nymous with an increase in solvatochromism. The average arrangement of solvent molecules will also differ from that in the mononuclear complex, as shown in (1).

Changes in bonding will alter the effective ground- and excited-state dipole moments, which will affect the strength of the solvent-solute interactions, i.e. the second and third terms of McRae's equation (eq 1). tom Dieck has demonstrated the effect of decreasing the difference between μ_g and μ_e, by increasing the amount of mixing of the metal and diimine ligand orbitals, in an extensive series of $Mo(CO)_4$(diimine) complexes (and phosphine-substituted analogues).[47-50] Increasing the mixing, by making the ligand a stronger π acceptor or by substituting phosphines for two of the carbonyls, gives the electronic transition less charge-transfer character and thus decreases the solvatochromism. This effect can be seen in the dinuclear complexes, the solvatochromism of $(CO)_5WpyzW(CO)_5$ being much greater than that of its PBu_3-substituted analogue (Table I).

The lowering of the π^* level when the second metal is coordinated may increase the metal-ligand orbital mixing and decrease the solvatochromism. However, both σ and π effects should be considered in this context. Unfortunately, there is little conclusive evidence to indicate what changes in bonding are occurring; changes in (C-O) force constants are small and variable, and metal oxidation potentials are irreversible.[13,20,26,51,52]

Conclusion

The available experimental evidence supports the view that the solvatochromism of centrosymmetric dinuclear metal carbonyl complexes is caused mainly by dipole-dipole interactions. However, the reasons for differences in the solvatochromism of the mono- and dinuclear species remain unclear. Clearly, more detailed studies, employing larger numbers of solvents and related series of bridging ligands, are necessary before the subtleties of the solvatochromism of these species can be properly understood.

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Binuclear Bis(μ-oxo)dimanganese(III,IV) and -(IV,IV) Complexes with *N,N'*-Bis(2-pyridylmethyl)-1,2-ethanediamine

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The magnetic susceptibility, EPR and visible spectra, and electrochemical properties of the mixed-valence complex $[(bispicen)MnO_2Mn(bispicen)](ClO_4)_3$ [bispicen = *N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine, $C_{14}H_{18}N_4$] are reported. The complex has a doublet ground state with $J = -140 \pm 1$ cm^{-1}; the EPR spectrum shows a 16-line pattern. The complex exhibits quasi-reversible waves at 191 and 798 mV (vs Ag/AgCl), corresponding to the III/III ↔ III/IV and III/IV ↔ IV/IV couples, respectively. The IV/IV complex $[(bispicen)MnO_2Mn(bispicen)](ClO_4)_4\cdot 2CH_3CN$ has been synthesized, and its crystal structure has been determined. The complex crystallizes in the monoclinic space group $C2/c$ with four centrosymmetric binuclear complexes in a cell of dimensions $a = 12.070$ (3) Å, $b = 15.871$ (3) Å, $c = 22.016$ (5) Å, and $\beta = 97.46$ (2)°. The structure has been refined to a final value of $R = 0.040$ based on 3078 independent intensities gathered at −100 °C. The Mn-Mn separation is 2.672 (1) Å, and the Mn-O-Mn bridging angle is 95.0 (2)°. The magnetic properties of the dimer are consistent with a singlet ground state, and $J = -125.6 \pm 0.2$ cm^{-1}. The electronic spectrum is in some ways similar to that of the III/IV complex, but there is no intervalence charge-transfer band.

Introduction

There is continuing interest in the bis(μ-oxo)dimanganese complexes, both because of the similarity of some of their physical properties to those of the water-oxidizing enzyme in photosystem II[2] and because of their inherent potential to act as redox catalysts. Gref et al.[3] have shown that the mixed-valent 2,2'-bipyridine complex $[(bpy)_2MnO_2Mn(bpy)_2]^{3+}$ and its 1,10-phenanthroline (phen) analogue serve as electrocatalytic oxidants for alcohols and ethers, and Ramaraj et al.[4] have reported that the bpy complex oxidizes water in the presence of a chemical oxidant. As a result of this work, and some preliminary results of our own,[5,6] we have undertaken a comprehensive synthetic program designed to produce bis(μ-oxo)dimanganese species whose electrochemical properties may permit their use as redox catalysts.

In order to stabilize the manganese(III) species that are formed during the presumed catalytic cycles, we have focused our attention on complexes formed with tetradentate ligands. We have provided brief preliminary accounts of the synthesis of the mixed-valent manganese(III,IV) species formed from the ligands *N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen)[5] and tris(2-pyridylmethyl)amine (tmpa),[6] and Suzuki et al. have subsequently described the oxidized manganese(IV,IV) form of the latter complex.[7] Other workers have structurally characterized the mixed-valent forms of the bpy[8] and phen[9] complexes and more recently the tris(2-aminoethyl)amine (tren),[10] 1,4,7,10-tetraaza-

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Table I. Crystallographic Data for $[(\text{bispicen})\text{MnO}_2\text{Mn}(\text{bispicen})](\text{ClO}_4)_4\cdot 2\text{CH}_3\text{CN}$

formula	$Mn_2C_{32}H_{42}Cl_4N_{10}O_{18}$	space group	*C*2/*c*
a, Å	12.070 (3)	*T*, °C	−100
b, Å	15.871 (3)	λ, Å	0.71073
c, Å	22.016 (5)	μ, mm^{-1}	0.92
β, deg	97.46 (2)	NO[a]	4391
V, Å^3	4181 (2)	NO[$>3\sigma(I)$]	3078
Z	4	*R*	0.040
fw	1106.45	R_w	0.054

[a] NO = number of observations.

cyclododecane (cyclen),[11] and *N,N*-bis(2-pyridylmethyl)glycinato[12] complexes. Very recently, both we[13] and Spreer and co-workers[14] have characterized salts of the 1,4,8,11-tetraazacyclotetradecane (cyclam) complex. In addition to the tmpa complex noted above,[7] the only Mn(IV,IV) forms to be structurally characterized are the phen complex[9] and a triazacyclononane complex.[15] Wieghardt et al.[15] have recently reported the formation and structure of a tris(μ-oxo)dimanganese(IV,IV) complex, which necessarily has a much shorter Mn···Mn separation than that found in these bis(μ-oxo) species.

We here report the synthesis and characterization of the III/IV and IV/IV forms of the bispicen complex, $[(\text{bispicen})\text{MnO}_2\text{Mn}(\text{bispicen})]^{3+}$ and $[(\text{bispicen})\text{MnO}_2\text{Mn}(\text{bispicen})]^{4+}$.

Experimental Section

Magnetic susceptibility measurements were performed by the Faraday method on equipment described elsewhere.[16] The molar susceptibilities were corrected for ligand diamagnetism by using Pascal's constants.

EPR spectra were recorded at liquid-helium temperature on a Bruker ESP 300 spectrometer operating at a frequency of 9.38 GHz. Samples were examined as frozen glasses in *N*-methylformamide solution.

Electronic spectra were obtained in aqueous solution and in acetonitrile on a Perkin-Elmer Lambda 17 spectrometer or on a Varian/Cary 2390 spectrometer.

Cyclic voltammograms were recorded in water on a BAS 100A electrochemical analyzer using a glassy-carbon working electrode, a platinum-wire auxiliary electrode, and a silver/silver chloride reference electrode. Solutions were approximately 2 mM, with 0.1 M sodium perchlorate as supporting electrolyte.

Synthesis of the Complexes. The synthesis of the III/IV complex has been reported earlier.[5] The IV/IV complex was initially synthesized electrochemically. In a typical experiment, 1.25 g (1.3 mmol) of $Mn_2O_2(\text{bispicen})_2(ClO_4)_3\cdot 3H_2O$ was dissolved in 150 mL of CH_3CN. An 8.61-g (0.0375 mol) amount of NEt_4ClO_4 was added, and the mixture was stirred until all the solids had dissolved. The solution was oxidized by using Pt-gauze electrodes starting at 0.9 V (vs Ag/AgCl) and increasing slowly to 1.2 V as the current allowed. A total of 156 C was counted in approximately 1 h. The dark solution was cooled in the refrigerator overnight. The red crystals that separated were collected by filtration and washed with cold acetonitrile. Yield: 0.76 g (52%). The complex crystallizes with 2 mol of acetonitrile/mol of dimer, $[(\text{bispicen})_2\text{Mn}_2\text{O}_2](\text{ClO}_4)_4\cdot 2\text{CH}_3\text{CN}$. Anal. Calcd for $Mn_2C_{32}H_{42}Cl_4N_{10}O_{18}$: C, 34.74; H, 3.83; Cl, 12.82; N, 12.66. Found: C, 34.91; H, 3.81; Cl, 12.64; N, 12.69.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^4) for $[(\text{bispicen})\text{MnO}]_2(\text{ClO}_4)_4\cdot 2\text{CH}_3\text{CN}$

	x	*y*	*z*	*U*(eq),[a] Å^2
Mn(1)	1116 (1)	8522 (1)	2572 (1)	141 (1)
O(1)	0	9293 (2)	2500	155 (9)
O(2)	0	7753 (2)	2500	164 (9)
N(1A)	1322 (2)	8486 (2)	3494 (1)	183 (8)
N(8A)	2407 (2)	9360 (2)	2792 (1)	212 (9)
N(1B)	1298 (2)	8578 (2)	1683 (1)	182 (8)
N(8B)	2380 (2)	7662 (2)	2518 (1)	203 (8)
C(2A)	1053 (3)	7826 (2)	3830 (2)	196 (10)
C(3A)	1222 (3)	7853 (3)	4461 (2)	274 (12)
C(4A)	1659 (3)	8576 (3)	4752 (2)	320 (12)
C(5A)	1933 (3)	9256 (3)	4402 (2)	295 (12)
C(6A)	1773 (3)	9190 (2)	3770 (2)	229 (10)
C(7A)	2111 (3)	9841 (2)	3332 (2)	257 (11)
C(9A)	3464 (3)	8874 (3)	2946 (2)	263 (11)
C(2B)	1007 (3)	9253 (2)	1321 (2)	213 (10)
C(3B)	1130 (3)	9236 (3)	706 (2)	282 (12)
C(4B)	1572 (3)	8525 (3)	466 (2)	329 (13)
C(5B)	1909 (3)	7850 (3)	845 (2)	297 (12)
C(6B)	1747 (3)	7892 (2)	1454 (2)	203 (10)
C(7B)	2066 (3)	7214 (2)	1925 (2)	249 (11)
C(9B)	3457 (3)	8121 (3)	2528 (2)	238 (11)
Cl(1)	231 (1)	1663 (1)	1260 (1)	315 (3)
O(3)	1218 (3)	2117 (2)	1167 (1)	389 (10)
O(4)	4 (3)	1022 (2)	803 (1)	477 (11)
O(5)	−692 (3)	2237 (3)	1224 (3)	815 (19)
O(6)	383 (4)	1268 (3)	1849 (2)	699 (16)
Cl(2)	3777 (1)	516 (1)	1558 (1)	270 (3)
O(7)	3729 (3)	−372 (2)	1650 (2)	468 (11)
O(8)	3355 (3)	721 (2)	938 (1)	514 (12)
O(9)	4899 (3)	790 (3)	1691 (2)	632 (14)
O(10)	3102 (3)	908 (3)	1971 (2)	607 (14)
N(1N)	3599 (4)	10931 (3)	4527 (2)	612 (17)
C(1N)	4232 (4)	10990 (3)	4946 (2)	400 (15)
C(2N)	5036 (4)	11058 (3)	5496 (2)	529 (18)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

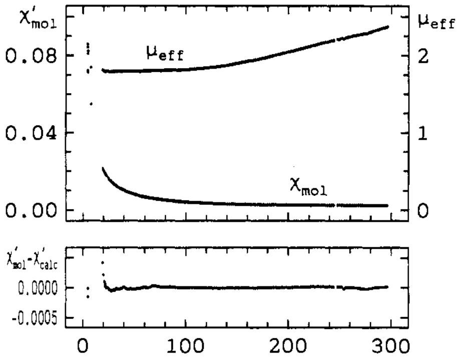

Figure 1. Magnetic susceptibility (left scale) and effective magnetic moment (right scale) of a powdered sample of the mixed-valent complex $[(\text{bispicen})\text{MnO}]_2(\text{ClO}_4)_3\cdot 3\text{H}_2\text{O}$.

The complex can also be formed chemically, by disproportionation of the III/IV dimer in acidic solution; this is in principle the method used by Goodwin and Sylva in the original synthesis of the phen IV/IV complex.[17] In a typical experiment, 300 mg (0.31 mmol) of $Mn_2O_2(\text{bispicen})_2(ClO_4)_3\cdot 3H_2O$ was extracted on a filter with the amount of 1 M hydrochloric acid necessary to dissolve the compound at ambient temperature (6 mL). A 10% solution of $NaClO_4$ (0.5 mL) and 1 M $HClO_4$ (0.5 mL) were added to the filtrate, and the resulting solution was cooled on ice for 2 h. The crystals that had separated were then filtered out and washed with a 1 M solution of $NaClO_4$ and with ethanol (95%). Yield: 73 mg (23%). The compound was recrystallized from 0.1 M $HClO_4$ to give 52 mg of $Mn_2O_2(\text{bispicen})_2(ClO_4)_4\cdot 3H_2O$. Anal. Calcd for $Mn_2C_{28}H_{42}Cl_4N_8O_{21}$: C, 31.21; H, 3.93; Cl, 13.10; N, 10.40. Found: C, 31.26; H, 3.34; Cl, 13.28; N, 10.42.

X-ray Structure Determination. The structure of the perchlorate salt of the IV/IV complex, $[(\text{bispicen})\text{MnO}_2\text{Mn}(\text{bispicen})](\text{ClO}_4)_4\cdot 2\text{CH}_3\text{CN}$, was determined at −100 °C (173 K) on a Nicolet R3m/V diffractometer equipped with a molybdenum tube [$\lambda(K\alpha_1)$ = 0.70926 Å; $\lambda(K\alpha_2)$ = 0.71354 Å] and a graphite monochromator. Crystal data and experi-

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mental parameters are tabulated in Table I. The data were corrected for Lorentz–polarization effects and for absorption. The structure was solved by Patterson and difference Fourier methods and refined by least-squares techniques; the programs used were from the SHELXTL system.[18]

The complex crystallizes in the centrosymmetric monoclinic space group $C2/c$ with four binuclear cations in the unit cell. All hydrogen atoms were placed in fixed calculated positions (C–H = 0.96 Å), while other atoms were refined anisotropically. The final values of the conventional R factors were $R = 0.0405$ and $wR = 0.0544$, based on 3078 independent data with $I > 3\sigma(I)$. The values of the agreement factors based on the entire data set are $R = 0.0666$ and $R_w = 0.0711$. The final values of the atomic positional parameters, along with their estimated standard deviations, are presented in Table II. Hydrogen atom parameters and anisotropic thermal motion parameters are available as supplementary material.

Results and Discussion

The Mixed-Valent Mn(III,IV) Complex. Magnetic Susceptibility. The temperature dependence of the magnetic susceptibility of a powdered sample of the mixed-valent III/IV complex was measured in the range 4–296 K. As is shown in Figure 1, the effective magnetic moment at room temperature is approximately 2.50 μ_B, declining monotonically to a value of 1.81 μ_B at 30 K; the moment is essentially constant below 30 K. The value of 1.81 μ_B corresponds well to the value of $\sqrt{3}$ μ_B expected for the spin-only moment of a complex with one unpaired electron and indicates that the ground state is a doublet.

The susceptibility data were analyzed by fitting them to the expression

$$\chi'_{\text{mol}} = -\frac{N}{H}\,\frac{\sum_i \frac{\delta E_i}{\delta H}\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} + K + \frac{C}{T}$$

where the E_i values are the energies of the 20 components of the ground-state manifold. The term C/T accounts for paramagnetic impurities, and K accounts for TIP (temperature-independent paramagnetism) and minor deviations in the correction for the diamagnetic contribution of the atoms. The fitting was accomplished with the isotropic spin Hamiltonian

$$H = -2J\vec{S}_1\cdot\vec{S}_2 + g_1\beta\vec{S}_1\cdot\vec{H} + g_2\beta\vec{S}_2\cdot\vec{H}$$

where $\vec{S} = \vec{S}_1 + \vec{S}_2$ and we have set $g_1 = g_2$. The Heisenberg term $-2J\vec{S}_1\cdot\vec{S}_2$ gives energies of the quartet, sextet, and octet states relative to the doublet ground state of $-3J$, $-8J$, and $-15J$, respectively. The fitting leads to a value of $2J = -280 \pm 2$ cm^{-1}. C was found to be 9.0×10^{-2}, which implies approximately 1% of a monomeric Mn(II) impurity.

This value of $J = -140 \pm 1$ cm^{-1} observed for the bispicen complex is similar to those of -150 ± 7, -148 ± 12, -146, and -151 cm^{-1} reported for the bpy,[19] phen,[9] tren,[10] and N$_3$O-py[12] complexes, respectively. The value of $J = -140$ cm^{-1} for the present complex means that the complex has a doublet ground state, with the quartet, sextet, and octet states lying at energies of 420, 1120, and 2100 cm^{-1}, respectively, higher than the ground state doublet.

EPR Spectra. The EPR spectrum of the III/IV complex was measured at 4.1 K and at 298 K. The spectra were recorded on a Bruker ESP-300 EPR spectrometer operating at 9.38 GHz (X-band) with magnetic field modulation of 100 kHz, modulation amplitude of 7 G, and microwave power of 10 mW. The room-temperature spectra of both solid- and solution-state samples were broad. The EPR spectrum of a frozen solution in N-methylformamide at 4.1 K is presented in Figure 2.

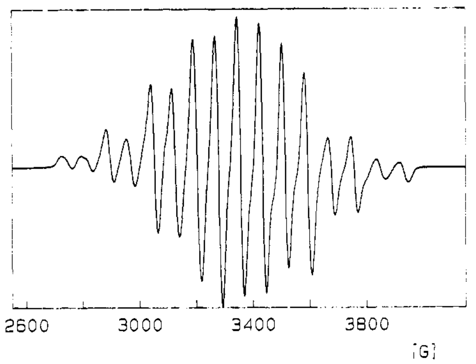

Figure 2. X-Band EPR spectrum of the mixed-valent complex [(bispicen)MnO]$_2$(ClO$_4$)$_3$·3H$_2$O (frozen solution in N-methylformamide) at 4.1 K.

The spectrum shown in Figure 2 consists of 16 lines. The EPR spectra of complexes of this type have traditionally been interpreted by means of the hyperfine term

$$H = (A_1I_1 + A_2I_2)\vec{S}$$

in the spin Hamiltonian, with $A_1 = 2A_2$. Here, $\vec{S}$ is the total spin given by $\vec{S} = \vec{S}_1 + \vec{S}_2$. In this interpretation,[19] the terms A_1 and A_2 are not local atomic hyperfine coupling constants but are transformed dimeric constants. Recently,[20] it was shown that use of the more physically appealing term

$$A_1\vec{S}_1\cdot\vec{I}_1 + A_2\vec{S}_2\cdot\vec{I}_2$$

in the spin Hamiltonian (where the hyperfine coupling constants are the normal local constants) with $S_1 = 2$, $S_2 = {}^3/_2$, and equal hyperfine constants $A_1 = A_2$ leads to a spectrum that should consist of 16 equally spaced lines with the intensity pattern 1,1,2,2,3,3,3,3,3,3,3,3,2,2,1,1. This is, of course, consistent with the result observed in Figure 2. The center of the spectrum corresponds to $g = 2.00 \pm 0.01$.

The observed spectrum comes exclusively from the doublet ($S = {}^1/_2$) ground state. The spacing between adjacent lines is equal to A, the hyperfine coupling constant, the pattern being centered around $(2g_1 - g_2)$. Hence, the present spectrum gives a value of $A = 78 \pm 1$ G. The spectrum reported here is similar to those reported for the phen and bpy complexes[19] and to those of related species, but it does not show the slight anisotropy seen in those previously reported spectra.

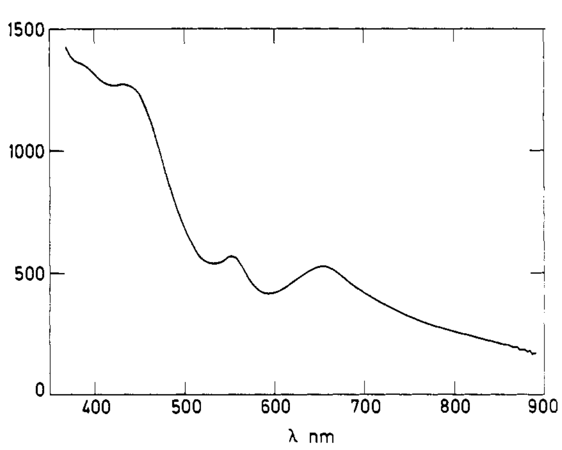

Figure 3. Absorption spectrum of the mixed-valent complex [(bispicen)MnO]$_2$(ClO$_4$)$_3$·3H$_2$O in water.

Electronic Spectra. The absorption spectrum of the III/IV complex was recorded in water, the complex being sufficiently stable in this medium. The spectrum in acetonitrile is virtually the same as that in water. It is noteworthy that the bpy and phen complexes are unstable in water and are rapidly hydrolyzed.

The spectrum is shown in Figure 3 and is compared with those reported earlier for other III/IV complexes in Table III. The present spectrum consists of two intense maxima in the UV region and two bands of medium intensity in the visible region. The visible spectrum is very similar to those of the bpy and phen analogues. In the bpy and phen complexes, however, the higher energy band is split into two resolvable peaks at 525 and 555 nm;

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Table III. Visible Spectra of Bis(μ-oxo)dimanganese(III,IV) Complexes

complex	λ, nm (ε)	solvent	ref
$[(bpy)MnO]_2(ClO_4)_3$	525 (530) 555 (455) 684 (561)	bpy buffer	21
$[(phen)MnO]_2(ClO_4)_3$	525 (509) 555 (427) 684 (553)	phen buffer	21
$[(phen)MnO]_2(PF_6)_3$	523 (580) 550 (460) 680 (550) ~800 (sh)	solid state	9
$[(cyclen)MnO]_2(ClO_4)_3$	556 (700) 650 (890) 740 (880)	water	11
$[(cyclam)MnO]_2Br_3$	550 644 800 (sh)	water	13a
$[(cyclam)MnO]_2(ClO_4)_3$	550 (760) 650 (780)	water	11
$[(tmpa)MnO]_2(ClO_4)_3$	443 (1490) 561 (760) 658 (620)	acetonitrile	7
$[(tren)MnO]_2(CF_3SO_3)_3$	380 (1170) 428 (sh) 526 (sh) 548 (440) 590 (sh) 638 (sh) 680 (570)	acetonitrile	10
$[(bispicen)MnO]_2(ClO_4)_3$	386 (1355) 432 (1270) 553 (569) 655 (526) 805 (250)	water	this work

Table IV. Cyclic Voltammetric Data for Bis(μ-oxo)dimanganese(III,IV) Complexes

ligand	III/III ↔ III/IV[a]	III/IV ↔ IV/IV[a]	ref
bpy	0.29	1.25	21
phen	0.10	1.04	9
	0.33	1.26	21
tmpa	0.20	0.90	6
	0.24	1.04	7
N_3O-py	-0.02	0.76	12
cyclen	0.15	0.90	11
cyclam	0.00	1.00	11
bispicen	0.14	0.75	5
	0.146	0.753	this work

[a] Values are in V vs SCE. Corrections applied to literature values are as follows: $E(SCE) = E(Ag/AgCl) - 0.045$; $E(SCE) = E(NHE) - 0.241$; $E(SCE) = E(Ag/Ag^+) + 0.35$. See text.

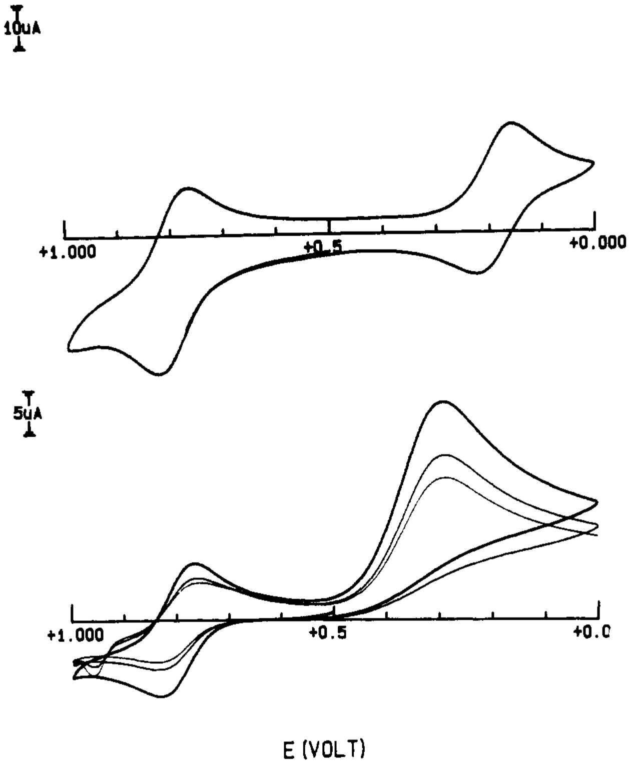

Figure 4. Cyclic voltammograms of $[(bispicen)MnO]_2^{3+}$ in 0.1 M $NaClO_4$: (a, top) pH = 7.4; (b, bottom) pH = 2.4. The scan rate is 100 mV/s. Voltages are vs Ag/AgCl.

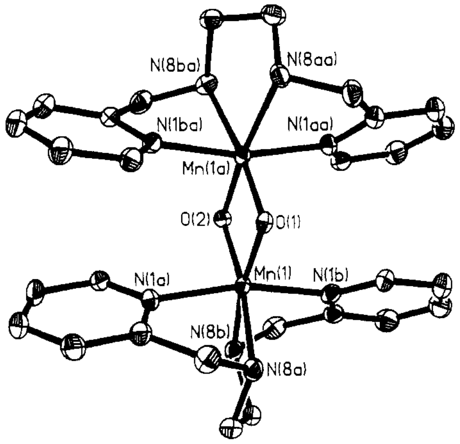

Figure 5. View of the oxidized Mn(IV,IV) complex $[(bispicen)MnO]_2^{4+}$ in the crystals of $[(bispicen)MnO]_2(ClO_4)_4{\cdot}2CH_3CN$. The top half of the molecule is related to the bottom half by the 2-fold axis passing through O(1) and O(2).

in the present complex a single peak is observed at 553 nm. The lower energy band in the present complex is at 655 nm, which is at higher energy than the corresponding band in the bpy and phen analogues.

Cyclic Voltammetry. A solution of the III/IV complex in 0.1 M $NaClO_4(aq)$ shows two waves in the cyclic voltammograms, one at 191 mV and the other at 798 mV vs Ag/AgCl. These $E_{1/2}$ values are virtually pH independent in the range $3.0 \leq pH \leq 9.5$. Above pH = 10, the complex appears to decompose during the scans; below pH = 2.5, the cyclic voltammograms are significantly different, which may indicate that the bridging oxo groups have been partially or fully protonated. A representative scan at pH = 7.4 is shown in Figure 4a, and a scan at pH = 2.4 is shown in Figure 4b.

The $E_{1/2}$ value of 191 mV corresponds to the one-electron couple III/IV ↔ III/IV, while that at 798 mV represents the couple III/IV ↔ IV/IV. These redox potentials are compared to those reported for related systems in Table IV. For purposes of comparison, we have reported all values relative to SCE in Table IV; the corrections for Ag/AgCl and NHE are from ref 22, while that for Ag/Ag^+ is as reported by the original authors in ref 11. The data in Table IV demonstrate that the $E_{1/2}$ values can be modulated by suitable ligand modification, as anticipated. In general, the complexes with tetradentate ligands are easier to oxidize than the bpy and phen complexes, and the bispicen complex is the easiest so far reported for the III/IV ↔ IV/IV couple. The work of Suzuki et al.,[12] however, demonstrates that the nature of the donor atoms also has a major impact on the redox potentials, and our own more recent work[23] shows that these potentials are also sensitive to steric effects.

The IV/IV Complex. Description of the Structure. The structure of the IV/IV complex consists of centrosymmetric $[(bispicen)MnO]_2^{4+}$ cations, perchlorate anions, and acetonitrile

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Table V. Bond Lengths (Å) for $[(\text{bispicen})\text{MnO}]_2(\text{ClO}_4)_4\cdot 2\text{CH}_3\text{CN}$

Mn(1)–O(1)	1.812 (2)	Mn(1)–O(2)	1.810 (2)
M(1)–N(1A)	2.013 (3)	Mn(1)–N(8A)	2.058 (3)
Mn(1)–N(1B)	2.001 (3)	Mn(1)–N(8B)	2.061 (3)
Mn(1)–Mn(1A)	2.672 (1)	O(1)–Mn(1A)	1.812 (2)
O(2)–Mn(1A)	1.810 (2)	N(1A)–C(2A)	1.347 (5)
N(1A)–C(6A)	1.352 (5)	N(8A)–C(7A)	1.494 (5)
N(8A)–C(9A)	1.492 (5)	N(1B)–C(2B)	1.353 (5)
N(1B)–C(6B)	1.343 (5)	N(8B)–C(7B)	1.492 (5)
N(8B)–C(9B)	1.488 (5)	C(2A)–C(3A)	1.377 (5)
C(3A)–C(4A)	1.385 (6)	C(4A)–C(5A)	1.391 (6)
C(5A)–C(6A)	1.384 (5)	C(6A)–C(7A)	1.505 (5)
C(9A)–C(9B)	1.509 (6)	C(2B)–C(3B)	1.383 (5)
C(3B)–C(4B)	1.382 (6)	C(4B)–C(5B)	1.386 (6)
C(5B)–C(6B)	1.381 (5)	C(6B)–C(7B)	1.509 (5)
Cl(1)–O(3)	1.430 (3)	Cl(1)–O(4)	1.432 (3)
Cl(1)–O(5)	1.434 (4)	Cl(1)–O(6)	1.430 (4)
Cl(2)–O(7)	1.427 (3)	Cl(2)–O(8)	1.431 (3)
Cl(2)–O(9)	1.415 (4)	Cl(2)–O(10)	1.439 (4)
N(1N)–C(1N)	1.121 (6)	C(1N)–C(2N)	1.455 (7)

Table VI. Bond Angles (deg) for $[(\text{bispicen})\text{MnO}]_2(\text{ClO}_4)_4\cdot 2\text{CH}_3\text{CN}$

O(1)–Mn(1)–O(2)	84.9 (1)	O(1)–Mn(1)–N(1A)	95.8 (1)
O(2)–Mn(1)–N(1A)	93.6 (1)	O(1)–Mn(1)–N(8A)	96.6 (1)
O(2)–Mn(1)–N(8A)	171.5 (1)	N(1A)–Mn(1)–N(8A)	77.9 (1)
O(1)–Mn(1)–N(1B)	93.4 (1)	O(2)–Mn(1)–N(1B)	96.8 (1)
N(1A)–Mn(1)–N(1B)	166.7 (1)	N(8A)–Mn(1)–N(1B)	91.5 (1)
O(1)–Mn(1)–N(8B)	171.6 (1)	O(2)–Mn(1)–N(8B)	95.5 (1)
N(1A)–Mn(1)–N(8B)	92.6 (1)	N(8A)–Mn(1)–N(8B)	84.2 (1)
N(1B)–Mn(1)–N(8B)	78.3 (1)	Mn(1)–O(1)–Mn(1A)	95.0 (2)
Mn(1)–O(2)–Mn(1A)	95.2 (2)	Mn(1)–N(1A)–C(2A)	124.7 (2)
Mn(1)–N(1A)–C(6A)	114.8 (2)	C(2A)–N(1A)–C(6A)	120.5 (3)
Mn(1)–N(8A)–C(7A)	105.4 (2)	Mn(1)–N(8A)–C(9A)	108.5 (2)
C(7A)–N(8A)–C(9A)	111.6 (3)	Mn(1)–N(1B)–C(2B)	123.9 (2)
Mn(1)–N(1B)–C(6B)	115.6 (2)	C(2B)–N(1B)–C(6B)	120.5 (3)
Mn(1)–N(8B)–C(7B)	105.1 (2)	Mn(1)–N(8B)–C(9B)	109.1 (2)
C(7B)–N(8B)–C(9B)	111.6 (3)	N(1A)–C(2A)–C(3A)	121.0 (3)
C(2A)–C(3A)–C(4A)	119.3 (4)	C(3A)–C(4A)–C(5A)	119.4 (3)
C(4A)–C(5A)–C(6A)	119.1 (4)	N(1A)–C(6A)–C(5A)	120.7 (3)
N(1A)–C(6A)–C(7A)	113.9 (3)	C(5A)–C(6A)–C(7A)	125.3 (3)
N(8A)–C(7A)–C(6A)	105.8 (3)	N(8A)–C(9A)–C(9B)	109.5 (3)
N(1B)–C(2B)–C(3B)	120.6 (3)	C(2B)–C(3B)–C(4B)	119.0 (4)
C(3B)–C(4B)–C(5B)	120.0 (4)	C(4B)–C(5B)–C(6B)	118.6 (4)
N(1B)–C(6B)–C(5B)	121.2 (3)	N(1B)–C(6B)–C(7B)	113.6 (3)
C(5B)–C(6B)–C(7B)	125.2 (3)	N(8B)–C(7B)–C(6B)	105.9 (3)
N(8B)–C(9B)–C(9A)	109.4 (3)	O(3)–Cl(1)–O(4)	110.1 (2)
O(3)–Cl(1)–O(5)	109.1 (2)	O(4)–Cl(1)–O(5)	109.7 (2)
O(3)–Cl(1)–O(6)	109.8 (2)	O(4)–Cl(1)–O(6)	108.4 (2)
O(5)–Cl(1)–O(6)	109.6 (3)	O(7)–Cl(2)–O(8)	110.1 (2)
O(7)–Cl(2)–O(9)	109.2 (2)	O(8)–Cl(2)–O(9)	109.9 (2)
O(7)–Cl(2)–O(10)	107.5 (2)	O(8)–Cl(2)–O(10)	110.2 (2)
O(9)–Cl(2)–O(10)	110.0 (2)	N(1N)–C(1N)–C(2N)	178.8 (5)

molecules. A view of the cation is given in Figure 5. Principal distances and angles are listed in Tables V and VI, respectively.

The geometry about each manganese center is roughly octahedral, the ligating atoms being two cis oxo bridges and four nitrogen atoms from the bispicen ligand. The trans angles at Mn fall in the range 166.7 (1)–171.6 (1)°, with the greatest deviation from linearity occurring at the intraligand N(1A)–Mn–N(1B) angle defined by the two axial pyridine nitrogen atoms. The Mn–Mn separation of 2.672 (1) Å is intermediate between those of 2.748 (2) and 2.625 (2) Å in the only other structurally characterized IV/IV complexes of this type. Interestingly, however, the present distance is only slightly longer than that of 2.659 (2) Å in the bispicen III/IV complex[5] and falls comfortably within the range 2.64–2.74 Å reported in recent summaries of structures of bis(μ-oxo)dimanganese(III,IV) complexes.[13a,24] The Mn–O–Mn bridging angle of 95.0 (2)° is much smaller than the value of 99.5 (2)° in the phen analogue, but is again similar to the value of 94.3 (1)° in the bispicen III/IV complex and within the range 94.0–97.7° found in the III/IV complexes.[13a,24]

The axial Mn–N bonds of 2.001 (3) and 2.013 (3) Å are slightly shorter than the equatorial values of 2.058 (3) and 2.061 (3) Å. While this difference might be attributable to the difference between pyridine (axial) and ethanediamine (equatorial) nitrogen atoms, it is also partially reflective of the trans influence of the bridging oxo groups on the equatorial nitrogen atoms. The average Mn–N (axial) and Mn–N (equatorial) distances of 2.007 (8) and 2.060 (2) Å are similar to the values of 2.010 (6) and 2.076 (4) Å in the phen analogue and are comparable to the values observed for the Mn(IV) center in the III/IV complexes; averages for these latter values range 2.013 (1)–2.107 (5) Å (axial) and 2.022 (8)–2.113 (3) Å (equatorial) in the reported ordered structures.[5,6,8-10,12,14] The similarity between the axial and equatorial distances is as expected for a d^3 Mn(IV) ion. The Mn–O distances of 1.810 (2) and 1.812 (2) Å are longer than the values of 1.797 (3)–1.805 (3) Å [average: 1.800 (4) Å] in the phen analogue but are within the range observed for the Mn(IV) center in the III/IV complexes.

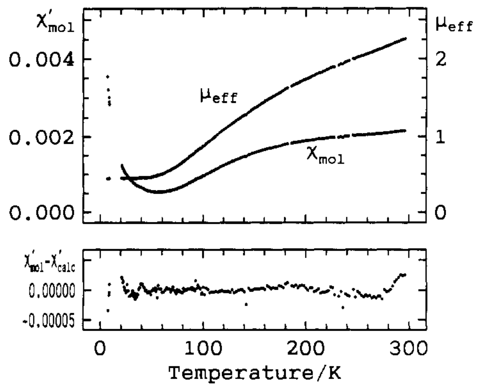

Figure 6. Magnetic susceptibility (left scale) and effective magnetic moment (right scale) of a powdered sample of the IV/IV complex $[(\text{bispicen})\text{MnO}]_2(\text{ClO}_4)_4\cdot 3\text{H}_2\text{O}$.

The geometry of the bispicen ligands is unremarkable. As was the case for the bispicen III/IV dimer, the isomer isolated here is the α,α form, in which the pyridine nitrogen atoms are trans at both metal centers. This is only one of the isomers possible with this ligand; the α,β form was found[25] in a chromium dimer containing this ligand, and the β,β form has been observed for the related ligand bispictn, in which the ethanediamine linkage is replaced by 1,3-propanediamine.[26] The perchlorate anions are ordered and well behaved, with Cl–O bond lengths in the range 1.415 (4)–1.439 (4) Å [average: 1.430 (7) Å] and O–Cl–O angles of 107.5 (2)–110.2 (2)° [average: 109.5 (8)°]. The acetonitrile molecule exhibits the anticipated linear geometry [C–C–N = 178.5 (2)°], with C—C and C≡N bonds of lengths 1.455 (7) and 1.121 (6) Å, respectively.

Magnetic Susceptibility. The magnetic susceptibility and effective magnetic moment of the IV/IV complex are shown in Figure 6. The effective magnetic moment of the IV/IV complex decreases from a value of about 2.3 μ_B at room temperature to about 0.45 μ_B at 45 K. Below 45 K, the effective magnetic moment is approximately constant. This magnetic behavior is consistent with the results obtained for the phen analogue.[9] The susceptibility data were fitted as above. Here, however, with two $S = {}^3/_2$ centers the Heisenberg term $-2JS_1 \cdot S_2$ gives rise to a singlet, a triplet, a quintet, and a septet with energies of 0, $-2J$, $-6J$, and $-12J$, respectively. The fitting leads to a value of $2J = -251.1 \pm 0.4$ cm^{-1}, or $J = -125.6 \pm 0.2$ cm^{-1}. This value of J can be compared to those of -144 ± 7 and -137 cm^{-1} reported for the phen[9] and tmpa[7] IV/IV complexes, respectively. The susceptibility tail at low temperatures was explained by the term C/T in the susceptibility expression. Here, C was found to be 2.45×10^{-2}, and if the paramagnetic impurity is assumed to be a monomeric Mn(II) compound, then the content of such impurity is 0.28%; if, however, the impurity is the Mn(III)/Mn(IV) dimer, the content of this species is 6.53%. As is also the case for the

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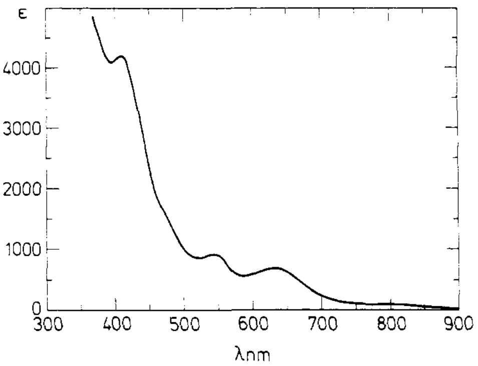

Figure 7. Absorption spectrum of the IV/IV complex [(bispicen)-$MnO]_2(ClO_4)_4 \cdot 3H_2O$ in acetonitrile.

phen complex,[19] the bispicen IV/IV complex does not give an EPR signal at 4 K or at higher temperatures; the only signal that is observed must be attributed to the presence of a mixture of a Mn(II) compound and small quantities of the Mn(III)/Mn(IV) dimer, which is consistent with the susceptibility data.

Electronic Spectra. The electronic spectrum of the IV/IV complex, shown in Figure 7, was recorded in acetonitrile; the complex is too unstable in water to allow the spectrum to be recorded in aqueous solution. The spectrum is similar to that of the III/IV complex, but the peaks are shifted. The spectrum exhibits two very intense peaks in the UV region and two medium intensity bands in the visible region at 544 (ϵ = 843 M^{-1} cm^{-1}) and 632 nm (ϵ = 657 M^{-1} cm^{-1}). The higher energy of the two intense UV peaks has a maximum below 350 nm, while the lower energy peak is at 411 nm (ϵ = 3956 M^{-1} cm^{-1}) with a shoulder at 470 nm (ϵ = 1544 M^{-1} cm^{-1}). These values may be compared with those at 394 and 470 nm (sh) observed in the tris(μ-oxo)-dimanganese(IV,IV) complex.[15] The intensity in the region near 800 nm, which has been attributed to the intervalence charge-transfer band in the III/IV complexes, is much lower in the IV/IV complex than in the III/IV analogue. The observation of a very weak band at 802 nm (ϵ = 159) in the present spectrum of the IV/IV complex may be due to the presence of a small amount of the III/IV form in solution. The present spectrum is similar to that reported for the tmpa analogue,[7] but very different from that of the phen complex in that the latter shows no peaks in the visible region.[9,21]

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Supplementary Material Available: For $[(bispicen)MnO]_2(ClO_4)_4 \cdot 2CH_3CN$, Tables S1 (hydrogen atom parameters) and S2 (anisotropic thermal parameters) (2 pages); Table S3 (observed and calculated structure amplitudes) (16 pages). Ordering information is given on any current masthead page.

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New Niobium Complexes with Alkynes. 1. Mono- and Dinuclear Complexes

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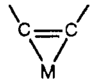
Four alkyne complexes of niobium are reported, and their structures, determined by X-ray crystallography, are presented. $NbCl_3(PhCCPh)(THF)_2$ (**1**), prepared by the reaction of $NbCl_4(THF)_2$, sodium amalgam, and PhCCPh in THF, crystallizes in the $P2_1/n$ space group with a = 12.013 (3) Å, b = 15.265 (4) Å, c = 13.520 (3) Å, β = 110.83 (2)°, V = 2317 (1) Å^3, and Z = 4. $NbCl_3(PhCCMe)(THF)_2$ (**2**), prepared by the reaction of $NbCl_4(THF)_2$, sodium amalgam, and PhCCMe in THF, crystallizes in the $P2_1/n$ space group with a = 13.751 (3) Å, b = 10.867 (2) Å, c = 14.592 (2) Å, β = 116.91 (1)°, V = 1944.5 (6) Å^3, and Z = 4. $[Mg_2Cl_3(THF)_6][NbCl_4(PhCCPh)(THF)] \cdot 0.5THF$ (**3**), prepared by the reaction of $NbCl_4(THF)_2$, Mg, and PhCCPh in THF, crystallizes in the $P\bar{1}$ space group with a = 10.310 (2) Å, b = 15.117 (2) Å, c = 17.148 (4) Å, α = 80.46 (2)°, β = 89.79 (2)°, γ = 87.24 (1)°, V = 2633 (1) Å^3, and Z = 2. $Nb_2OCl_4(PhCCPh)(THF)_4$ (**4**), prepared by the same reaction as for **3**, or two other reactions, crystallizes in the $C2/c$ space group with a = 20.581 (3) Å, b = 9.829 (2) Å, c = 19.176 (3) Å, β = 119.406 (9)°, V = 3379 (2) Å^3, and Z = 4.

Introduction

Previous work in this laboratory led to the preparation and characterization of the first η^2-alkyne complexes of tantalum. One of these[1] was the anion $[TaCl_4py(PhCCPh)]^-$, in which a central flat pyramid, $TaCl_4$, has a py ligand below and a side-on PhCCPh ligand above. From the bond lengths (Ta-C = 2.07 Å; C-C = 1.33 Å) it was concluded that the alkyne was so strongly bonded to the tantalum atom that the oxidation state of the latter should be considered to be V and the bonding represented by I with an



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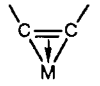

II

appreciable contribution from II as well. Shortly thereafter we reported a dinuclear tantalum compound[2] containing two such metal-alkyne linkages, this time with the alkyne CH_3CCCH_3, where the Ta-C distances were even shorter (2.03 Å). In addition, with Me_3CCCMe_3 we obtained a dinuclear compound in which the alkyne formed a skewed (i.e., neither parallel nor perpendicular) bridge across a Ta-Ta bond.[3] The Ta-Ta distance (2.68 Å) was shorter than any previously reported, and the Ta-C distances (2.21 and 2.42 Å) seemed consistent with appreciable Ta-C bond orders.

We now report the preparation and structural characterization of some alkyne complexes of niobium that are very similar to those of tantalum just mentioned. In 1984 Dehnicke and co-workers[4] reported one compound of niobium containing similar, strongly bonded PhCCPh groups. Beyond this, our search of the literature, including the two detailed reviews by Holloway and Melnick,[5] reveals that only two further reports of alkyne complexes of niobium and tantalum have appeared. One deals with $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(PhCCPh)$, for which a structure was reported.[6]

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