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# Evidence for Time-Dependent Valence Detrapping in a Mixed-Valent Dimanganese Fulvalenyl Cation[†]

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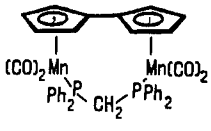
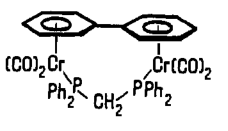
We report the preparation of a mixed-valent monocation derived from (fulvalenyl)$Mn_2(CO)_4(\mu$-dppm) (**1**) (dppm = $Ph_2P$-$CH_2$-$PPh_2$) that appears to exhibit valence detrapping in solution which can be resolved by spectral probes of inherently different time scales. Cyclic voltammetric and ESR spectroscopic measurements on $\mathbf{1}^+$ are consistent with delocalization between the two metals; IR spectra, however, argue for a *trapped-valent* description of $\mathbf{1}^+$.



**1**



**2**

The bridging dppm ligand confines the two $Mn(CO)_2$ moieties in **1** to a syn configuration, with the cyclopentadienyl (Cp) rings rotated by 65.4° from coplanarity in the neutral complex.[1] Oxidation occurs in two reversible one-electron steps ($CH_2Cl_2$/0.1 M $Bu_4NPF_6$) with $E°_1 = -0.055$ V *vs* $Fc^{0/+}$ and $E°_2 = +0.40$ V, $\Delta E° = 0.455$ V, the large separation of $E°$ values being suggestive of a strong interaction between the redox centers.[2] The monocation [**1**][$BF_4$] is readily isolated when **1** is oxidized with $AgBF_4$.[3] X-ray crystal analysis[4] shows that the rings are rotated toward coplanarity (dihedral angle 5.5°) with concomitant shortening of the Mn–Mn distance from 4.588 Å in **1**[1] to 4.07(1) Å in $\mathbf{1}^+$ (Figure 1).

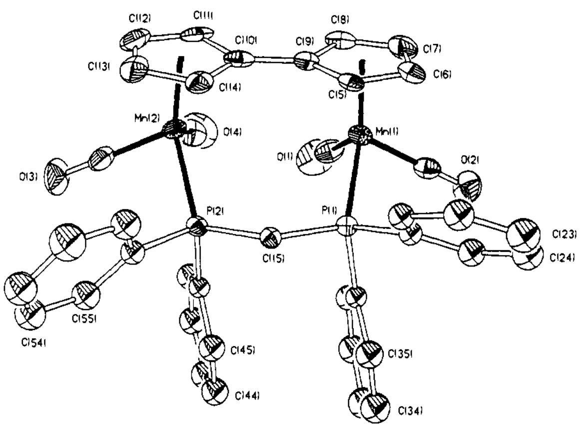


**Figure 1.** Molecular structure and atom labeling scheme for $\mathbf{1}^+$.

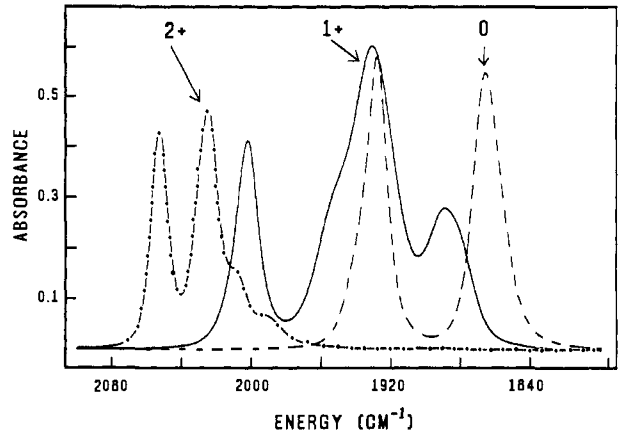


**Figure 2.** Carbonyl-region IR spectra of three oxidation states of complex **1**. Original solution 2.8 mM **1** in $CH_2Cl_2$/0.5 M $[Bu_4N][PF_6]$, $T = 273$ K. (- -), **1**; (—), $\mathbf{1}^+$; (- · ·), $\mathbf{1}^{2+}$.

ESR spectra of $\mathbf{1}^+$ in fluid $CH_2Cl_2$ are indicative of delocalization between the two metal sites, with hyperfine splittings to pairs of equivalent Mn and P atoms ($\langle a \rangle_{Mn} = 17.1 \times 10^{-4}$ cm$^{-1}$, $\langle a \rangle_P = 8.6 \times 10^{-4}$ cm$^{-1}$, $\langle g \rangle = 2.0245$). Spectra at 77 K appear to confirm delocalization in frozen solutions.

The properties of $\mathbf{1}^+$ discussed to this point parallel those of $\mathbf{2}^+$, a biphenyl analogue in which the monocation appears to be intrinsically delocalized (one pair of CO bands in the IR spectrum of $\mathbf{2}^+$).[5] Vibrational spectra of $\mathbf{1}^+$ in $CH_2Cl_2$, however, show evidence of trapped valency.

IR-transparent thin-layer electrode transmission spectroscopy[6] in the carbonyl region revealed clean and reversible transformations among the three oxidation states (Figure 2):

$$\mathbf{1} \overset{-e}{\rightleftharpoons} \mathbf{1}^+ \overset{-e}{\rightleftharpoons} \mathbf{1}^{2+}$$

The two outlying members of the electron-transfer series, **1** and $\mathbf{1}^{2+}$, display the expected *pairs* of prominent CO bands[7] shifted to higher energy by over 100 cm$^{-1}$ in the dication ($\nu_{CO}$ = 1928, 1865 for **1**, 2051, 2022 for $\mathbf{1}^{2+}$), consistent with formation of two equivalent Mn(II) sites.[8]

The IR spectrum of $\mathbf{1}^+$ was interpreted with the aid of a Lorentzian band-fitting program as four intense absorptions with

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[†] Structural Consequences of Electron-Transfer Reactions. 26. For part 25, see: Geiger, W. E.; Rieger, P. H.; Corbato, C.; Edwin, J.; Fonesca, E.; Lane, G. A.; Mevs, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 2314.

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(3) **1**[1] (115 mg) and 30 mg of $AgBF_4$ were reacted in 100 mL of $CH_2Cl_2$ under $N_2$ in the dark. The dark purple solution was filtered and partially evaporated, diluted with THF, reduced in volume, and filtered to give [**1**][$BF_4$], yield of 110 mg (86%). Anal. C, 55.76 (calcd 57.04); H, 4.07 (calcd 3.68).

(4) Crystal data for [**1**][$BF_4$] (from $CH_2Cl_2$/pentane):graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.7107$ Å; $C_{39}H_{30}BF_4Mn_2O_4P_2$, MW = 821.3, monoclinic, space group $P2_1/n$, $a = 17.138(6)$ Å, $b = 10.665(4)$ Å, $c = 20.094(7)$ Å, $\beta = 101.68(3)°$, $V = 3596.6(23)$ Å$^3$, $Z = 4$, $D = 1.517$ g/cm$^3$, $\mu = 8.53$ cm$^{-1}$. Photographic analysis revealed $2/m$ Laue symmetry. No correction for absorption required, structure solved by direct methods using the SHELXTL (Version 5.1, 1989) program library [G. Sheldrick, Nicolet (Siemens), Madison, WI] to residuals of $R = 0.084$ and $R_w = 0.102$ for 3843 observed reflections.

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(7) The two low-energy shoulders in the IR spectrum of $\mathbf{1}^{2+}$ (Figure 2) do not arise from impurities. The dication may contain a Mn–Mn bond which allows vibrational coupling of the dicarbonyl groups on adjacent metals.

(8) Oxidation of $CpMn(CO)_2(PPh_3)$ to $CpMn(CO)_2(PPh_3)^+$ results in a shift of the CO bands from (cm$^{-1}$) 1931 and 1864 to 2048 and 1966 under our conditions. Original observation: Connelly, N. G.; Demidowicz, Z.; Kelly, R. L. *J. Chem. Soc., Dalton Trans.* **1975**, 2335.

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energies of 2003, 1952, 1929, and 1885 cm$^{-1}$. The number of bands and their energies are strongly indicative of a *localized* mixed-valent cation, formally Mn(II)/Mn(I). Although four bands could, in principle, arise from a delocalized complex of low symmetry with four vibrationally coupled CO groups,[9] this is an unlikely scenario in the present case. Owing to the absence of a direct metal–metal bond in **1**$^+$, the vibrational coupling of the two dicarbonyl groups would have to occur through a minimum of four bonds. Thus, the four absorptions are instead ascribed to two pairs of symmetric and asymmetric $(CO)_2$ stretches, one for a Mn(II) site and one for a Mn(I) site. The lowest frequency band is particularly diagnostic, since its shift of 20 cm$^{-1}$ from that of $\nu_{asym}$ of **1** (which has two Mn(I) sites) is typical of *valence trapped* dinuclear metal carbonyls.[10] Identical spectra for **1**$^+$ were obtained with different solvents, ionic strengths, counteranions (including a large nickel dithiolene anion[11]), and temperatures (295–202 K).

Our evidence suggests that **1**$^+$ is valence trapped on the time scale of IR spectroscopy (ca $10^{-12}$ s)[12] but delocalized on a time scale longer than that of ESR spectroscopy ($10^{-8}$ s),[13] implying that the rate, $k_{et}$, of valence detrapping (i.e., intramolecular electron transfer) in **1**$^+$ is $10^{12}$ s$^{-1}$ > $k_{et}$ > $10^8$ s$^{-1}$.

Optical absorption spectra (relevant time scale ca. $10^{-15}$ s) do not afford the unambiguous conclusions drawn from ESR and IR measurements. Powdered [**1**][BF$_4$] (in Nujol) has a near-IR absorption centered at 6350 cm$^{-1}$ which is assigned as an intervalence transition (IT) band based on its breadth (roughly that expected of a Class II mixed-valent system) and its energy. In solution, however, this intense absorption ($\bar{\nu}$ = 6940 cm$^{-1}$, $a_M$ = 5130 M$^{-1}$ cm$^{-1}$) is too narrow to fit the dielectric continuum model for a trapped-valent system.[14] This appears to be one of a growing number of examples in which application of the usual IT band diagnostics is indecisive in assigning mixed-valency type.[16] We intend to comment further on the optical spectra in due course.

Compounds like **1**$^+$ and **2**$^+$ are attractive for the study of valence detrapping in fluid media because of the range of spectral probes available to study their charge and spin localization. Since identical electrolyte media were employed to obtain the data on these two ions, their differences in behavior do not appear to be linked to local medium effects, known to be important in other examples of valence trapping.[17] The structural and electronic factors affecting delocalization in these systems, including the possibility that valence detrapping may be triggered by conformational changes, remain under study. It is clear, however, that *syn*-dinuclear complexes may possess strongly interacting metals, even though they are separated by >4 Å, and thus can contribute to our understanding of strongly-coupled metals.[18]

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**Supplementary Material Available:** Tables of anisotropic thermal parameters, hydrogen atom coordinates, bond distances, and bond angles for [**1**][BF$_4$] (15 pages); listings of observed and calculated structure factors for same (27 pages). Ordering information is given on any current masthead page.

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(9) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975; pp 81 ff.

(10) Geiger, W. E.; Van Order, N., Jr.; Pierce, D. T.; Bitterwolf, T. E.; Rheingold, A. L.; Chasteen, N. D. *Organometallics* **1991**, *10*, 2403 and references therein.

(11) Oxidation of **1** by equimolar Ni[$S_2C_2(CF_3)_2$]$_2$ (Davison, A.; Edelstein, N.; Holm, R. H.; Maki, A. H. *Inorg. Chem.* **1963**, *2*, 1227) in $CH_2Cl_2$ gave identical CO-region IR spectra.

(12) If the narrowest line in the IR spectrum of **1**$^+$ is assumed to be the natural line width of the sample, unbroadened by chemical (i.e., electron) exchange, an upper lifetime of 3 × $10^{-13}$ s is calculated for the lifetime of the trapped-valent species on the basis of the uncertainty principle (see Drago, R. S. *Physical Methods of Chemistry*; Saunders College Publishing: Philadelphia, PA, 1977; pp 86 ff). For another approach to the time scale argument, see: Strauss, H. L. *J. Am. Chem. Soc.* **1992**, *114*, 905.

(13) Calculated on the basis of the observation of a ca. 4-G minimum line width for **1**$^+$ in $CH_2Cl_2$ at ambient temperatures.

(14) Width at half-height for the solution band was 2.45 × $10^3$ cm$^{-1}$, significantly less than that prediicted (4.0 × $10^3$ cm$^{-1}$) by the Hush model (*Prog. Inorg. Chem.* **1967**, *8*, 391) for an IT band of this energy from a Class II[15] trapped-valent system. See also: Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(15) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

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(18) Borderline class II/class III systems remain under active investigation in mixed-valence chemistry. See: (a) Hupp, J. T.; Kober, E. M.; Neyhart, G. A.; Meyer, T. J. In *Mixed Valency Systems: Applications in Chemistry, Physics, and Biology*; Prassides, K., Ed.; Kluwer Academic Publishers: Dordrecht, 1991; p 51. (b) McManis, G. E.; Nielson, R. M.; Weaver, M. J. *Inorg. Chem.* **1987**, *27*, 1827.