

- (7) F. Basolo, B. M. Hoffman, and J. A. Ibers, *Acc. Chem. Res.*, **8**, 384 (1975), and references therein.
- (8) S. K. Cheung, C. J. Grimes, J. Wong, and C. A. Reed, *J. Am. Chem. Soc.*, **98**, 5028 (1976).
- (9) C. J. Weschler, B. M. Hoffman, and F. Basolo, *J. Am. Chem. Soc.*, **97**, 5278 (1975).
- (10) J. Almog, J. E. Baldwin, R. L. Dyer, J. Huff, and C. J. Wilkinson, *J. Am. Chem. Soc.*, **96**, 5600 (1974), and references therein.
- (11) C. K. Chang and T. G. T aylor, *J. Am. Chem. Soc.*, **95**, 5811, 8477 (1973).
- (12) J. P. Collman, R. R. Gagne, C. A. Reed, T. R. Halbert, C. Lang, and W. T. Robinson, *J. Am. Chem. Soc.*, **97**, 1427 (1975).
- (13) D. L. Anderson, C. J. Weschler, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 5599 (1974).
- (14) G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, **19**, 1 (1976), and references therein.
- (15) J. S. Valentine, Y. Tatsuno, and M. Nappa, *J. Am. Chem. Soc.*, **99**, 3522 (1977).
- (16) N. Farrell, D. H. Dolphin, and B. R. James, *J. Am. Chem. Soc.*, **100**, 324 (1978).
- (17) F. A. Walker, *J. Am. Chem. Soc.*, **95**, 1150, 1154 (1973).
- (18) H. C. Stynes and J. A. Ibers, *J. Am. Chem. Soc.*, **94**, 1559 (1972).
- (19) D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 1796 (1973); **96**, 1358 (1974).
- (20) D. V. Stynes, H. C. Stynes, J. A. Ibers, and B. R. James, *J. Am. Chem. Soc.*, **95**, 1142 (1973).
- (21) F. A. Walker, *J. Am. Chem. Soc.*, **92**, 4235 (1970).
- (22) F. A. Walker, D. Beroiz, and K. M. Kadish, *J. Am. Chem. Soc.*, **98**, 3484 (1976).
- (23) V. L. Goedken, N. K. Kildahl, and D. H. Busch, *J. Coord. Chem.*, **7**, 89 (1977).
- (24) R. H. Bailes and M. Calvin, *J. Am. Chem. Soc.*, **69**, 1886 (1947), and previous publications in this series.
- (25) F. Calderazzo, C. Floriani, and J. J. Salzman, *Inorg. Nucl. Chem. Lett.*, **2**, 379 (1966).
- (26) C. Floriani and F. Calderazzo, *J. Chem. Soc. A*, 946 (1969).
- (27) M. Calligaris, G. Nardin, and L. Randaccio, *Chem. Commun.*, 763 (1969).
- (28) G. Tazher, G. Amiconi, E. Antonini, M. Brenori, and G. Costa, *Nature, New Biol.*, **241**, 222 (1973).
- (29) D. Diemente, B. M. Hoffman, and F. Basolo, *Chem. Commun.*, 467 (1970).
- (30) A. L. Crumbliss and F. Basolo, *J. Am. Chem. Soc.*, **92**, 55 (1970).
- (31) B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Am. Chem. Soc.*, **92**, 61 (1970).
- (32) G. A. Rodley and W. T. Robinson, *Nature (London)* **235**, 438 (1972).
- (33) M. J. Carter, D. P. Rillema, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 392 (1974).
- (34) R. M. C. Wei and S. C. Cummings, *Inorg. Nucl. Chem. Lett.*, **9**, 43 (1973).
- (35) Earlier abbreviations for this ligand and its metal complexes included $H_2(sacac)_2en$, $M(sacac)_2en$, $H_2(sacacen)$, and $M(sacacen)$. We have decided to use $sacsacenH_2$ and $M(sacsacen)$ to be consistent with abbreviations now commonly accepted for related systems.
- (36) P. R. Blum, R. M. C. Wei, and S. C. Cummings, *Inorg. Chem.*, **13**, 450 (1974).
- (37) D. R. Treter, M. S. Thesis, Wright State University, Aug 1973.
- (38) P. R. Blum, R. M. C. Wei, and S. C. Cummings, *Inorg. Syn.*, **16**, 225-228 (1976).
- (39) L. S. Chen and S. C. Cummings, *Inorg. Chem.*, **17**, 2358 (1978).
- (40) M. E. Koehler and S. C. Cummings, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Tex., April 1973.
- (41) M. E. Koehler, M. S. Thesis, Wright State University, Aug 1973.
- (42) Full names of the complexes are as follows: $Co(benacen)$, N,N' -ethylenebis(benzoylacetone iminato)cobalt(II); $Co(CH_3benacen)$, N,N' -ethylenebis(*p*-methylbenzoylacetone iminato)cobalt(II); $Co(CH_3Obenacen)$, N,N' -ethylenebis(*p*-methoxybenzoylacetone iminato)cobalt(II); $Co(Br(benacen))$, N,N' -ethylenebis(*p*-bromobenzoylacetone iminato)cobalt(II); $Co(Cl(benacen))$, N,N' -ethylenebis(*p*-chlorobenzoylacetone iminato)cobalt(II); $Co(bensacen)$, N,N' -ethylenebis(benzoylmonothioacetone iminato)cobalt(II); $Co(CH_3bensacen)$, N,N' -ethylenebis(*p*-methylbenzoylmonothioacetone iminato)cobalt(II); $Co(CH_3Obensacen)$, N,N' -ethylenebis(*p*-methoxybenzoylmonothioacetone iminato)cobalt(II); $Co(Br(bensacen))$, N,N' -ethylenebis(*p*-bromobenzoylmonothioacetone iminato)cobalt(II); $Co(Cl(bensacen))$, N,N' -ethylenebis(*p*-chlorobenzoylmonothioacetone iminato)cobalt(II).
- (43) P. J. McCarthy, R. J. Hovey, K. Ueno, and A. E. Martell, *J. Am. Chem. Soc.*, **77**, 5820 (1955).
- (44) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969, p 11.
- (45) Initial studies using DMF were reported: B. C. Pestel, M.S. Thesis, Wright State University, Dec 1974.
- (46) H. C. Stynes and J. A. Ibers, *J. Am. Chem. Soc.*, **94**, 5125 (1972).
- (47) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, N.Y., 1963, pp 162-177.
- (48) R. J. Hovey and A. E. Martell, *J. Am. Chem. Soc.*, **82**, 2697 (1960).
- (49) D. R. Roberts, M.S. Thesis, Wright State University, Aug 1978.
- (50) D. R. Roberts and S. C. Cummings, to be submitted for publication.

Mixed Valence Interactions in Di- μ -oxo Bridged Manganese Complexes. Electron Paramagnetic Resonance and Magnetic Susceptibility Studies

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Abstract: EPR examination of the class II (deeply trapped) mixed valence complexes $[(bpy)_2MnO_2Mn(bpy)_2]^{3+}$ (the bipyridyl(III,IV) dimer) and its phenanthroline analogue in acetonitrile solution verifies that these complexes possess inequivalent Mn ions at room temperature. Isotropic hyperfine structure for two Mn ions is resolved with $A_1 = 167 \pm 3$ G and $A_2 = 79 \pm 3$ G for both complexes. The hyperfine pattern with $|A_1| \approx 2|A_2|$ and the small g anisotropy are consistent with high-spin Mn(III) antiferromagnetically coupled to Mn(IV), producing an $S = 1/2$ ground state. At room temperature a rate of less than 10^8 s $^{-1}$ is estimated for the thermally activated intramolecular electron transfer, consistent with an upper limit of 10^6 s $^{-1}$ calculated from Hush's theory. The magnetic susceptibility of the (III,IV) complexes is characteristic of a strongly antiferromagnetically coupled $S = (2, 3/2)$ pair. The temperature dependence of the data was in good agreement with the isotropic Heisenberg exchange Hamiltonian $H = -2JS_1S_2$, yielding $J = -150 \pm 7$ cm $^{-1}$ for the bipyridyl(III,IV) dimer and $J = -134 \pm 5$ cm $^{-1}$ for the phenanthroline analogue.

Introduction

Since the 1964 reviews of Hush,¹ Allen and Hush,² and Robin and Day,³ mixed valence compounds have received considerable attention, prompted in some part by interest in synthesis of new conducting materials and the occurrence of

mixed valence complexes in biology, notably the ferredoxins. One of the most interesting properties of a mixed valence compound is the extent of electron delocalization, expressed as an electron delocalization rate. The classification scheme of Robin and Day³ divides mixed valence compounds into three groups—those exhibiting no delocalization (class I), those with complete electron delocalization (class III, the molecular ion case), and those with intermediate delocalization (class II).

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Class II ions possess discrete oxidation states, and the optical spectra of these ions generally closely approximate the sum of spectra of the constituents. However, an additional broad, low-energy transition which has been assigned to an intervalence transfer absorption, a photon-assisted electron transfer between the ions, has often been observed. Hush's treatment of these transitions considers the electron as coupled to two harmonic oscillators, leading to the potential energy surfaces shown in Figure 1 for a Mn(III)-Mn(IV) pair. In addition to the optical, or Franck-Condon, electron transfer with energy E_{op} , an associated thermally activated adiabatic process is also predicted, with activation energy E_{th} (ref 1).

In a previous paper⁴ we examined the electronic structure of di- μ -oxo-tetrakis(2,2'-bipyridine)dimanganese(III,IV) perchlorate [(bpy)₂MnO₂Mn(bpy)₂](ClO₄)₃ (hereafter called the bipyridyl(III,IV) dimer), its 1,10-phenanthroline analogue, and the corresponding phenanthroline(IV,IV) complex.⁵ The bipyridyl(III,IV) dimer, first synthesized by Nyholm and Turco,⁶ was found by Plaksin et al.⁷ to have inequivalent Mn ions from the considerable differences in bond lengths about the ions in the crystalline state. Our physical studies were consistent with this observation. Both the bipyridyl and phenanthroline(III,IV) dimers have broad mixed valence bands at approximately 830 nm as expected for class II, or deeply trapped systems. From Hush's theory¹ this value of E_{op} implies a thermal activation barrier to electron transfer of $E_{th} = 8.6$ kcal/mol, neglecting splitting of the potential energy surfaces. Assuming no activation entropy and a transmission coefficient of unity, this theory places an upper bound of 10^6 s⁻¹ on the thermal electron transfer rate. No thermal averaging of bond lengths was reported in the crystal structure determination for the bipyridyl(III,IV) dimer as might be anticipated from this thermal electron transfer rate. We previously suggested⁴ that lattice polarization might contribute significantly to electron trapping in the crystal. To estimate the thermal electron transfer rate in the absence of lattice effects we have examined the EPR of the mixed valence (III,IV) complexes in frozen and fluid solution and report herein the

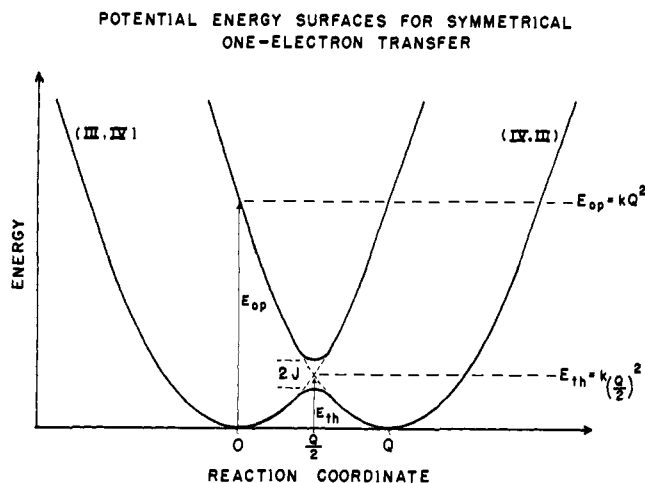


Figure 1. Potential energy surfaces for (III,IV) to (IV,III) electron transfer. E_{op} is the energy of the optical, or Franck-Condon, process; E_{th} the activation energy of the corresponding thermal, or adiabatic, electron transfer.

paramagnetic impurity were the only parameters allowed to vary. The paramagnetic impurity constituted less than 0.1% of the sample on a molar basis (assuming it to be Mn(II)) for both bipyridyl and phenanthroline(III,IV) samples. For the phenanthroline(IV,IV) dimer there was sufficient paramagnetic impurity to preclude meaningful fitting of our data and those of earlier workers⁵ to the appropriate exchange Hamiltonian.

Results

Magnetic Behavior. The temperature dependence of the molar magnetic susceptibility χ_M and magnetic moment μ (both per dimer) of the bipyridyl(III,IV) dimer is shown in Figure 2. Both the bipyridyl and phenanthroline(III,IV) dimers exhibit essentially the same behavior. In both cases the room temperature moment of approximately $2.5 \mu_B$ (ref 4, 7) decreases to $1.74 \mu_B$ at low temperature. The susceptibility data were fitted to eq 1 (derived for an $S = (2, 3/2)$ pair)

$$\chi_M = \frac{Ng^2\beta^2}{12kT} \left[\frac{3 + 30 \exp(-3J/kT) + 105 \exp(-8J/kT) + 252 \exp(-15J/kT)}{1 + 2 \exp(-3J/kT) + 3 \exp(-8J/kT) + 4 \exp(-15J/kT)} \right] + N\alpha \quad (1)$$

results. The temperature-dependent magnetic susceptibility of bipyridyl and phenanthroline(III,IV) dimers from 250 to 4 K reported here confirms that these complexes are strongly antiferromagnetically coupled ($J \gg g\beta H$).⁴⁻⁶ Previous workers have reported susceptibility studies from 298 to 77 K for the bipyridyl(III,IV)⁷ and phenanthroline(IV,IV)⁵ complexes.

Experimental Section

The complexes [(bpy)₂MnO₂Mn(bpy)₂](ClO₄)₃·2H₂O, [(phen)₂MnO₂Mn(phen)₂](ClO₄)₃·CH₃COCH₃, and [(phen)₂MnO₂Mn(phen)₂](ClO₄)₄·H₂O⁵ were prepared as previously described.⁴

EPR spectra were obtained at X-band (9.15 GHz) on a Varian E-9 spectrometer with magnetic field modulation at 100 kHz. Frozen solutions of the complexes in spectrograde acetonitrile were examined in cylindrical quartz tubes, while flat EPR cells were used for fluid samples. Magnetic measurements were performed on a Foner-type⁸ Princeton Applied Research Model 155 vibrating sample magnetometer for measurements below 200 K. Lack of instrumental sensitivity obviated precise measurements above this temperature. The temperature at the sample was measured with a calibrated GaAs diode. The magnetometer was calibrated with HgCo(SCN)₄ (ref 9) and operated at 12.5 kG. No field dependence was observed for any of the complexes.¹⁰ Diamagnetic corrections were applied using Pascal's constants.¹⁰ Magnetic susceptibility data were fitted to the isotropic Heisenberg exchange Hamiltonian $H = -2JS_1S_2$ by a nonlinear least-squares program. No biquadratic exchange was employed to fit the data. The exchange integral J and the amount of

where $N\alpha$, the temperature-independent paramagnetism term, was estimated to be 120×10^{-6} cgs emu, using $10 Dq = 20000$ cm⁻¹ for the Mn(III) ion and 1.5 times this value for the Mn(IV). All terms have their usual significance.¹⁰ The best fit to the above equation was $J = -150 \pm 7$ cm⁻¹ for the bipyridyl(III,IV) dimer and $J = -134 \pm 5$ cm⁻¹ for the phenanthroline(III,IV) dimer. The error limits represent the standard deviations observed from the fitting process—the error incurred in the measurements is probably somewhat greater, owing to the inability to pursue the magnetic measurements to higher temperature. Previous workers⁷ reported a J value of -101 cm⁻¹ for the former complex—we are unable to account for the appreciable discrepancy. In both cases g values of 2.0 were employed, as determined from the EPR spectra (vide infra). The magnetic data are tabulated in Tables I and II.

EPR Spectra. The EPR spectra of the bipyridyl and phenanthroline(III,IV) dimers were examined between 12 and 298 K and found to be identical over this temperature range; that of the phenanthroline complex is shown in Figure 3a. Spectra obtained in acetonitrile or aqueous solution with excess ligand as buffer⁴ are also essentially identical. Upon electrochemical oxidation⁴ of the phenanthroline(III,IV) complex in CH₃CN to the (IV,IV) complex the EPR intensity diminishes with increasing extent of oxidation. No EPR spectrum is observed for the (IV,IV) complex from 12 to 298 K.

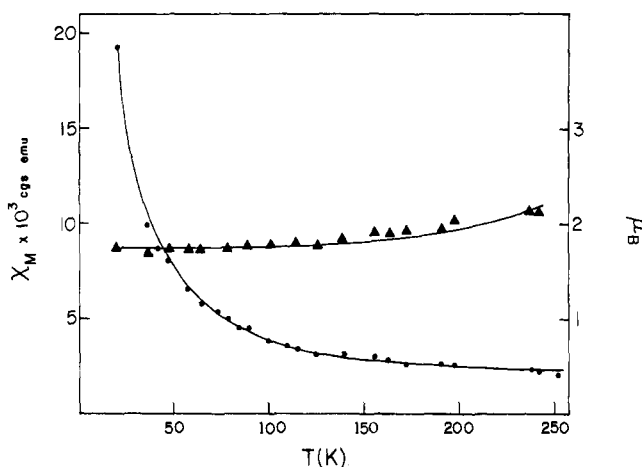


Figure 2. Molar magnetic susceptibility (circles) and magnetic moment (triangles), both per dimer, for the bipyridyl(III,IV) dimer. Points are experimental data; susceptibility curve is best fit to isotropic Heisenberg exchange Hamiltonian for $S = (2, \frac{3}{2})$ system.

Discussion

Magnetic Behavior. Both the phenanthroline(III,IV) and (IV,IV) dimers are presumed to have a di- μ -oxo structure like the bipyridyl(III,IV) dimer, which has been structurally characterized.⁷ All three complexes have an IR band in the 688–692- cm^{-1} region which has been assigned previously to a vibrational mode of the Mn_2O_2 moiety by isotopic labeling studies.⁴ All three complexes are strongly antiferromagnetically coupled. The interaction is presumed to occur via a superexchange pathway, although the Mn–Mn distance is short (2.716 Å for the bipyridyl(III,IV) complex⁷) and a direct exchange contribution cannot be excluded. The small difference in J values between the bipyridyl and phenanthroline(III,IV) complexes may be due to a more favorable exchange interaction geometry for the flexible bipyridyl ligand.

The limiting low-temperature magnetic moment of 1.74 μ_B (Tables I and II) is close to the $S = \frac{1}{2}$ spin-only moment of 1.73 μ_B and indicates that the Mn(III) ion is high spin, i.e., the dimer is well described as an $S = (2, \frac{3}{2})$ system, in agreement with the optical data.⁴ An orbital contribution to the moment would be anticipated for low-spin Mn(III) ($^3T_{1g}$ in O_h symmetry) which would be manifest in the dimer since the exchange coupling and spin-orbit interaction are of comparable magnitude ($\sim 100 \text{ cm}^{-1}$).

EPR Spectra. The predominant features of the EPR spectrum in Figure 3a are accounted for by the spin Hamiltonian

$$g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + (A_1 I_1 + A_2 I_2)S - 2JS_1 S_2$$

where S_1 and I_1 are the electron spin and nuclear spin operators, respectively, and A_1 is the hyperfine coupling tensor for the Mn(III) ion, while terms with subscript 2 refer to the Mn(IV) ion. The total spin $S = S_1 + S_2$, g_{\parallel} and g_{\perp} are principal g tensor components for axial symmetry, and J is the isotropic spin exchange energy between Mn(III) and Mn(IV). Consistent with the susceptibility results, the EPR spectra demonstrate that the largest term in the spin Hamiltonian is the exchange interaction, as can be deduced from the spectrum in Figure 3a, which is free of the forbidden hyperfine transitions $\Delta m = \pm 1, \pm 2$ common to d^3 and d^5 systems such as Mn(IV) and Mn(II).¹¹ These forbidden transitions have been shown to occur when both a hyperfine splitting and a fine structure splitting of comparable magnitude are present, and as such arise from the competition between magnetic and electrostatic forces in aligning the nuclear spins. Since such

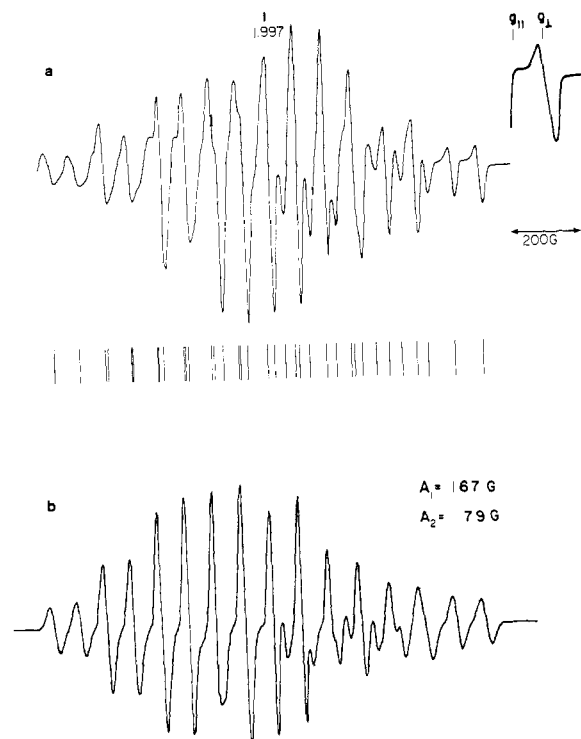


Figure 3. (a) EPR spectrum of phenanthroline(III,IV) dimer (10^{-3} M) in CH_3CN at 18 K. Microwave power 1.0 mW with 2 G modulation amplitude (100-kHz modulation frequency); microwave frequency 9.165 GHz. The inset shows an expanded region about the hyperfine peak at the high-field end of the spectrum. (b) Computer simulation of the (III,IV) EPR spectrum. The simulation was performed using a Gaussian line width which was a function of the nuclear quantum numbers m_1 and m_2 : $\Delta = \Delta_0 + b_1 m_1 + b_2 m_2$, where $\Delta_0 = 5.5$ G, $b_1 = 2b_2 = 2.35$ G, and $2^{1/2}\Delta = \Delta H_{ms} =$ first derivative at maximum slope.

multipole effects can only be observed in systems with $S \geq 1$, their absence in this case is consistent with the ground spin state of $S = \frac{1}{2}$. The absence of an EPR spectrum for the (IV,IV) complex also indicates appreciable exchange coupling in the oxidized analogue, consistent with the magnetic results of Goodwin and Sylva.⁵

The expression for the transition energies for the allowed transitions $\Delta M = \pm 1$, $\Delta m_1 = \Delta m_2 = 0$ within the ground doublet (obtained through second-order perturbation theory) is (ref 12)

$$E_M - E_{M-1} = g\beta H + (A_1 m_1 + A_2 m_2) + (2g\beta H)^{-1}(A_1^2(I_1(I_1 + 1) - m_1^2) + A_2^2(I_2(I_2 + 1) - m_2^2))$$

where $g^2 = g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta$, where θ is the angle between the symmetry axis and the external magnetic field, and m_1 and m_2 are the nuclear spin quantum numbers. Anisotropic hyperfine structure is not considered in this expression.

The hyperfine structure is readily accounted for by coupling to two nonequivalent ^{55}Mn nuclei ($I = \frac{5}{2}$) with $A_1 = 167 \pm 3$ G and $A_2 = 79 \pm 3$ G. The increase in separation between lines and the resolution of additional lines at the high-field end of the spectrum are a consequence of the second-order corrections to the hyperfine energy. This asymmetric hyperfine structure arises because the hyperfine interaction is not small in comparison with the Zeeman interaction. A stick spectrum and a computer simulation predicted from the hyperfine terms in the expression above are given in Figures 3b and 3c. The very large difference between the hyperfine constants indicates that the unpaired electron in the ground spin state is localized on one of the Mn ions or transferred between them at a rate much slower than $(|A_1| - |A_2|)$.

Table I. Molar Magnetic Susceptibility and Moment of the Bipyridyl(III,IV) Dimer

<i>T</i> , K	χ_M	μ_B^a
298	2540	2.46 ^b
251	2151	2.07
241	2348	2.13
231	2446	2.15
196	2642	2.04
189	2642	2.00
171	2741	1.94
163	2839	1.92
154	3036	1.93
139	3134	1.86
124	3232	1.79
115	3527	1.80
109	3625	1.77
101	3920	1.78
98	3920	1.75
89	4509	1.79
84	4608	1.76
78	4902	1.75
72	5394	1.76
64	5788	1.73
57	6622	1.74
47	8145	1.74
42	8735	1.70
36	9914	1.69
20	19 347	1.75
14	27 994	1.77
4	94 320	1.74

^a Corrected for paramagnetic impurity. ^b Reference 4.

The line width of the individual transitions is insensitive to temperature below 120 K, with the narrowest line width being 10 G. This implies that electron transfer between the Mn ions is slower than $\sim 3 \times 10^7 \text{ s}^{-1}$ below 120 K. At 298 K where the solution is fluid and lattice trapping cannot be a factor, a similar spectrum is observed except for an increased minimum line width of 30 G and a reduction in overall intensity due to population of EPR-silent excited states of the spin state manifold. The thermal electron transfer rate must be less than 10^8 s^{-1} at 298 K. The line width is due in part to unresolved ^{14}N superhyperfine structure, as indicated by preliminary experiments on the bipyridyl N,N' -dioxide analogue (in preparation).

The presence of line width anisotropy can be deduced from the difference in line width of the nondegenerate transitions observed at the outer extremes of the spectrum in Figure 3a. This anisotropy is partially resolved in the extreme high-field peak and is shown in the inset in Figure 3a. The line shape is that expected for axial symmetry and is due in part to hyperfine anisotropy as was deduced from the experimental spectrum which shows a line width increasing with $|m_1|$ and $|m_2|$. Although orientational anisotropy was not explicitly considered in the simulation, its effects on the spectrum were partially introduced by assuming a line width which increased with $|m_1|$ and $|m_2|$ (see Figure 3 legend). This improved the fit to the experimental spectrum. The remaining discrepancies between the experimental and simulated spectra are small and due to the approximation of a symmetric line shape, neglect of g anisotropy, and the presence of a small contamination of Mn(II) ($\sim 0.1 \text{ mol } \%$). No attempt was made to extract the anisotropic component of the g and hyperfine tensors, although this can be done in principle from a full simulation.¹² It is important to recognize that the increase of line width with $|m_1|$ and $|m_2|$ is due to hyperfine anisotropy and not a relaxation effect at the low temperature reported in Figure 3.

An average g value equal to 2.003 was estimated from the spectrum by comparison to diphenylpicrylhydrazyl radical (DPPH) and taking into account the second-order shift of the

Table II. Molar Magnetic Susceptibility and Moment of the Phenanthroline(III,IV) Dimer

<i>T</i> , K	χ_M	μ_B^a
298	2975	2.66 ^b
215	2654	2.14
210	2658	2.11
205	2712	2.11
200	2721	2.09
195	2747	2.07
190	2775	2.05
185	2828	2.04
180	2868	2.03
175	2882	2.01
170	2945	2.00
165	3012	1.99
160	3038	1.97
155	3083	1.95
150	3128	1.94
145	3217	1.93
140	3262	1.91
135	3351	1.90
120	3798	1.91
115	3753	1.86
110	4111	1.90
105	4246	1.89
100	4424	1.88
95	4203	1.79
90	4533	1.81
85	4816	1.81
80	5093	1.81
75	5428	1.80
70	5852	1.81
65	6418	1.83
60	6842	1.81
55	7360	1.80
50	8020	1.79
43.8	9810	1.85
39.6	10 612	1.83
35	11 931	1.83
31.1	13 203	1.81
28.1	14 476	1.80
25.9	15 559	1.80
22.4	17 727	1.78
18.2	21 497	1.77
15.8	24 372	1.75
13.2	28 707	1.74
11.1	34 644	1.75

^a Corrected for paramagnetic impurity. ^b Reference 4.

spectrum. The presence of a rather small g anisotropy indicates that in the ground spin state the d^4 Mn(III) ion is in a high-spin configuration. An appreciable departure from the free spin g value is observed for low-spin d^4 ions in octahedral fields.¹⁴

For exchange coupled ions in which the exchange energy is much larger than the Zeeman and hyperfine energies, the electron spin of the component ions may be added vectorially to arrive at the total electron spin. The component spins are said to be quantized along the total spin. We may therefore express the magnetic parameters of the cluster (effective g and A values) in terms of the values expected for the isolated ions.¹⁵ In terms of the projection along each spin these are

$$g = g_1 \frac{(S_1 S)}{S^2} + g_2 \frac{(S_2 S)}{S^2} = 2g_1 - g_2$$

$$A_1 = A_1' \frac{(S_1 S)}{S^2} = 2A_1'$$

$$A_2 = A_2' \frac{(S_2 S)}{S^2} = -A_2'$$

where g , A_1 , and A_2 are effective g and hyperfine constants for the cluster and g_1 , g_2 , A_1' , and A_2' identify those for the

isolated ions. The projections have been evaluated for the high-spin case $S_1 = 2$, $S_2 = 3/2$, and $S = 1/2$. The observed average g value of 2.003 agrees with the expression above using the reported g values of Mn(IV) and an estimated g value for Mn(III) based on isoelectronic analogues.^{12,14} The hyperfine expressions show that a large coupling constant of twice the isolated ion value is expected. The 167 G coupling in Figure 3 is very close to twice the value expected for Mn(III).¹⁵ A coupling constant opposite in sign but the same in magnitude to that for the isolated ion is predicted for one hyperfine component. This agrees with the 79 G coupling observed in Figure 3 (75 G is found for Mn(IV) in Al_2O_3 ¹⁴) but the sign cannot be determined from the spectrum. The negative sign arises because the two ions are antiferromagnetically coupled, and is consistent with the magnetic susceptibility results. The hyperfine structure and g anisotropy are not consistent with low-spin Mn(III) ($S_1 = 1$).

Conclusions

EPR studies on the mixed valence (III,IV) dimers have shown conclusively that the Mn ions are inequivalent at room temperature in solution, and that an upper bound of 10^8 s^{-1} can be placed on the thermal electron transfer rate. This value is consistent with that predicted by Hush's theory from the energy of the intervalence transfer absorption in these complexes. The slowness of the thermal electron transfer can be attributed to the high-spin nature of the Mn(III), which is inferred from optical data⁴ as well as EPR and magnetic studies (this work). The odd electron is antibonding (e_g in O_h) and hence its transfer necessitates considerable changes in bond lengths about the Mn ions (as shown by the crystallographic results of Plaksin et al.⁷) leading to slow electron transfer. An alternate description considers the potential energy surfaces in Figure 1 to be characterized by much greater steepness (i.e., a large force constant for the redox-active mode) for electrons in bonding and antibonding orbitals than those in nonbonding orbitals, with concomitant increase in E_{th} , the thermal activation energy.

Note: Since submission of this manuscript, a report on the (III,IV) complexes by Sawyer and co-workers has appeared.¹⁶ We must take serious exception to several points in that report.

(1) The (III,IV) dimers are expected to yield 11 lines in the fast exchange limit or up to 36 lines in the slow exchange limit. The 6-line spectrum presented by Sawyer et al. for the (III,IV) complex is inconsistent with that complex but is consistent with Mn(II), an impurity which is both difficult to remove and which yields an EPR spectrum identical with that shown by these authors.

(2) Similar objections obtain for the putative (IV,IV)

spectrum presented by these authors, which again is more consistent with Mn(II). We have not observed any EPR signals from the (IV,IV) complex over the temperature range 298 to 12 K.

(3) The magnetic data of Goodwin and Sylva⁵ (specifically a moment *per dimer* of $1.86 \mu_B$ at 298 K) indicate that the phen(IV,IV) dimer complex is strongly antiferromagnetically coupled, in contrast to the statement that there is "no significant electron pairing" between the Mn(IV) ions. (The EPR evidence upon which this conclusion is based is addressed in (2).) A room temperature spin-only moment of $5.5 \mu_B$ would be expected for the (IV,IV) dimer in the limit as J goes to zero.

Note Added in Proof. Recently M. Inoue has published EPR studies of pure single crystals of the bipyridyl(III,IV) dimer and reported weak signals attributable to the excited quartet state. These signals are unobservable in our solution studies, no doubt due to the much lower concentrations involved. In addition, J was estimated to be -143 cm^{-1} , in agreement with our value of -150 cm^{-1} .

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References and Notes

- (1) N. S. Hush, *Prog. Inorg. Chem.*, **8**, 391 (1967).
- (2) G. C. Allen and N. S. Hush, *Prog. Inorg. Chem.*, **8**, 357 (1967).
- (3) M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, **10**, 247 (1967).
- (4) S. R. Cooper and M. Calvin, *J. Am. Chem. Soc.*, **99**, 6623 (1977).
- (5) H. A. Goodwin and R. A. Sylva, *Aust. J. Chem.*, **20**, 629 (1967).
- (6) R. S. Nyholm and A. Turco, *Chem. Ind. (London)*, 74 (1960).
- (7) P. M. Plaksin, R. C. Stouffer, M. Mathew, and G. J. Palenik, *J. Am. Chem. Soc.*, **94**, 2121 (1972).
- (8) S. Foner, *Rev. Sci. Instrum.*, **30**, 548 (1959).
- (9) H. St-Rade, *J. Phys. Chem.*, **77**, 424 (1973).
- (10) F. E. Mabbs and D. J. Machin, "Magnetism and Transition Metal Ions", Chapman and Hall, London, 1973, p 5.
- (11) B. Bleaney and R. S. Rubins, *Proc. Phys. Soc., London*, **77**, 103 (1961).
- (12) A. Abragam and B. Bleaney, "Electron Paramagnetic Resonance of Transition Metal Ions", Oxford University Press, London, 1970, pp 429-430 and 435.
- (13) R. H. Sands and W. R. Dunham, *Q. Rev. Biophys.*, **7**, 443 (1975).
- (14) S. Geschwind, P. Kisliuk, M. P. Klein, J. P. Reineika, and D. L. Wood, *Phys. Rev.*, **128**, 1684 (1962).
- (15) In isolated ions the hyperfine field per electron is expected to be nearly constant based on the spin polarization of the core electrons by the outer d electrons. Accordingly, the hyperfine fields for Mn(II), Mn(III), and Mn(IV) should all be about the same except somewhat reduced for the higher oxidation states owing to increased effects of covalency. This is essentially what is found and implies a Mn(III) hyperfine field of 80 G.
- (16) M. M. Morrison and D. T. Sawyer, *Inorg. Chem.*, **17**, 333 (1978).