spectra at higher temperatures; in fact, for several H_4WL_4 tungsten complexes, where L is a phosphine or arsine ligand, the nonrigidity limit is reached above room temperature.[7]

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Mixed Valence Interactions in Di-μ-oxo Bridged Manganese Complexes

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Abstract: The complexes $[(L)_2MnO_2Mn(L)_2]^{3+}$ where L = 2,2′-bipyridine or 1,10-phenanthroline, have been examined, in addition to the corresponding (IV, IV) complex of phenanthroline. The crystal structure of the mixed valence (III, IV) compound with L = 2,2′-bipyridine demonstrated that this complex has deeply trapped valences, corresponding to class II in the classification of Robin and Day since the bond lengths differ considerably about the manganese ions. We have examined the electronic spectrum of the (III, IV) complexes and observed broad bands in the near infrared which we have assigned to the mixed valence band expected for a class II system. No comparable band is observed for the phenanthroline(IV, IV) complex. Lowering the pH of (III, IV) dimer solutions reversibly cleaves the antiferromagnetically coupled (III, IV) dimers as determined by the increase in solution magnetic susceptibility; loss of the near infrared band occurs with dimer cleavage, although the remainder of the visible spectrum is substantially unaltered. Both absorbance and solution magnetic susceptibility changes with pH are reversible. The solvent dependence of the near infrared band is small but apparently opposite to that predicted by Hush's theory. However, the bandwidths agree well with those predicted from Hush's treatment (e.g., 0.53 μm^{-1} predicted, 0.46 μm^{-1} observed). A band at 688 cm^{-1} in the infrared spectrum of the bipyridyl(III, IV) dimer is shifted by isotopic substitution with ^{18}O, and has been assigned to one of the stretching modes of the Mn_2O_2 bridge; analogous bands are found for the phenanthroline(III, IV) and -(IV, IV) complexes. Pertinent aspects of the electrochemistry are also discussed.

In 1972 Plaksin et al.[1] reported the crystal structure of di-μ-oxo-tetrakis(2,2′-bipyridyl)dimanganese(III, IV) perchlorate (hereafter termed the bipyridyl(III, IV) dimer) which was originally synthesized by Nyholm and Turco[2] in 1960. This complex, which Nyholm and Turco had formulated as a Mn(III)–Mn(IV) compound, was found by Plaksin et al. to have discrete Mn(III) and Mn(IV) ions from the inequivalence of the bond lengths about the ions. The electronic structure of such complexes with mixed oxidation states has excited considerable interest since the 1967 reviews of Robin and Day,[3] Hush,[4] and Allen and Hush.[5]

Robin and Day[3] have classified mixed valence complexes into three categories. Class I compounds exhibit essentially no interaction between the ions, while class III ions are fully delocalized, resonance stabilized compounds. The electronic spectra of class I ions are the sum of the spectra of the constituent ions; those of class III are due to transitions between molecular orbitals and bear no necessary relation to the spectra of the components. Class II ions have weak but nonnegligible interactions between the ions; thus, in addition to contributions typical of both constituent ions, the electronic spectrum of a class II ion is expected to exhibit a new absorption due to a photon-driven electron transfer between the ions. Such electron transfer bands, termed mixed valence or intervalence transfer absorption bands, are typically broad and low in energy. In addition to the optical process, an associated thermally activated electron transfer is also predicted. Hush[4] has described such intervalence transfer absorption in terms of a multiphonon-assisted electron transfer reaction, in which the electron is coupled to two harmonic oscillators and the solvent is considered as a continuous dielectric. From this approach predictions regarding bandwidth, solvent dependence, extent of delocalization, and barrier to thermal electron transfer can be made.

Boucher and Coe[6] have recently reported the properties of μ-oxo-μ-hydroxo-dimanganese(III, IV) complexes of Schiff base ligands and assigned a band at 2.2 μm^{-1} to an intervalence transfer band.

In their report of the crystal structure of the bipyridyl(III, IV) dimer Plaksin et al.[1] made no mention of an intervalence transfer absorption, although one is expected for this class II system. In order to clarify this situation we have examined the electronic structure of this complex and its phenanthroline analogue.

Experimental Section

Solvents and Reagents. The ligands 2,2′-bipyridyl and 1,10-phenanthroline were purchased from Aldrich and recrystallized from petroleum ether and water, respectively. Acetone and acetonitrile were distilled from potassium permanganate; the acetonitrile was subsequently distilled from phosphorus pentoxide. Tetraethylammonium perchlorate was prepared by reaction of ethyl bromide with triethylamine, recrystallized three times from water, and vacuum dried at 100 °C for 24 h. All other chemicals were of reagent grade and were used without further purification.

$[(bipy)_2MnO]_2(ClO_4)_3 \cdot 2H_2O$ (bipy = 2,2′-Bipyridyl). A solution of 4.3 g of $Mn(OAc)_2 \cdot 4H_2O$ (OAc = CH_3COO^-) (17.5 mmol) in 60 mL of H_2O was added to 8.2 g of 2,2′-bipyridyl (52.5 mmol) in 30 mL of acetone. Eighty milliliters of 1 M acetate buffer (pH 4.5) was added to the yellow solution, and the pH adjusted to 4.5 with glacial acetic acid. After the solution was cooled to 0 °C in an ice bath 1.18 g of $KMnO_4$ (7.5 mmol) in 50 mL of H_2O was added dropwise with stirring. The resulting green solution was stirred for 15 min at 0 °C after addition was complete before it was filtered and concentrated sodium perchlorate solution added to precipitate the product as a green powder. The product was collected on a medium frit and washed with ethanol and diethyl ether, yield 11.2 g, 80%. The product can be recrystallized from acetonitrile or 0.05 M bipyridyl/bipyridinium nitrate buffer at pH 4.5. The complex is unstable in aqueous solutions at temperatures greater than approximately 80 °C; hence recrystallizations should be performed below this temperature. Alternatively, the complex can be recrystallized at room temperature by slurrying it with Dowex AG1-X8 (200–400 mesh) in the nitrate form to bring it into solution, filtering off the resin, and very slowly adding sodium perchlorate solution with stirring to the point of incipient crystallization of the complex. Cooling the solution leads to isolation of pure product. The latter method has been found useful for preparing spectral samples, since an impurity absorbing in the visible is much more soluble as the perchlorate salt than the desired product. (The ratio of the absorbances at 684 and 600 nm, $A_{684}:A_{600}$, is 1.76 for the pure compound; values less than this are indicative of impurity). On the other hand, recrystallization from hot bipyridyl buffer is better for preparation of samples for magnetic measurements, since virtually all Mn(II) is removed in this fashion. Recrystallization from hot bipyridyl buffer followed by recrystallization at room temperature using the resin technique removes both impurities. Anal. Calcd for $C_{40}H_{36}N_4O_{16}Cl_3Mn_2$: C, 43.63; H, 3.30; N, 10.18; Cl, 9.66. Found: C, 43.85; H, 3.12; N, 10.21; Cl, 9.75.

The bipyridyl(III, IV) dimer can also be prepared by disproportionation of $Mn(bipy)(OH_2)(Cl)_3$ in bipyridyl buffer at pH 4.5. The starting material (80 mg) was dissolved in 12 mL of 0.1 M bipyridyl buffer at pH 4.5. The complex was added in small portions with stirring and continuous monitoring of the pH, which was kept between 4.4 and 4.5 with concentrated sodium acetate solution. The red-brown starting material dissolved in the buffer to form a deep green solution with optical spectrum identical with that of genuine bipyridyl(II, IV) dimer. Concentrated sodium perchlorate solution was added dropwise with stirring after filtration to precipitate a green powder which was recrystallized as described above. Infrared analysis confirmed optical identification of the product as the bipyridyl(III, IV) dimer, yield 52 mg, 40% from $Mn(bipy)(OH_2)(Cl)_3$.

In addition to elemental analysis, the metal:ligand:counterion ratio, (1:2.01:1.57), oxidizing equivalents per Mn (1.49 ± 0.03), and molecular weight were determined (1108 ± 23). Manganese and bipyridyl were determined spectrophotometrically as MnO_4^- and $bipyH^+$, respectively; perchlorate was determined gravimetrically as the tetraphenylarsonium salt. Redox titrations were performed by addition of the bipyridyl(III, IV) dimer to excess primary standard grade As_2O_3 as described by Vogel[7a] and back-titrated with standard potassium permanganate solution. The molecular weight was determined by vapor pressure osmometry in acetonitrile on a Mechrolab 301 osmometer; $[(bipy)_2Co(NH_2,O_2)Co(bipy)_2](ClO_4)_3 \cdot 2H_2O$, synthesized by the method of Sasaki and Fujita,[8] was used as a calibration standard.

$[[(phen)_2MnO]_2MnO]_2(ClO_4)_3 \cdot CH_3COCH_3$. The phenanthroline(III, IV) dimer was prepared in a fashion analogous to the bipyridyl(III, IV) dimer.

Recrystallization of the product by a procedure similar to that used for the bipyridyl(III, IV) dimer proved difficult owing to the low solubility of phenanthrolium perchlorate. It is possible to recrystallize the phenanthroline(III, IV) dimer by dissolution in 0.01 M phenanthroline buffer at pH 4.5 and 70 °C, filtering, cooling to room temperature, and making the solution 20% by volume in acetone (in which phenanthrolium perchlorate is very soluble). Black crystals were deposited overnight, and washed with ice-cold acetone. Anal. Calcd for $C_{48}H_{38}N_4O_{13}Cl_3Mn_2$: C, 50.24; H, 3.14; N, 9.19; Cl, 8.72. Found: C, 50.21; H, 3.34; N, 9.02; Cl, 8.69.

The phenanthroline(III, IV) dimer can also be synthesized by adding $Mn(phen)(OH_2)(Cl)_3$ to phenanthroline buffer at pH 4.5 to yield a product identical by infrared and optical analysis with the above product.

$[(phen)_2MnO]_2(ClO_4)_4 \cdot H_2O$. This complex was synthesized by the method of Goodwin and Sylva.[9]

$Mn(L)(OH_2)(Cl)_3$, Where L = 2,2′-Bipyridine and 1,10-Phenanthroline. These complexes were synthesized by the method of Goodwin and Sylva.[10]

Physical Measurements. Cyclic voltammograms were recorded using three-electrode circuitry with a platinum disk working electrode, platinum wire auxiliary, and a saturated calomel reference electrode (Radiometer) and are uncorrected for liquid junction potentials. The latter was calibrated with an anaerobic solution of quinhydrone (National Technical Laboratories) in 0.05 M phosphate buffer at pH 7.00 in a cell thermostated at 25.0 °C and purged with argon. Triangular waves were generated by the Princeton Applied Research (PAR) 175 programmer in conjunction with the PAR 380 controlled potential coulometry system, which included the PAR 173 potentiostat. Controlled potential coulometry was performed on a platinum mesh electrode with the Model 179 digital coulometer which is included in the controlled potential coulometry system. Scan rates too rapid to be recorded on a Houston Instruments Omnigraphic 2000 X-Y recorder were photographed from a Tektronix 549 storage oscilloscope trace.

Optical absorption spectra were recorded in the ultraviolet and visible regions on a Cary 118 spectrophotometer; visible and near-infrared spectra were recorded on a Cary 14 spectrophotometer, and all measurements were made at ambient temperature, approximately 23 °C. Hydrogen ion activities were determined by a Radiometer GK 2321 C combination electrode in conjunction with the pH module of the Radiometer Titrator TTT2. For the bipyridyl(III, IV) dimer the total ligand concentration was 0.05 M, while for phenanthroline(III, IV), 0.01 M ligand sufficed to stabilize the complex. All solutions were 1 M in $NaNO_3$ to swamp salt effects. Solutions were allowed to equilibrate for 12 h, at which time no further change was evident. The pH 0 solutions are subject to appreciable decomposition in this time, particularly for the phenanthroline(III, IV) dimer. Since low pH solutions equilibrate more rapidly than those at higher pH, the pH 0 solution of the phenanthroline complex was allowed to equilibrate only 2 h. This time represented the best compromise between equilibration and decomposition.

Magnetic susceptibilities in solution were determined by the NMR method[11] (using 2% v/v acetone) on a Varian A-60 NMR spectrometer which was calibrated by sideband modulation. The temperature at the sample was adjusted to 25 °C and measured by the shift between the methyl protons and the hydroxyl protons of methanol. Nickel chloride solutions yielding shifts comparable to those of

Table I. Infrared Bands of Manganese(III, IV) and -(IV, IV) Complexes (cm^{-1})

Bipy(III, IV)·$2H_2O$	Phen(III, IV)·CH_3COCH_3	Phen(IV, IV)·H_2O
3400 b	3400 b	3400 b
3080	3080	3080
1632 sh	1697 s	1635
1609	1626	1619
1600	1605	1600
1575	1582	1544
1566	1518	1521 s
1496	1494	1498
1472	1457	1471
1447 s	1427 s	1454
1385 w	1383 w	1427 s
1316	1367	1418 sh
1275 w	1340	1369 w
1244	1310	1338
1226 sh	1253 w	1320
1177 sh	1212 sh	1287 w
1165	1144 sh	1243 w
1080 vs, b	1080 vs, b	1226 w
1040 w, sh	1033 w, sh	1190 w, sh
1030	1000 sh	1158 sh
1019	938 w	1143 sh
929 w	930 w	1090 vs, b
895 w, b	912 w	992 w, sh
811 w	874 sh	940 w
802 w	863 sh	931 w
768 s	844 vs	883
733	776	874 w
727	738 sh	847 s
688	721 vs	815
668 w	686	778
654	655	741 w, sh
642 w, sh	644	717 s
633 sh	634	692
621 s	622 s	656
589 w	578	645 w
479 w, b	556	633 sh
448 w	531 w	623
428 w, sh	509 w	620
418	490 w	542 w
389	435	498 w
365 w, sh	422	466
358	366	437
281	287 w	421
234	225	413
		399
		367
		242
		225

experimental samples were used as standards. The $NiCl_2$ concentration was determined gravimetrically as the dimethylglyoxime complex.[7b] The correction for density changes was found to be negligible.

Infrared spectra were recorded on a Perkin-Elmer 283 grating spectrophotometer, which was calibrated with water vapor (in the far IR) and polystyrene. Samples were run as 0.5% by weight potassium bromide pellets; mineral oil mulls gave equivalent results. Cesium iodide plates were used to run mineral oil mulls in the far infrared region owing to absorption by KBr. Isotopically enriched $H_2{}^{18}O$ was purchased from the Weizmann Institute and distilled before use. Mass spectral analysis showed the distillate to be 53 atom % ^{18}O. Gymkowski et al.[12] have reported that the KI used for IR pellets is subject to solid state reactions involving oxidation of iodide to IO_4^- and IO_3^-. Since the manganese complexes reported here are all powerful oxidants the infrared spectra of these compounds were examined for artifacts from oxidation of the KBr. Oxidation of the KBr *was* observed, but proceeded at a significant rate only at elevated temperatures (~100 °C). At room temperature KBr oxidation was appreciable only after 1 month.

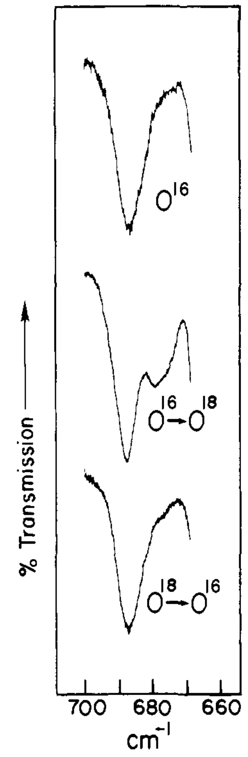


Figure 1. Infrared spectrum of bipyridyl(III, IV) dimer (KBr pellet). Top, spectrum before isotopic substitution. Center, spectrum after heating in 53 atom % enriched $H_2{}^{18}O$. Bottom, spectrum following recrystallization from $H_2{}^{16}O$ solution of sample isolated from $H_2{}^{18}O$ solution. All solutions were buffered by 0.05 M bipyridyl, pH 4.5.

Results

Infrared Spectra. Infrared spectral data of the bipyridyl(III, IV), phenanthroline(III, IV), and phenanthroline(IV, IV) dimers are summarized in Table I. The infrared bands in the ligand ring mode region are typical of bipyridyl and phenanthroline coordinated to metal ions[13] and will not be discussed further. The IR of the phenanthroline(III, IV) complex verifies the presence of acetone of crystallization from the intense band at 1697 cm^{-1} which is lost on heating to 110 °C for 3 h, with no other change in IR or visible spectrum.

Recrystallization of the bipyridyl(III, IV) dimer at room temperature from 53 atom % $H_2{}^{18}O$ bipyridyl buffer caused no noticeable splittings in any of the IR bands. Recrystallizing the bipyridyl complex at higher temperatures (~80 °C) produces a shoulder on the 688-cm^{-1} band of the complex (Figure 1), which is lost on back substitution with $H_2{}^{16}O$. All recrystallizations were conducted in bipyridyl buffer (0.05 M) at pH 4.5. The new band appears at 676 cm^{-1}; no other bands are observed to be sensitive to isotopic substitution.

Electronic Spectra. The visible spectrum of the bipyridyl(III, IV) dimer in 0.05 M aqueous bipyridyl buffer (pH 4.5) is shown in Figure 2. The spectrum of the phenanthroline analogue is essentially identical. Both complexes have shoulders at 525 and 555 nm and a maximum at 684 nm (1.90, 1.80, and 1.45 μm^{-1}, respectively; Table II). A broad band in the near infrared appears as a shoulder on the 684-nm band, which subsequent measurements (vide infra) revealed to have a maximum at approximately 830 nm. The absorption spectrum of the phenanthroline(IV, IV) dimer reveals no bands in the visible region. The (III, IV) dimers were found to obey Beer's law over the concentration range from 10^{-1} to 10^{-5} M.

Small solvent shifts are observed for the near infrared band when dissolved in D_2O-bipyridyl buffer, acetonitrile, and nitrobenzene, although the 684-nm band appearing as a high-energy shoulder renders quantitation of the shifts difficult.

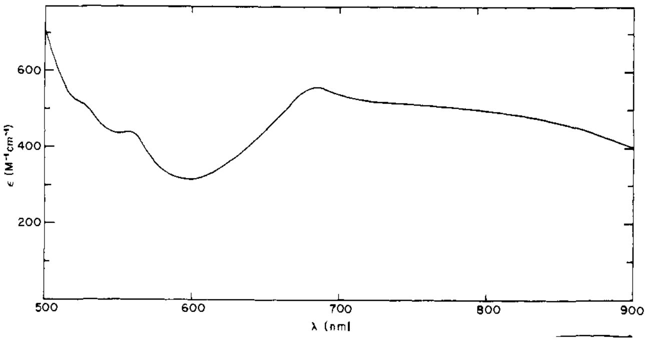


Figure 2. Visible spectrum of bipyridyl(III, IV) dimer in aqueous 0.05 M bipyridyl buffer, pH 4.5.

Table II. Visible Spectra of (III, IV) Ions in Aqueous Buffer Solution

Complex	λ, nm	ν, cm^{-1} × 10^{-3}	ε, M^{-1} cm^{-1}
Bipy(III, IV)·2H_2O	525	19.0	530
	555	18.0	455
	684	14.5	561
Phen(III, IV)·CH_3COCH_3	525	19.0	509
	555	18.0	427
	684	14.5	553

Solution Chemistry. Lowering the pH of (III, IV) dimer solutions causes a rapid decrease in absorbance of the near infrared band for both bipyridyl and phenanthroline complexes (Figure 3). Difference spectra (vide infra) indicate that the absorbance of the 684-nm band is decreased by the diminished contribution from the overlapping near infrared band. The remainder of the visible spectrum is relatively unaffected by the change in pH, although the higher energy features at 525 and 55 nm are obscured by the tail of ultraviolet bands which shift toward the visible region. The originally green (III, IV) dimer solutions are observed to become red upon acidification—this change in appearance, like the change in absorption spectrum, is reversible upon addition of sodium acetate solution. Addition of strong bases such as sodium hydroxide produces hydrous manganese oxides unless added extremely gradually. The pH-induced changes are not found strictly to be reversible—addition of base qualitatively returns the absorption spectrum to that of the original solution, but with slight (<5%) loss of intensity. Subsequent observations revealed that solutions of the (III, IV) dimers are unstable at low pH—if allowed to stand for several days, low pH (<4) solutions become colorless, and all Mn is present in the divalent state. The decomposition rate increases with decreasing pH. Hence the failure of the spectrum completely to return to that of the initial solution can be ascribed to instability of the species present at low pH.

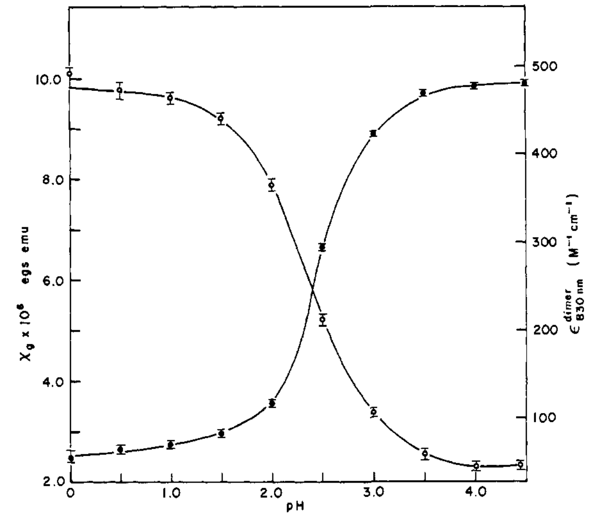


Figure 4. pH dependence of solution specific susceptibility (open circles) and ϵ_{830nm} (closed circles) for bipyridyl(III, IV) dimer in 0.04 M aqueous bipyridyl, 1 M $NaNO_3$ solutions at 25.0 °C.

Difference spectra of the bipyridyl(III, IV) dimer at high and low pH and those of the phenanthroline analogue are very similar. Both spectra exhibit the broad near infrared band as the salient feature, with a broad maximum at approximately 830 nm. The difference spectra underscore the great breadth of the near IR band, estimated from these data to be 0.46 μm^{-1} (using the bandwidth definition of Hush[4]).

Plaksin et al.[1] reported that the bipyridyl(III, IV) dimer is strongly antiferromagnetically coupled, such that the room temperature magnetic moment per dimer is 2.5 μ_B, decreasing to 1.8 μ_B at 77 K. Our measurements down to 4 K find a limiting value of 1.74 μ_B for this complex.[14] The magnetic properties of the phenanthroline analogue are essentially identical with those of the bipyridyl complex. To determine the extent to which the (III, IV) dimers remain dimeric in solution the solution magnetic susceptibility was measured by the NMR method. In Figure 4 is shown the pH dependence of the near infrared band maximum as determined from the pH difference spectra, and that of the specific susceptibility, as measured by the NMR method. The data are tabulated in Table III. It is evident that the *decrease* in absorbance at the near infrared band maximum is well correlated with the *increase* in specific susceptibility. The change in specific susceptibility, like the spectral change, is essentially reversible with pH, although the final value is slightly higher than the initial susceptibility, again indicative of some reduction of Mn(III) and Mn(V) to divalent manganese at low pH.

Electrochemistry. The electrochemistry of the manganese complexes was studied by cyclic voltammetry and controlled

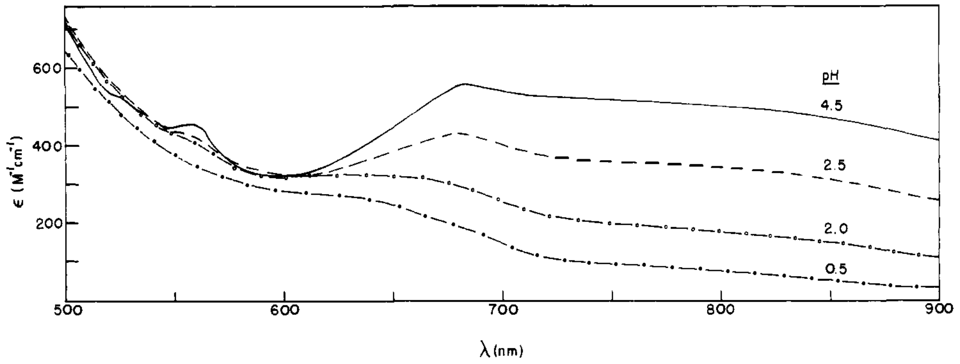


Figure 3. pH dependence of bipyridyl(III, IV) dimer visible spectrum in 0.05 M aqueous bipyridyl, 1 M $NaNO_3$ solution.

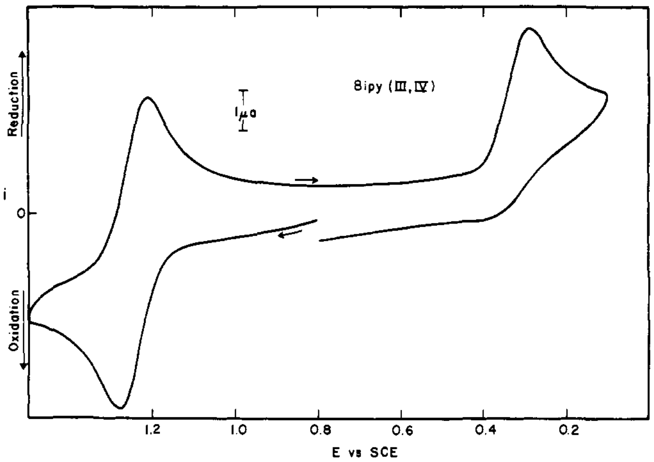


Figure 5. Cyclic voltammogram of bipyridyl dimer in CH_3CN on Pt disk. Scan rate 100 mV s^{-1}, supporting electrolyte 0.3 M tetraethylammonium perchlorate, potential vs. SCE.

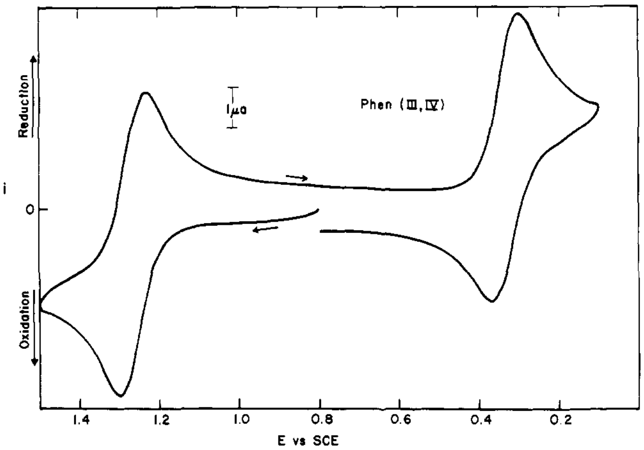


Figure 6. Cyclic voltammogram of phenanthroline(III, IV) dimer in CH_3CN on Pt disk. Scan rate 100 mV s^{-1}, supporting electrolyte 0.3 M tetraethylammonium perchlorate, potential vs. SCE.

Table III. Specific Solution Susceptibility (χ_g) and ϵ_{830nm} for Bipyridyl and Phenanthroline(III, IV) Complexes of Manganese

	Bipy(III,IV)·$2H_2O$		Phen(III, IV)·$(CH_3)_2CO$	
pH	ϵ_{830nm}	$\chi_g \times 10^6$, cgs emu	ϵ_{830nm}	$\chi_g \times 10^6$, cgs emu
4.5	476	2.27	508	2.44
4.0	470	2.33	508	2.44
3.5	460	2.54	502	2.85
3.0	410	3.37	473	2.98
2.5	280	5.22	368	4.21
2.0	123	7.89	176	5.97
1.5	91	9.23	96	8.14
1.0	80	9.63	85	9.09
0.5	73	9.76	70	9.63
0.0	67	10.16	50	9.93

potential coulometry to characterize the oxidation states available to these complexes. The cyclic voltammogram of the bipyridyl(III, IV) dimer in acetonitrile is presented in Figure 5. Examination of the cyclic voltammogram in water is not possible owing to the large background current from the competing oxidation of water. At a scan rate of 100 mV s^{-1} the bipyridyl(III, IV) dimer is found to undergo a reversible redox process at 1.25 V vs. the aqueous SCE, with peak anodic to cathodic current ratio very near unity. The separation between extrema is 65 mV, while a separation of 59/*n* mV is predicted for an electrochemically reversible *n*-electron process.[15] The difference is ascribable to instrumental factors since known reversible couples also yield waves separated by 65 mV.

Another wave is located at 0.29 V, presumably corresponding to the reduction of the (III, IV) complex to the (III, III). However, it is apparent that the subsequent anodic scan finds no (III, III) present to be reoxidized to (III, IV), since the anodic to cathodic peak current ratio is essentially zero. Scan rates up to 5 V s^{-1} have failed to find any evidence for oxidation of the putative (III, III) complex back to the (III, IV) dimer.

By contrast, the cyclic voltammogram of the phenanthroline(III, IV) dimer, shown in Figure 6, exhibits an anodic wave at 0.37 V associated with the reduction wave at 0.30 V to the (III, III) state. The reductions for both bipyridyl and phenanthroline(III, IV) dimers are assumed to be to the (III, III) state because the currents involved are nearly the same as those observed for the oxidation of these complexes, a process which is known to involve one electron (vide infra). Observation of the (III, III) to (III, IV) oxidation shows that at 100 mV s^{-1} scan rate the phenanthroline(III, III) complex exists long enough to be reoxidized to the (III, IV) state. The peak to peak separation is 70 mV, indicating that the couple is only quasi-reversible, while the ratio of peak anodic to cathodic currents is 0.6, a reflection of the limited stability of the (III, III) state on the cyclic voltammetric time scale. The phenanthroline(III, IV)/(IV, IV) couple yields anodic and cathodic waves corresponding to those observed for the bipyridyl(III, IV/(IV, IV) couple, with $E = 1.26$ V, peak to peak separation of 65 mV, and peak anodic to cathodic current ratio of approximately unity.

All cyclic voltammmetry experiments were performed in 0.3 M tetraethylammonium perchlorate. At lower electrolyte concentrations both the (III, IV)/(IV, IV) and (III, III)/(III, IV) couples shift to higher potential and become more irreversible. This effect is thought to be due to ion pairing of perchlorate with the highly charged cationic manganese complexes. The conproportionation constant for (III, III) + (IV, IV) = 2(III, IV), estimated from the cyclic voltammetry data, is $10^{15.6}$.

Controlled potential coulometry of the (III, IV) complexes in acetonitrile after drying in a vacuum oven demonstrates that both oxidations are one-electron processes, definitively identifying the products as the (IV, IV) dimers.

Electrolysis of aqueous solutions of the complexes at 1.2 V on a platinum mesh electrode oxidized the green (III, IV) solutions to red-brown solutions, spectral examination of which revealed an isosbestic point at 642 nm. Attempts to oxidize the (III, IV) dimers chemically with dichlorine or cerium(IV) in acetonitrile were partially successful. In both cases the redox potential of the oxidant is not sufficiently greater than that of the (III, IV)/IV, IV) couple to permit complete oxidation without a huge excess of oxidant. Optical spectra of the products of chemical oxidation are identical with those of (III, IV) solutions partially oxidized electrochemically.

Discussion

Infrared Spectra. Assignment of the bridging modes of the complexes was sought to permit the identification of the di-μ-oxo bridging group in the complexes which have not yet been examined by x-ray diffraction. Assignment of the bridging modes of the bipyridyl(III, IV) dimer would allow a more confident presumption of a similar structure in the phenanthroline complexes if the same bridging mode were found.

To determine the position of the bridge stretching modes, isotopic substitution experiments were performed. Mixed isotopic substitution was employed in order to provide an internal reference between labeled and unlabeled oxo bridges. Recrystallizing the bipyridyl(III, IV) dimer from ^{18}O-enriched aqueous bipyridyl buffer at 80 °C produces a shoulder on the 688-cm^{-1} band, which is lost on back substitution. No effect on the infrared spectrum of similarly treated $Fe(bipy)_3(ClO_4)_2$ was observed. Recrystallizing the complex from deuterated buffer under otherwise identical conditions causes no change in the 688-cm^{-1} band. In light of these results the 688-cm^{-1} band is considered to be one of the four expected bridging modes of the bipyridyl(III, IV) dimer. The 688-cm^{-1} band had been suggested to be a bridging mode by Castrillo,[16] as had several other bands, but no evidence supporting these assignments was reported.

Assignment of the Mn_2O_2 stretching mode to a band in this region is reasonable by comparison with a number of di-μ-oxo bridged complexes reported in the literature.[17] Boucher and Coe[17] have assigned bands in the 655–642-cm^{-1} region to the Mn_2O_2 stretch in manganese Schiff base complexes. A doublet centered at 660 cm^{-1} in the polymeric complex thought to be a di-μ-oxo bridged Mn(IV)-picolinate complex has been tentatively assigned to the stretch of the bridging Mn_2O_2 group.[18]

Considering these results assignment of the 688-cm^{-1} band to a stretching mode of the di-μ-oxo bridge is reasonable. A similar band appears at 686 cm^{-1} for the phenanthroline(III, IV) complex, and at 692 cm^{-1} for the phenanthroline(IV, IV) complex; hence a di-μ-oxo bridged structure is indicated for these complexes.

Electronic Spectra. Nyholm and Turco[2] recorded the visible spectrum of an aqueous solution of bipyridyl(III, IV); they reported no absorption maximum but a continuous decrease in extinction coefficient from 200 at 500 nm to 50 at 750 nm, a situation which subsequently has been recognized to be due to hydrolysis. Upon dissolution in water, the originally green (III, IV) complexes rapidly yield a red solution (with spectrum like that described by Nyholm and Turco) which deposits red hydrous manganese oxides within a few hours.

Although the (III, IV) dimers are unstable in water, it has proven possible to work with the complexes in aqueous bipyridyl or phenanthroline buffer at pH 4.5. Neither buffering (with acetate) nor presence of ligand alone suffices to stabilize the complexes; the ligand *as* the buffer is the sole condition under which the spectrum of the complex is not time dependent.

The bands at 525, 555, and 684 nm are analogous to those in other bis(bidentate)diaquoMn(III) complexes,[19] and appear to be characteristic. Note that since the 525- and 555-nm bands are shoulders, the maxima actually lie at higher energy. Comparison of the (III, IV) dimer spectra with that of bis(malonato)diaquoMn(III)[19] suggests that the bands in the latter at 446, 461, and 741 nm (2.24, 2.17, and 1.35 μm^{-1}) correspond to the 525-, 555-, and 684-nm bands of the (III, IV) dimers. The 525- and 555-nm bands are tentatively assigned as d–d bands to split components of the $^5T_{2g}$ state in octahedral symmetry. The 684-nm band is interesting because a similar band is found at nearly the same energy for other bis(bidentate)diaquoMn(III) complexes, suggesting that it is due to the water ligands. The 684-nm band has been previously assigned as a ligand to metal charge transfer band from oxygen to Mn(III).[19]

Despite the considerable similarity between the spectra in the higher energy region, the broad feature in the near IR of the (III, IV) dimers lacks a counterpart in the bis(malonato)diaquoMn(III) ion. Lowering the pH of (III, IV) solutions to approximately pH 1 yields a spectrum similar to bis(malonato)diaquoMn(III); the most striking difference is the loss of the near infrared band. This change is reversible—upon raising the pH, the original dimer spectrum returns.

Furthermore, the near IR band is not attributable to the Mn(IV). As pointed out by Plaksin et al.,[1] the greater charge on the Mn(IV) than the Mn(III) ion is expected from simple electrostatic considerations to generate a greater ligand field splitting. This expectation is verified for the phenanthroline(IV, IV) dimer, which has no absorption bands in the visible region. The spin allowed d–d bands of the Mn(IV) ion are evidently all shifted to higher energy, out of the visible region and into the ultraviolet, where they are obscured by the much more intense $\pi \rightarrow \pi^*$ bands of the ligand.

Thus the broad near IR band lacks an analogue in both monomeric Mn(III) ions of the same symmetry and in the phenanthroline(IV, IV) dimer, and therefore can be due to neither the Mn(III) nor Mn(IV) ion alone. It is considered that this band is due to a mixed valence, or intervalence transfer absorption transition. Mixed valence transitions correspond to displacing an electron from the more reduced metal, Mn(III), to the more oxidized, Mn(IV). Similar bands found in other polynuclear complexes constitute the subject of several reviews.[3-5]

The crystal structure results[1] and the appearance of electronic absorption bands attributable to the Mn(III) ion establish that the ions retain discrete identities, and thus belong to class II in the classification scheme of Robin and Day.[3]

Solution Chemistry. The pH dependence observed for the solution susceptibility and extinction coefficient of the near IR band maximum at 830 nm establish that the near IR band is found only in the dimeric spin-coupled (III, IV) complexes. Evidently at low pH protonation of the oxo bridge occurs, leading to dimer cleavage, which both renders the intervalence transfer absorption impossible and destroys the magnetic coupling of the ions. Isolation of one of the low pH products (vide infra) demonstrates that bridge cleavage, and not merely protonation, is responsible for the optical and magnetic changes at low pH. Thus lowering the pH should *decrease* the intensity of the near IR band with concomitant *increase* in the solution susceptibility, as observed. Both changes with pH are reversible, indicating that lowering the pH shifts the position of a proton-dependent equilibrium. A plot of log $[X - X(\text{pH } 0)/X(\text{pH } 4.5) - X]$ (where $X = \chi_g$ or $\epsilon_{830\text{nm}}$ at a particular pH) vs. pH yields a value for n, the number of protons involved in the equilibrium, of 1.3 H$^+$/dimer. This probably indicates one proton in the equilibrium, since the decomposition which occurs at low pH will tend to decrease $\epsilon_{830\text{nm}}$(pH 0) and increase χ_g(pH 0), in both cases increasing the observed value for n. Cleavage of the (III, IV) dimers into the monomeric constituents does not account quantitatively for the solution susceptibility data, however, since a limiting low pH specific susceptibility of approximately 14 × 10^{-6} cgs emu is predicted for both bipyridyl and phenanthroline cases. This calculation assumes the Mn(III) ion to be high spin; the limiting low temperature magnetic moment of 1.74 μ_B which we observed[14] lacks the orbital contribution expected for a low spin Mn(III). If the Mn(III) were low spin, a low pH susceptibility of 8.6 × 10^{-6} cgs emu would be predicted.

From the known magnetic moment of the phenanthroline(IV, IV) dimer at 298 K (1.86 μ_B),[9] and assuming the same moment for the bipyridyl(IV, IV) complex, it is calculated that the specific susceptibility should increase to 9.74 × 20^{-6} cgs emu at low pH for the bipyridyl case, and to 10.05 × 10^{-6} cgs emu for the phenanthroline case, again assuming the Mn(III) ion to be high spin (for low spin Mn(III) $\chi_g \simeq 3.6 \times 10^{-6}$ cgs emu). The observed values are 10.16 and 9.93 × 10^{-6} cgs emu, respectively, for the pH 0 solutions. The low pH solutions are unstable, readily reducing to Mn(II)—for this reason the susceptibilities will tend to be high.

The observed limiting low pH susceptibilities of approximately 10 × 10^{-6} cgs emu are readily explained by an equilibrium involving (IV, IV) dimeric ions, thus:

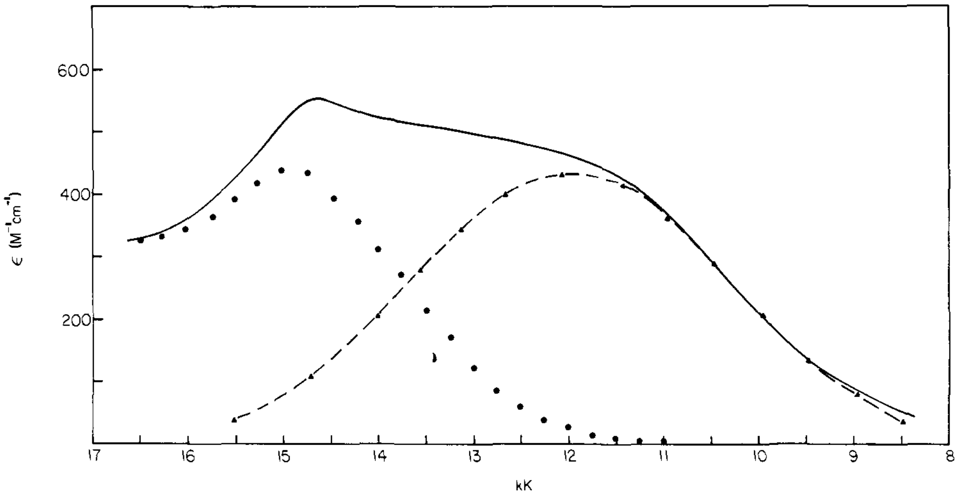
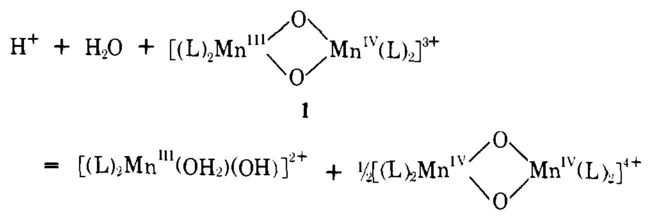


Figure 7. Near infrared spectrum of bipyridyl(III, IV) dimer in deuterated bipyridyl buffer, pD 4.1.



$$H^+ + H_2O + [(L)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(L)_2]^{3+} = [(L)_2Mn^{III}(OH_2)(OH)]^{2+} + \tfrac{1}{2}[(L)_2Mn^{IV}(\mu\text{-}O)_2Mn^{IV}(L)_2]^{4+}$$

1

The work of Goodwin and Sylva[9] corroborates this suggestion nicely. These workers found that dissolution of $Mn(phen)(OH_2)(Cl)_3$ in slightly acidified aqueous phenanthroline solution leads to a green solution which becomes red upon addition of concentrated perchloric acid and deposits the phenanthroline(IV, IV) dimer in yields approaching 50%. In our investigation of this reaction we have isolated the green intermediate and determined it from electronic and infrared spectral data to be the phenanthroline(III, IV) complex, produced by disproportionation of the starting material. Acidification of phenanthroline(III, IV) as described by Goodwin and Sylva thus leads to phenanthroline(IV, IV) dimer in a reaction strictly analogous to that postulated here for the bipyridyl(III, IV) dimer. Isolation of the bipyridyl(IV, IV) complex as the ClO_4^- salt was foiled by the much greater solubility of bipyridyl(IV, IV) than the phenanthroline analogue. Numerous other anions were tried to isolate the product but without success.

Mixed Valence Bands. Hush[4] has predicted that the energy of an intervalence transfer band should vary with solvent as $1/n^2 - 1/D$, where n is the refractive index and D the dielectric constant of the solvent. Only small shifts are predicted for these complexes since the metal-metal distance is short (2.716 Å);[1] electron transfer from one ion to the other thus entails a much smaller dipole moment change than in the ruthenium complexes previously examined, where the metal-metal distance is approximately 7 Å.[20-22]

For the (III, IV) dimers the 684-nm band precludes observation of the mixed valence band maximum, but the position of the low-energy shoulder of the bands depends on solvent in a fashion opposite to that predicted by Hush, in contrast to the behavior observed for other mixed valence complexes.[20-24] The reason for this discrepancy is not known—specific interactions with solvent or solvent dependent changes in bandwidth could explain this result within the framework of Hush's theory.

The near infrared band in Figure 7 can be approximated by a Gaussian with $\bar{\nu}_{max} = 1.20\ \mu m^{-1}$, $\epsilon_{max} = 430\ M^{-1}\ cm^{-1}$, and full width at half maximum of 0.40 μm^{-1}. The band half-width is defined by Hush[4] as that value of $\bar{\nu}$ at which $A(\bar{\nu})\bar{\nu}_{max} = \frac{1}{2}A_{max}\bar{\nu}$ (where $A(\bar{\nu})$ is the absorbance at $\bar{\nu}$). For the (III, IV) dimers the experimental band width is 0.46 μm^{-1}, compared to the 0.53 μm^{-1} value calculated from $\bar{\nu}_{max} = (\Delta\bar{\nu}_{1/2})^2/2.31$, where $\Delta\bar{\nu}_{1/2}$ is the band half-width as defined above.[4] This value is 87% of that calculated; similar comparisons on class II systems have shown ratios of observed half-width to calculated half-width of 1.17 for $[(bipy)_2ClRu(pyz)RuCl(bipy)_2]^{3+}$,[20] 1.3 for $[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{4+}$,[21,22] 1.08 for $[(NH_3)_5Ru(pyz)Ru(bipy)_2(pyz)Ru(NH_3)_5]^{8+}$ [25] (where pyz = pyrazine), and 1.44 for biferrocene(II, III) picrate.[26] Thus the observed bandwidth of the near IR band of the (III, IV) dimers agrees well with Hush's prediction.

From estimates of the energy and extinction coefficient of the mixed valence band in the (III, IV) dimers and their known Mn–Mn distance the delocalization coefficient, α^2, can be calculated from

$$\alpha^2 = \frac{(4.25 \times 10^{-4})\epsilon_{max}\Delta\bar{\nu}_{1/2}}{\bar{\nu}_{max}r^2}$$

where r is the distance between the metal ions (in Å), $\Delta\bar{\nu}_{1/2}$ the bandwidth as depicted above, and other terms have their usual significance.[4] For the (III, IV) dimers, using $r = 2.72$ Å, $\bar{\nu}_{max} = 1.205\ \mu m^{-1}$, $\epsilon_{max} = 430$, and $\Delta\bar{\nu}_{1/2} = 0.46\ \mu m^{-1}$, value of $\alpha^2 = 0.01$ is obtained, which is consistent with a class II description. This value of α^2 implies that the electron spends 99% of the time on the Mn(III) ion.[4] Comparison with selected values in the literature[20,22,25] reveals that the extent of delocalization calculated is relatively high for this complex, largely as a result of the short metal-metal distance. Although the intervalence transfer absorption of the (III, IV) dimers is comparable with other mixed valence complexes in intensity, bandwidth and energy, the short metal-metal distance leads to high calculated values of the delocalization coefficient. This is particularly evident in comparison with $[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{4+}$ ($\alpha^2 = 0.0026$),[22] where the close parallel in optical parameters is broken by the metal-metal distance of approximately 7 Å for the Ru complex, vs. 2.7 Å for the Mn complex.

The calculated delocalization coefficient of the (III, IV) dimers is close to that estimated for $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$ ($\mu^2 = 0.009$).[27] However, the optical properties[28] of the latter complex do not conform to Hush's predictions and probably reflect a delocalized ground state,[29] invalidating comparison between them. Hush[4] has also shown that for class II systems the energy of the optical intervalence transfer is predicted to be approximately four times greater than the activation energy of the associated thermally activated adiabatic electron transfer. For the (III, IV) dimers, a thermal activation energy of 8.6 kcal mol^{-1} is calculated, from which a maximum thermal electron transfer rate of $10^6\ s^{-1}$ is estimated,[4] assuming no activation entropy, and a transmission coefficient of unity (in addition to neglecting any splitting of the potential energy surfaces). This estimate suggests that lattice polarization participates in the valence trapping which occurs in the solid state, since the crystallographic data of Plaksin et al.[1] lack any indication of the thermally average bond lengths expected from such an electron transfer rate. Thus classification of complexes in the scheme of Robin and Day[3] from solid state data may be subject to ambiguities from lattice effects.

The solution spectral data, as well as the crystallographic results, indicate class II behavior for these complexes. The deep trapping observed in solution (from the presence of a mixed valence band) can be explained by the proposed high spin nature of the Mn(III). Electron transfer from Mn(III) to Mn(IV) alters the population of the antibonding e_g orbitals (in octahedral symmetry) on both ions, changing bond orders and necessitating changes in bond lengths. The energy necessary to do this contributes to the thermal activation energy, and is sufficiently great to make electron transfer slow at room temperature for the solution case as well as in the solid state.

In light of this, the reversible electron transfer observed in the cyclic voltammogram is surprising. The isoelectronic high spin Cr(II)/Cr(III) couple (e.g., $Cr(OH_2)^{2,3+}$) is very irreversible at all electrodes, whereas the low spin $Cr(bipy)_3{}^{2,3+}$ couple is reversible.[30] Thus the electrochemical behavior of the (III, IV) complexes is more consistent with low spin Mn(III), while the magnetic, crystallographic, and optical data are more consonant with high spin Mn(III). It may be that the bond length rearrangements accompanying oxidation of high spin Mn(III) to Mn(IV) are sufficiently fast relative to the cyclic voltammetric time scale that they are not rate limiting. The reason for the difference in behavior between Cr and Mn complexes is not clear.

Conclusions

Our observations on some of the first Mn(III)–Mn(IV) complexes to be examined in detail indicate that the electronic structure of these complexes is compatible with that of other class II systems. A broad mixed valence band is found in the near IR which appears to conform closely to Hush's predictions regarding bandwidth, although it does not exhibit the expected solvent dependence. The reason for the latter discrepancy is not clear but may be attributable to specific interactions with the solvents. In addition, it appears as though valence trapping by the lattice may render assignment of class II behavior from solid state data ambiguous. The results of magnetic susceptibility and EPR studies[14] will be reported in a subsequent publication.[31]

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