, of the dinuclear systems. This appears to be the strongest evidence to date that the values of $\Delta E_{1/2}$ for a closely related series of compounds may be used to make quantitative conclusions about the site-to-site interactions in homodinculear complexes.

Note Added in Proof: A good review of “almost delocalized” systems has recently appeared. See: Nelsen, S. F. *Chem. Eur. J.* **2000**, *6*, 581.

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