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Accessibility of Manganese Oxidation States. Control by Pentaaza Macrocyclic Ligands

JAMES C. DABROWIAK,*[1a] LAURENCE A. NAFIE,[1a] PHILIP S. BRYAN,*[1b] and ANDREW T. TORKELSON[1b]

The synthesis and characterization of a series of manganese(II) and -(III) and zinc(II) complexes with 15–17-membered pentaaza and 14-membered tetraaza macrocyclic ligands are reported. Except for two of the complexes with the largest ring, [17]pydieneN₅, all of the divalent compounds incorporating the pentadentate ligands appear to exhibit pentagonal-type coordination geometry in the solid state. Solution infrared and NMR studies (^{1}H and ^{13}C) on the diamagnetic Zn(II) complexes indicate that in solution all of the pentadentate ligands display a pentagonal coordination geometry. The Mn(II) complexes with the 15-membered pentadentate ligand can be oxidized by NOPF₆ to stable Mn(III) products. The pentagonal-bipyramidal coordination geometry displayed by the new complexes is highly unusual and has not been previously observed for Mn(III). These high-spin d⁴ complexes are deeply colored and exhibit d–d spectra which have been interpreted using a simple one-electron model. The accessibility of the trivalent oxidation state as a function of ligand structure is discussed.

Introduction

The importance of manganese in photosynthesis is well-known.[2] Although its detailed function in the photosynthetic process remains obscure, it has been established that the metal is important in the oxygen evolution part of the cycle. On this basis Calvin[3] proposed that a manganese porphyrin complex having the metal in a high oxidation state [Mn(IV)] may be involved in dioxygen binding in photosystem II. With the emphasis on a manganese–dioxygen interaction and the attainment of a high oxidation state of the metal a number of model systems have been explored.[4] In an effort to examine the oxidation states accessible to this metal as a function of ligand structure, we have synthesized and studied a number of macrocyclic complexes of manganese.[5-8] Since macrocyclic compounds are generally more stable than their acyclic analogues,[9,10] they are well suited for a systematic study of the effects of ligand charge, geometry, and donor type on the properties of the bound metal ion. In previous reports we have shown that a dinegatively charged unsaturated macrocyclic ligand stabilizes Mn(III) relative to a ligand that is uncharged and saturated.[5,7] Moreover, oxidation of the manganese complexes containing a dianionic ligand does not result in the formation of Mn(IV) compounds.[8] For this series of complexes, ligand oxidation occurs before the tetravalent oxidation

state of the metal can be reached. In this report, we will examine the effects of macrocyclic ring size as well as the number of nitrogen donor atoms on the coordination geometry and oxidation states available to the metal ion. By focusing on a series of manganese complexes containing the tetra- and pentadentate cyclic ligands shown below, some of these important metal–ligand relationships have been delineated.
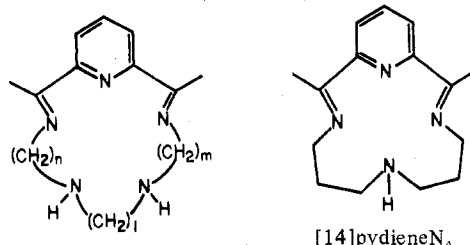
n	l	m	
2	2	2	[15]pydieneN₅
2	3	2	[16]pydieneN₅
3	2	3	[17]pydieneN₅

[14]pydieneN₄

The metal template synthesis of a pentadentate macrocyclic ligand was first reported by Busch et al.[11] Condensation of 2,6-diacetylpyridine with triethylenetetramine in the presence of Fe(III) yields seven-coordinate Fe(III) complexes containing

[15]pydieneN$_5$. This relatively rare coordination geometry was confirmed via x-ray structural analysis.[12,13] The template reaction also proceeds on Mn(II) generating the corresponding, presumably seven-coordinate manganese compounds.[14,15] The manganese(II) complexes of [16]pydieneN$_5$ as well as the zinc(II) compounds with both the 15- and 16-membered pentadentate ligands have received only brief attention in the literature.[16] None of their physical or chemical properties have yet been discussed. Although a number of transition metal complexes with [14]pydieneN$_4$ exist,[9,17] no manganese complexes with this ligand have yet been reported. Finally, the 17-membered ligand, [17]pydieneN$_5$, is a new macrocyclic ligand and its synthesis on Mn(II) and Zn(II) is reported here for the first time.

Experimental Section

Physical Measurements. The infrared spectra were determined using Nujol mulls with either a Perkin-Elmer 521 or a 137 spectrometer. Visible absorption spectra were recorded in spectral quality acetonitrile using a Cary 14 spectrophotometer. The low-temperature (77 K) solid-state mull spectra of the Mn(III) complexes from 0.40 to 3.00 μm^{-1} were obtained in a previously described manner.[18]

The ^{1}H and ^{13}C NMR spectra for the Zn complexes were recorded using a Varian T-60 and a CFT-20 NMR spectrometer, respectively. All chemical shifts are reported relative to TMS. The magnetic moments were measured at room temperature using the Faraday method. The diamagnetic corrections for the various macrocyclic ligands were calculated based on the measured value of -110×10^{-6} cgsu for [14]pyaneN$_4$.[19] Pascal's constants[20] were employed for evaluating the diamagnetic corrections for the unsaturated macrocyclic ligands and the various anions. Conductivity measurements were made on 10^{-3}–10^{-4} M solutions using a Model 1665-A General Radio impedance comparator. Values of Λ for 1:1 electrolytes in acetonitrile, nitromethane, and DMSO are 120–160, 60–115, and 23–70 Ω^{-1} cm^2 mol^{-1}, respectively.[21] Elemental analyses were performed by Instranal Laboratories, Rensselaer, N.Y. All of the compounds gave acceptable analytical results.

Synthesis. All of the divalent complexes were synthesized via a metal template reaction involving 2,6-diacetylpyridine and a tetrafunctional amine. Except for the complexes of [14]pydieneN$_4$ and [17]pydieneN$_5$ the initially isolated products, hereafter referred to as precursor complexes, were solvates which gave variable analytical results. However, these complexes could easily be converted to other derivatives (primarily thiocyanato complexes), which gave acceptable analytical data. A procedure for the preparation of Mn^{II}[15]-pydieneN$_5$(NCS)$_2$ which is typical of that used for the synthesis of all of the Mn(II) compounds as well as for Zn^{II}[15]pydieneN$_5$(NCS)$_2$ is given below.

Mn^{II}[15]pydieneN$_5$(NCS)$_2$. The precursor complex was prepared by dissolving 3.26 g of 2,6-diacetylpyridine in 250 ml of methanol and adding 2.5 g of anhydrous MnCl$_2$. To the resulting orange solution was added 2.92 g of triethylenetetramine. After refluxing for 3 h the solution was filtered and 1.8 g of NH$_4$PF$_6$ added to the filtrate. Reduction of the solution volume in vacuo initiated the crystallization of the precursor complex. The solution was cooled (0–5 °C) and the orange solid which formed was removed by filtration, washed with a few milliliters of cold methanol and ether, and finally air-dried. The yield was 7.2 g. On the basis of analytical and IR data the precursor complex is best formulated as [Mn^{II}[15]pydieneN$_5$(CH$_3$OH)Cl]PF$_6$.

To 0.5 g of [Mn^{II}[15]pydieneN$_5$(CH$_3$OH)Cl]PF$_6$ dissolved in 50 ml of methanol was added 0.75 g of LiSCN. The solution was warmed for 30 min and its volume reduced to 20 ml under a stream of N$_2$ gas. Cooling caused the orange crystalline thiocyanate to form. The complex was removed by filtration, washed with a few milliliters of cold methanol, and air-dried. The yield was 0.33 g.

[Mn^{II}[15]pydieneN$_5$Cl$_2$]PF$_6$. To 4 g of [Mn^{II}[15]pydieneN$_5$-(CH$_3$OH)Cl]PF$_6$ dissolved in 250 ml of degassed acetonitrile was added 1.7 g of NOPF$_6$. A vigorous evolution of NO gas took place. After the reaction ceased (1 h), the volume of the solution was reduced to near dryness and 25 ml of methanol was added. The green crystalline solid which formed was removed by filtration, washed with ether, and air-dried. The yield was 1.6 g.

[Mn^{III}[15]pydieneN$_5$Br$_2$]PF$_6$. To 0.5 g of [Mn^{II}[15]pydieneN$_5$-(ClO$_4$)$_2$][14] dissolved in 50 ml of acetone was added a second acetone solution (50 ml) containing 1.5 g of LiBr. Reducing the solution
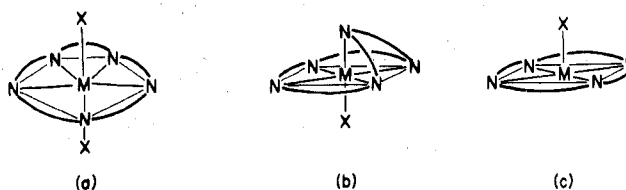

Figure 1. Coordination geometry of the macrocyclic ligands [15–17]pydieneN$_5$ and [14]pydieneN$_4$: (a) pentagonal bipyramidal; (b) folded octahedral; (c) planar coordination geometry of [14]pydieneN$_4$.

volume to 25 ml in vacuo resulted in the crystallization of the crude hygroscopic dibromide salt. This procedure was repeated to give a combined yield of 0.6 g of complex.

The Mn(III) complex was prepared by dissolving 0.5 g of the crude dibromide in methanol and oxidizing with 5 drops of bromine. After the addition of a methanol solution containing 0.1 g of NH$_4$PF$_6$, the solution was allowed to stand overnight to crystallize. The red-brown product which formed was removed by filtration, washed with ether, and air-dried. The yield of [Mn^{III}[15]pydieneN$_5$Br$_2$]PF$_6$ was 0.37 g.

Zn[15–17]pydieneN$_5$(NCS)ClO$_4$. To 3.74 g of zinc perchlorate hydrate in 125 ml of methanol was added 1.63 g (0.01 mol) of 2,6-diacetylpyridine. This was followed by the slow addition of 0.01 mol of the appropriate tetrafunctional amine. After refluxing for 5 h, the orange solution was filtered using filter aid to remove a small amount of tarry solid. Approximately 2 g of lithium thiocyanate in 20 ml of methanol was added to the filtrate. The resulting solution was cooled (0–5 °C) and the white solid which formed was filtered, washed with methanol and ether, and dried in vacuo with P$_4$O$_{10}$. The yield was 2.4 g.

Results and Discussion

Structural Considerations. Molecular models show that the coordination geometries which can be adopted by the pentadentate macrocyclic ligands [15–17]pydieneN$_5$ are dependent on ring size. The 15-membered ring system can only exhibit planar pentagonal-type coordination geometry (Figure 1(a)). The requirements of coplanarity of the pyridine ring and the two imine functions along with the sp^2 hybridization of the imine nitrogen atoms do not allow the ligand donor atoms to occupy the vertices of an octahedron in a pentadentate fashion (Figure 1(b)). Similar arguments apply to the 16-membered ring, [16]pydieneN$_5$. Although models show that a folded structure may be possible for this ligand, the coordination polyhedron is highly strained relative to that shown in Figure 1(a). X-ray structural analysis has substantiated the planar pentagonal geometry for both [15]- and [16]-pydieneN$_5$[12,13] in their Fe(III) complexes. The 17-membered ring on the other hand appears to have both coordination geometries (Figure 1(a) and (b)) accessible to it. This macrocyclic ligand has three methylene groups (instead of two) between the imine functions and the secondary amine nitrogen atoms which allow it sufficient freedom to form a planar pentagonal as well as a relatively unstrained folded structure. In the absence of knowledge of crystal field effects it is difficult to assess which of the two structures will predominate. The 14-membered tetradentate macrocyclic ligand [14]pydieneN$_4$ has been extensively studied and it invariably displays the planar-type coordination geometry shown in Figure 1(c).[9,22]

The Divalent Complexes. The reaction of 2,6-diacetylpyridine with the appropriate polyfunctional amine in the presence of Mn(II) or Zn(II) salts leads to the formation of the ring systems [14]pydieneN$_4$ and [15–17]pydieneN$_5$. The Mn(II) complexes are high spin and have magnetic moments in the range 5.90–5.95 μ_B (Table I). Both the Mn(II) and Zn(II) complexes are weakly colored but give strong absorptions (ϵ_M (4–5) $\times 10^3$) in the UV region. Since the bands are independent of the nature of the anions present as well as the metal ion, they are probably associated with transitions localized on the pyridine–imine framework. Except for small

Table I. Physical Properties of the Complexes

Complex	Color	μ_{eff}, μ_B	Λ, Ω cm^2 mol^{-1}	Absorption spectra, μm^{-1} (ϵ_M)^a
Mn^{II}[15]pydieneN$_5$(NCS)$_2$	Orange	5.95	22,^{b} 83^c	3.36 (5060), 3.43 (4870), 4.31 (25 300)
[Mn^{III}[15]pydieneN$_5$Cl$_2$]PF$_6$	Green	4.94	91,^{b} 150^c	1.07 (52), 1.66 (92), 2.61 sh, 3.33 sh, 3.68 (11 400); 0.70, 1.03, 1.69, 2.62^e
[Mn^{III}[15]pydieneN$_5$Br$_2$]PF$_6$	Red-brown	4.94	96,^{b} 149^c	0.99 (31), 1.53 (68), 2.15 (820), 2.78 sh, 3.20 sh, 3.44 sh, 3.88 (14 800); 0.66, 0.93, 1.57, 2.21, 2.96, 3.21^e
Mn^{II}[16]pydieneN$_5$(NCS)$_2$	Yellow	5.92	9.3,^{b} 58^c	3.24 sh, 3.38 (4970), 3.44 (4870), 4.27 (24 700)
Mn^{II}[17]pydieneN$_5$ClPF$_6$	Yellow	5.90	87,^{b} 144^c	3.18 sh, 3.29 (5410), 3.37 (5330), 4.17 (18 700)
Mn^{II}[17]pydieneN$_5$(NCS)$_2$	Yellow	5.95	68,^{b} 113^c	3.17 sh, 3.30 (5370), 3.38 (5300), 4.26 (28 900)
Mn^{II}[14]pydieneN$_4$(NCS)$_2$	Orange	5.94	45,^{b} 69^c	3.43 (4500), 4.08 (22 500)
Mn^{II}[14]pydieneN$_4$ClPF$_6$	Tan	5.94	87,^{b} 148^c	3.41 (4260), 4.18 (16 500)
Zn^{II}[15]pydieneN$_5$(NCS)$_2$	Pale yellow	Diamag	61,^{b} 112^c	3.40 (4330)
Zn^{II}[15]pydieneN$_5$(NCS)ClO$_4$	Pale yellow	Diamag	86,^{b} 151,^{c} 71^d	3.40 (4880)
Zn^{II}[16]pydieneN$_5$(NCS)ClO$_4$	Pale yellow	Diamag	82,^{b} 141,^{c} 68^d	3.40 (4850)
Zn^{II}[17]pydieneN$_5$(NCS)ClO$_4$	Pale yellow	Diamag	89,^{b} 147,^{c} 60^d	3.32 (5060)

^{a} Absorption spectra in acetonitrile solution unless otherwise noted. ^{b} Nitromethane. ^{c} Acetonitrile. ^{d} Me$_2$SO. ^{e} Solid-state mull spectrum at 77 K.

Table II. NMR Data for the Zinc Complexes^a

	^{1}H			^{13}C			
	py (s)	CH$_3$ (s)	–CH$_2$– (m)^b	–CH$_3$	–CH$_2$–	Aromatic and imine	NCS$^-$
[Zn[15]pydieneN$_5$(NCS)]ClO$_4$	8.37	2.57		15.1	46.4, 47.3, 48.2	124.8, 142.6, 148.0, 161.9	131.8
[Zn[16]pydieneN$_5$(NCS)]ClO$_4$	8.37	2.53	1.87	15.0	27.7, 48.0. 49.1, 49.8	124.6, 142.2, 148.2, 161.4	131.9
[Zn[17]pydieneN$_5$(NCS)]ClO$_4$	8.40	2.50	1.93	13.9	28.4, 48.3, 49.9 (2)	124.6, 143.4, 149.7, 162.4	135.8

^{a} The spectra were recorded in Me$_2$SO-d_6 and the shifts are relative to TMS. ^{b} The center methylene group in the six-membered chelate ring.

changes in band position, the absorptions obtained in the solid state at 77 K are identical with those observed in acetonitrile solution (Table I).

In contrast to the solution behavior of a series of earlier reported[11] seven-coordinate Fe(III) complexes with [15]-pydieneN$_5$, the Mn(II) and Zn(II) complexes with the 14–17-membered rings easily solvate in solution. Since the conductance values for the bis-thiocyanato derivatives are intermediate between those expected for a nonelectrolyte and a 1:1 electrolyte in acetonitrile, nitromethane, or dimethyl sulfoxide (Table I), at least one anion is easily displaced by a solvent molecule. Neither high-spin d^5 (Fe(III), Mn(II)) nor d^{10} (Zn(II)) exhibit crystal field stabilization, suggesting that the facile displacement of charged ligands is related to reduced electrostatic forces present in the divalent systems. Similar conductance behavior was observed for two manganese(II) complexes containing a tetradentate saturated amine.[5] If one of the counterions is very weakly coordinating, e.g., ClO$_4^-$ or PF$_6^-$, the observed conductance value is in the range for that expected for a 1:1 electrolyte.

Through the use of infrared and NMR techniques the coordination geometrics adopted by the M^{II}[15–17]pydieneN$_5$ complexes have been defined. All of the isolated complexes exhibit two strong bands in the IR region at 1570–1650 cm^{-1}. These absorptions are associated with the pyridine and imine portions of the macrocyclic ligand. In addition intense bands are observed for the uncoordinated anions ClO$_4^-$ ($\sim$1100, $\sim$600 cm^{-1}) and PF$_6^-$ ($\sim$850, $\sim$550 cm^{-1}). However, the C–S stretching mode of SCN$^-$ which is diagnostic of N- or S-bonded thiocyanate[23] is apparently obscured by ligand vibrations.

All but two of the complexes have a single IR absorption at 3200–3300 cm^{-1} due to the secondary amine functions. For [Zn^{II}[17]pydieneN$_5$(NCS)]ClO$_4$ and [Mn^{II}[17]-pydieneN$_5$Cl]PF$_6$ this absorption splits into two distinct bands at 3290, 3262 cm^{-1} and 3315, 3220 cm^{-1}, respectively. This evidence suggests that the ligand is folded in the solid state (Figure 1(b)) and that the IR bands are due to the two nonequivalent secondary amine functions. In DMSO solution both complexes exhibit only a single broad N–H absorption (3200 cm^{-1}) which is consistent with the presence of the pentagonal-type coordination geometry. The infrared time scale ($\sim$10^{-12} s) excludes the possibility of a rapid intramolecular rearrangement between the folded and planar forms. The IR data for these two complexes contrast with those of the third 17-membered system, Mn^{II}[17]pydieneN$_5$(NCS)$_2$, which has only one NH absorption in solution and in the solid state. It thus appears that the presence of two good donor groups (e.g., Cl$^-$, NCS$^-$, DMSO) is sufficient to cause this ligand to revert to the pentagonal geometry in solution and in the solid state.

The ^{1}H as well as ^{13}C NMR data for the zinc complexes, Zn^{II}[15–17]pydieneN$_5$(NCS)(ClO$_4$), are given in Table II.[24] For all three complexes only a single methyl resonance ($\sim$2.50 ppm) in the proton spectrum is observed. The ^{13}C spectra are more informative and show that all of the complexes possess either a mirror plane or a twofold symmetry axis. This observation taken with the earlier presented infrared results demonstrates that the geometry shown in Figure 1(b) is not possible and the coordination polyhedron in solution must be that of the pentagonal structure, Figure 1(a).

Oxidation Behavior of the Manganese Complexes. The manganese(III) complexes with the pyridine-containing macrocyclic ligands do not appear to be oxygen sensitive either in solution or in the solid state. However, addition of the strong oxidant NOPF$_6$ to acetonitrile solutions containing Mn(II) complexes of [15]- and [16]pydieneN$_5$ results in the formation of Mn(III) products. The complexes with [15]pydieneN$_5$,
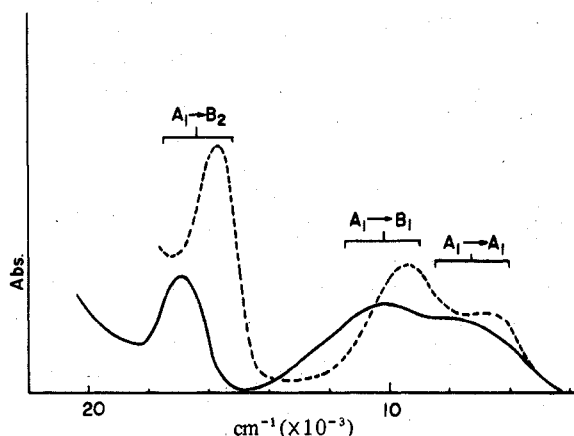
Figure 2. Solid-state spectra (77 K) of $[Mn^{III}[15]pydieneN_5Cl_2]PF_6$ (—) and $[Mn^{III}[15]pydieneN_5Br_2]PF_6$ (---).

$[Mn^{III}[15]pydieneN_5(X)_2]PF_6$ where X^- is Cl^- and Br^-, are stable and have been isolated and fully characterized. Oxidation of $Mn^{II}[16]pydieneN_5(NCS)_2$ or its precursor complex, $[Mn^{II}[16]pydieneN_5Cl(CH_3OH)]PF_6$, in the presence of Cl^- with excess $NOPF_6$ leads to green solutions indicative of the higher oxidation state. However, after the excess oxidant is exhausted, the solution color quickly fades. Spectroscopically these solutions appear to contain large amounts of a Mn(II) macrocyclic complex. Addition of $NOPF_6$ or H_2O_2 to an acetonitrile solution containing the divalent manganese complexes of [14]pydieneN₄ and [17]pydieneN₅ and excess Cl^- ion is without effect. Thus, based on chemical evidence the stability of the complexes containing trivalent manganese and the pentadentate macrocyclic ligands increases in the order [17]pydieneN₅ < [16]pydieneN₅ < [15]pydieneN₅. Since all of these ring systems exhibit pentagonal-type coordination geometry in solution, Figure 1(a), the stability of the higher oxidation state appears to be related to the folding ability of the ligand.[25] If folding is not possible, e.g., as in [15]-pydieneN₅, a stable seven-coordinate monocationic Mn(III) complex results. If on the other hand a folded structure is accessible, e.g., as in [16]- or [17]pydieneN₅, the Mn(III) complexes have only a transient existence or do not form at all. It is possible that in the case of the larger rings, oxidation yields a seven-coordinate Mn(III) compound which, driven by crystal field stabilization energy[26] and/or by minimization of steric interactions, reverts to a six-coordinate divalent cationic complex (Figure 1(b)). Divalent cationic manganese(III) complexes are inherently unstable and none have been isolated to date.[27] Although Mn(II) bound to a 14-membered tetraaza cyclic amine can be readily oxidized to Mn(III) by NO^+ and O_2,[5] the Mn^{II}–[14]pydieneN₄ complexes are resistant to oxidation by these reagents. The presence of three electron-withdrawing functions in [14]pydieneN₄, the pyridine nitrogen atom and two imine groups, is most likely responsible for stabilizing the lower oxidation state.

The Seven-Coordinate Manganese(III) Complexes. The two Mn(III) complexes with [15]pydieneN₅ have magnetic moments consistent with four unpaired electrons, 4.94 μ_B.[28] The planar pentadentate geometry of the ligands combined with the conductance values (Table I) and spectral interpretation given below show that the compounds are monovalent cations in solution and must contain seven-coordinate Mn(III). This type of coordination geometry is extremely rare for Mn(III) and has only previously been suggested for the solution behavior of a Mn^{III}–EDTA complex.[29]

The new Mn(III) compounds are deeply colored and give three bands which appear to be of d–d origin (Table I and Figure 2). Assuming that the complex is pentagonal bipyramidal and that the donor strengths of the five nitrogen atoms

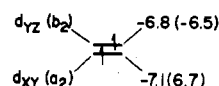**Figure 3.** Energy level diagram for a seven-coordinate $MA_3B_2C_2$, C_{2v} complex. The energy levels for $[Mn^{III}[15]pydieneN_5Cl_2]^+$ are given in $cm^{-1} \times 10^3$ with those for $[Mn^{III}[15]pydieneN_5Br_2]^+$ in parentheses.

Table III. Observed and Calculated Electronic Spectral Data for $[Mn^{III}[15]pydieneN_5X_2]^+$

	Band position, μm^{-1}			Band position, μm^{-1}	
X^-	$Obsd^a$	Calcd	X^-	$Obsd^a$	Calcd
Cl^-	1.69	1.65^b	Br^-	1.57	$1.57^{b,c}$
	1.00	0.79		0.94	0.74
	0.77	0.71		0.66	0.66

^{a} Solid-state mull spectra at 77 K. ^{b} The transition from the average of d_{yz} and d_{xy} to d_{z^2} is given. ^{c} This value is set equal to the observed value for the calculation.

are equivalent only two (not three) electronic transitions for the d^4 ion should be observed.[30] However, extensive spectral studies on cobalt(III) complexes containing various macrocyclic and noncyclic ligands have shown that the donor strengths of the imine and pyridine ligands are significantly greater than that of a secondary amine.[10,31] Since the crystal field strength of the halides is much lower than the amine donor groups[31] the chromophoric symmetry of the Mn(III) compounds reduces to $MA_3B_2C_2$, C_{2v}. Using the basic method developed by Companion and Komarynsky[32] for calculating crystal field splitting diagrams and its extension to low-symmetry d^1 and d^9 metal ions[30,33] we have determined the one-electron splitting diagram for $[Mn^{III}[15]pydieneN_5X_2]^+$. For this calculation it was assumed that the crystal field strengths of the donor groups as determined on Co(III) have the same *relative* values for Mn(III). The Dq values on Co(III) for the various groups are as follows (cm^{-1}): pyridine, imine, 2800; secondary amine, 2480; Cl^-, 1420; Br^-, 1270.[10,31,34] It is further assumed that the highest energy band in the spectrum of the dibromide complex corresponds to the transition from the average of the d_{yz} and d_{xy} orbitals (these levels are not degenerate in C_{2v} symmetry) to d_{z^2}. The energy level diagram for the Mn(III) complexes is shown in Figure 3 and the agreement between the observed and calculated transitions is given in Table III.[35] The diagram shows that four transitions are possible. In order of increasing energy they are $A_1 \rightarrow A_1$, $A_1 \rightarrow B_1$, $A_1 \rightarrow B_2$, and $A_1 \rightarrow A_2$. The close degeneracy of the last two transitions (~ 200-cm^{-1} separation) combined with the fact that the $A_1 \rightarrow A_2$ is symmetry forbidden suggests that only three transitions will in fact be observed. In addition the simple model predicts that all of the bands of the chloro complex will be shifted to higher energy relative to that of the bromo analogue. Since both of these predictions are realized (Table III and Figure 2), a simple

one-electron model appears to be useful for explaining the spectral properties of these low-symmetry d^4 systems. Thus, the successful spectral interpretation establishes that the chemical oxidation is primarily metal centered and that the products contain Mn(III).

In this report we have shown that the attainment of a high oxidation state of the manganese ion (in this case Mn(III)—no evidence was found for higher oxidation states) can have a strong dependence on ligand structure. If the ligand is uncharged and unsaturated as in [14]pydieneN$_4$, the Mn(II) complexes resist chemical oxidation to Mn(III) products. If however, the [14]pydieneN$_4$ ring system is expanded to include an additional donor group such as a secondary amine, [15]pydieneN$_5$, stable seven-coordinate Mn(III) complexes can be synthesized. Larger macrocyclic rings, [16]- and [17]pydieneN$_5$, jeopardize the stability of the trivalent oxidation state. The extension of these principles to other oxygen and mixed nitrogen–oxygen ligands is being explored.

Registry No. Mn^{II}[15]pydieneN$_5$(NCS)$_2$, 61318-74-9; [Mn^{III}-[15]pydieneN$_5$Cl$_2$]PF$_6$, 61318-76-1; [Mn^{III}[15]pydieneN$_5$Br$_2$]PF$_6$, 61318-78-3; Mn^{II}[16]pydieneN$_5$(NCS)$_2$, 61318-79-4; [Mn^{II}[17]-pydieneN$_5$Cl]PF$_6$, 61348-45-6; [Mn^{II}[17]pydieneN$_5$(NCS)$_2$, 61318-80-7; Mn^{II}[14]pydieneN$_4$(NCS)$_2$, 61348-43-4; [Mn^{II}[14]-pydieneN$_4$Cl]PF$_6$, 61318-82-9; Zn^{II}[15]pydieneN$_5$(NCS)$_2$, 61318-83-0; [Zn^{II}[15]pydieneN$_5$(NCS)]ClO$_4$, 61318-85-2; [Zn^{II}[16]-pydieneN$_5$(NCS)]ClO$_4$, 61318-87-4; [Zn^{II}[17]pydieneN$_5$(NCS)]ClO$_4$, 61318-89-6; 2,6-diacetylpyridine, 1129-30-2; triethylenetetramine, 112-24-3; [Mn^{II}[15]pydieneN$_5$(CH$_3$OH)Cl]PF$_6$, 61363-46-0; Mn^{II}[15]pydieneN$_5$(ClO$_4$)$_2$, 27680-13-3; ^{13}C, 14762-74-4.

Supplementary Material Available: Elemental analyses for the compounds (1 page). Ordering information is given on any current masthead page.

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