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Synthesis and Characterization of Manganese Complexes Containing a Synthetic Macrocyclic Ligand

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A number of manganese(II) and -(III) complexes with the uncharged 14-membered macrocyclic ligand, *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ([14]aneN$_4$) have been synthesized and fully characterized. The Mn(II) compounds are oxygen sensitive and are easily destroyed by exposure to pH extremes. The manganese(III) complexes appear to be air stable and less sensitive to pH effects than the Mn(II) derivatives. The solid-state esr spectra of the divalent complexes indicate that the metal ion is experiencing a relatively small tetragonal distortion. The observed tetragonal spitting parameter, D, is 0.1–0.2 cm^{-1}. Chemical and electrochemical investigations show that the Mn^{III}–[14]aneN$_4$ complexes are easier to reduce than a number of manganese(III)–porphyrin complexes. These complexes also display magnetic moments and electronic absorption bands consistent with high-spin, tetragonally distorted d^4 systems.

Introduction

Although complexes of many cyclic tetraaza ligands have been prepared with a variety of transition metal ions,[2] there have been few reports of Mn complexes of this type. This kind of ligand possesses a number of readily accessible structural features which can serve to alter the chemistry of the coordinated metal ion. The availability of various macrocyclic frameworks coupled with the number of obtainable oxidation states for manganese[3] emphasizes the possibility of these systems as useful redox agents. In this regard it has been shown[4] that a manganese(II) complex containing the cyclic ligand, phthalocyanine, is effective in converting cyclohexadiene to benzene in the presence of nitrobenzene. Manganese(II) phthalocyanine and oxygen gas have also been employed in the oxidation of cumene to cumene hydroperoxide.[5] The specific function of the complex in these systems is essentially unknown. Perhaps most interesting is the role manganese macrocyclic complexes may play in plant[6] as well as animal[7] physiology. Although there is no direct evidence for the existence of manganese–porphyrin complexes in the photosynthetic process, Calvin[6] has suggested that they may be essential to oxygen evolution. Manganese–porphyrin complexes under certain conditions are themselves photoactive and conversion between the II, III, and IV oxidation states may be important in the oxygen evolution part of the cycle.

As part of a study to examine the chemistry of manganese macrocyclic systems as a function of ligand structure, we have synthesized a number of manganese(II) and -(III) complexes with *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, [14]aneN$_4$,[8] Figure 1. This ligand is a saturated, tetradentate, uncharged macrocycle which can be easily synthesized in gram quantities.[9] Furthermore, its stereochemistry has been extensively documented and planar coordination is preferred.[10]

Experimental Section

Reagents and Equipment. All of the chemicals used were reagent grade unless otherwise noted. A Vacuum Atmospheres controlled-atmosphere drybox was used for the synthesis of the manganese(II) complexes. Solution absorption spectra were recorded using a Cary 14 spectrophotometer. Solid-state mull spectra were obtained using filter paper impregnated with Halocarbon 25-S5 grease and the compound. The absorption spectrum (4.3–30 kK) was recorded at 77°K in a manner previously described.[8]

The esr spectra between 500 and 8500 G were obtained using a Varian E-9 spectrometer operating at a microwave energy of 0.316 cm^{-1}. The $CF_3SO_3^-$ and $CH_3CO_2^-$ derivatives were run as undiluted powdered samples at room temperature.

Infrared spectra were obtained on Nujol mulls between KBr disks using a Perkin-Elmer 521 spectrophotometer. Polyethylene plates were used for measurements below 400 cm^{-1}. Conductivities at room temperature on 10^{-3}–10^{-4} M solutions were obtained using a Yellow Springs Instrument Co. Model 31 conductivity bridge. Magnetic moment measurements were done on 10–20 mg of sample in the solid state using the Faraday method.[11] The diamagnetic correction for [14]aneN$_4$ as determined was -254×10^{-6} cgsu.

The electrochemistry was carried out under nitrogen in acetonitrile. The polarographic and cyclic voltammetric behavior of the Mn(II) derivatives was examined with dropping mercury and hanging mercury drop electrodes, respectively. A platinum electrode was used for the Mn(III) complexes. Solutions were 10^{-3} M in complex and 0.10 M in tetra-*n*-butylammonium perchlorate as the supporting electrolyte. All potentials were determined at room temperature *vs.* an Ag-AgCl (sat NaCl) reference electrode. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Instranal Laboratories, Rensselaer, N. Y.

Preparation of [14]aneN$_4$. The synthesis of this ligand has been previously described.[9] For all the manganese syntheses the free ligand was dried for 2 days under vacuum (0.02 mm) over P_4O_{10}. The absence of water was checked using infrared spectroscopy.

Synthesis of Mn^{II}[14]aneN$_4$(SO$_3$CF$_3$)$_2$. The metal salt $Mn(SO_3CF_3)_2 \cdot CH_3CN$ necessary for the synthesis of the complex was synthesized from manganese metal and HSO_3CF_3 in acetonitrile. Thus, to 20 g of anhydrous HSO_3CF_3 in 400 ml of rapidly stirred acetonitrile was added 10.0 g of manganese metal (60 mesh). The stirred suspension was heated to 60° under nitrogen for 2 hr. After filtering the cool solution with the help of filter aid, the volume was reduced to 100 ml. Addition of 800 ml of ether, which was dried with $LiAlH_4$, caused the precipitation of the white hygroscopic manganese(II) salt. The salt was removed by filtration, and dried over P_4O_{10} under vacuum. The yield was 10.5 g. Although three elemental analyses showed variable composition, infrared evidence coupled with

Table I. Physical Properties of Some Mn(II) and -(III) Macrocyclic Complexes

Complex	X^-	Y^-	Color	μ_{eff}, BM	Λ, ohm^{-1} cm^2 mol^{-1}	Ir, cm^{-1}
$Mn^{II}[14]aneN_4(X)_2$	$CF_3SO_3^-$		White	5.94	78,[a] 290[b]	3270, 3250, N–H
$Mn^{II}[14]aneN_4(X)_2$	$CH_3CO_2^-$		White	6.02	1,[a] 18[b]	3210, 3150, N–H
$[Mn^{III}[14]aneN_4(X)_2]Y$	NCS^-	NCS^-	Red	4.90	80[a]	3190, N–H; 795, C–S
$[Mn^{III}[14]aneN_4(X)_2]Y$	Cl^-	BF_4^-	Green	4.89	94,[a] 150[b]	3180, 3130 N–H; 291, Mn–Cl
$[Mn^{III}[14]aneN_4(X)_2]Y$[c]	Cl^-	Cl^-	Green	5.01	76[a]	291, Mn–Cl
$[Mn^{III}[14]aneN_4(X)_2]Y$	Br^-	PF_6^-	Greenish yellow	4.90	87,[a] 148[b]	3140, N–H
$[Mn^{III}[14]aneN_4(X)_2]Y$	Cl^-	PF_6^-	Green	4.90	82,[a] 149[b]	3180, 3150, N–H; 291, Mn–Cl

[a] Nitromethane. [b] Acetonitrile. [c] Isolated as the trihydrate.

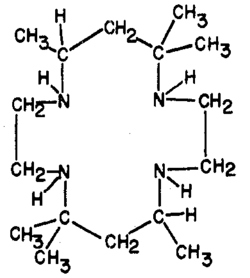

Figure 1. *meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane ([14]aneN$_4$).

the analytical figures suggests that the formulation is $Mn^{II}(SO_3CF_3)_2 \cdot \sim 1CH_3CN$. To 1.97 g (5 mmol) of $Mn(SO_3CF_3)_2 \cdot CH_3CN$ dissolved in 100 ml of degassed hot (70°) acetonitrile was added 1.42 g (5 mmol) of dry [14]aneN$_4$. After heating for 1 hr, the solution was cooled and filtered to remove a small amount of white insoluble material. The volume was reduced until crystallization commenced. After standing for 1 day, the crude, very pale yellow, air-sensitive product was collected by filtration and recrystallized from hot acetonitrile. The yield was about 1 g.

Anal. Calcd for $MnC_{16}H_{36}N_4(SO_3CF_3)_2$: C, 33.90; H, 5.66; N, 8.76. Found: C, 33.81; H, 5.85; N, 8.72.

Mn^{II}[14]aneN$_4$(CH_3CO_2)$_2$. This synthesis employing $Mn(CH_3CO_2)_2$, was identical with the procedure described above. The pale blue air-sensitive complex was recrystallized from an acetonitrile–chloroform solution. The yield was about 1 g.

Anal. Calcd for $MnC_{16}H_{36}N_4(CH_3CO_2)_2$: C, 52.50; H, 9.25; N, 12.25. Found: C, 52.61; H, 9.28; N, 12.48.

[Mn^{III}[14]aneN$_4$(Cl)$_2$]X (X^- = PF_6^-, BF_4^-) and [Mn^{III}[14]aneN$_4$(Br)$_2$]PF_6. To 8 mmol of anhydrous $Mn(CH_3CO_2)_2$ dissolved in 125 ml of degassed acetonitrile was added 2.00 g (7 mmol) of dry [14]aneN$_4$. After refluxing 4 hr with stirring, the solution was cooled and was treated with 9 mmol of $NOPF_6$ or $NOBF_4$. The solution turned dark green and NO gas was evolved vigorously. The NO was collected by periodically trapping it with liquid nitrogen *in vacuo*. After 1 hr the solution was filtered in the atmosphere to remove approximately 0.5 g of white solid (ligand salt). The solvent was removed *in vacuo* and the resulting oil was allowed to solidify. The impure solid was heated with 50 ml of absolute ethanol and filtered. The filtrate was treated with HCl or HBr to yield pure pale green air-stable solids. About 2 g of each complex was obtained.

Anal. Calcd for $MnC_{16}H_{36}N_4Cl_2BF_4$: C, 38.65; H, 7.30; N, 11.27; Cl, 14.26. Found: C, 38.45; H, 7.27; N, 11.27; Cl, 14.25.

Anal. Calcd for $MnC_{16}H_{36}N_4Cl_2PF_6$: C, 34.61; H, 6.54; N, 10.09; Cl, 12.77. Found: C, 34.74; H, 6.71; N, 10.22; Cl, 12.58.

Anal. Calcd for $MnC_{16}H_{36}N_4Br_2PF_6$: C, 29.83; H, 5.63; N, 8.70; Br, 24.81. Found: C, 30.42; H, 5.92; N, 8.88; Br, 24.75.

[Mn^{III}[14]aneN$_4$(NCS)$_2$]NCS. Two grams of [Mn^{III}[14]aneN$_4$(Cl)$_2$]BF_4 was suspended in 50 ml of methanol with rapid stirring. To the suspension was added 10 ml of a saturated solution of LiSCN in methanol. The resulting red solution was chilled in an ice bath for 30 min resulting in the crystallization of the red thiocyanate complex. The yield was about 1 g.

Anal. Calcd for [$MnC_{16}H_{36}N_4(NCS)_3$]: C, 44.43; H, 7.06; N, 1909. Found: C, 44.28; H, 7.15; N, 18.72.

[Mn^{III}[14]aneN$_4$(Cl)$_2$]Cl·3H_2O. The free ligand (7 mmol) and anhydrous $MnCl_2$ (8 mmol) were heated to reflux under nitrogen gas for 4 hr in anhydrous methanol. The suspension was chilled in an ice bath and purged with chlorine gas for 15 min. The air-stable yellow-green solid which appeared was removed by filtration and washed with small amounts of methanol and ether and air-dried. About 2 g of the crude [Mn^{III}[14]aneN$_4$(Cl)$_2$]Cl was redissolved in 75 ml of H_2O. Slow evaporation of the solution in the atmosphere over a 2-week period yielded large green plates (about 1 g) of the dichloro chloride.

Table II. Esr Absorptions (G) for $Mn^{II}[14]aneN_4(X)_2$[a]

Axial ligand X^-			
$CF_3SO_3^-$	$CH_3CO_2^-$	$CF_3SO_3^-$	$CH_3CO_2^-$
1650	1400	4850	5050
2950	3300	5450	6800
4200	4250	7250	

[a] Spectra were run in the solid state at room temperature using X-band frequency.

Anal. Calcd for $MnC_{16}H_{36}N_4Cl_3 \cdot 3H_2O$: C, 38.45; H, 8.47; N, 11.21; Cl, 21.28. Found: C, 38.68; H, 8.83; N, 11.35; Cl, 21.50.

Results and Discussion

Manganese(II) Complexes. The synthetic procedure for complexation of manganese(II) salts with [14]aneN$_4$ is more demanding than those encountered for other first-row transition metal ions. In addition to the manganese(II) complexes being O_2 and H_2O sensitive, the synthesis is hampered by the apparent low affinity of the metal ion (zero crystal field stabilization energy) for the macrocyclic ligand. The isolated solids are frequently contaminated with either the free ligand or excess metal salt. Attempts to prepare chloride and bromide derivatives gave solids of variable composition which could not be purified by repeated recrystallization.

The lability of these systems is further demonstrated by the conductance data presented in Table I. Although Mn^{II}[14]aneN$_4$(SO_3CF_3)$_2$ crystallizes unsolvated from acetonitrile, conductance measurements of the complex in the nitrile indicate that the anions are not bound. A conductance value consistent with a 2:1 electrolyte is observed. Nitromethane is also effective in axial ligand displacement and a 1:1 conductance value is observed for this complex. The acetate anion should be a stronger ligand than $CF_3SO_3^-$ toward any metal ion and the conductance values bear this out.

Both of the manganese(II) complexes that were prepared are oxygen sensitive in solution. Nitromethane and acetonitrile solutions of the complexes slowly oxidize to manganese(III) products. Extended exposure (days) produces dark insoluble materials which appear to be hydrous oxides of manganese, possibly MnO_2. In the solid state the complexes are slow to react with oxygen and can be handled for short periods of time in the atmosphere without noticeable color change.

Both of the manganese(II) complexes are very sensitive to pH extremes. Addition of 1 *M* NaOH to ethanol solutions of either complex results in the immediate precipitation of a gelatinous material. On the other hand, addition of small amounts of strong mineral acids such as hydrochloric or perchloric causes the formation of a white solid. Infrared analysis shows the solid is the protonated form of the macrocyclic ligand. The sensitivity to pH sharply contrasts with the greater stability of the Fe(II), Co(III), and Ni(II) complexes of [14]aneN$_4$.[2]

The esr spectra for the Mn(II) derivatives are shown in

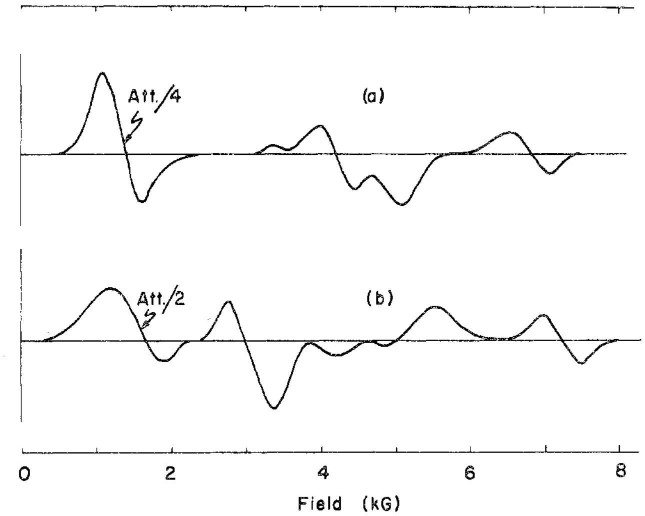

Figure 2. The solid-state esr spectra of (a) Mn^{II}([14]aneN$_4$)(SO$_3$CF$_3$)$_2$ and (b) Mn^{II}([14]aneN$_4$)(CH$_3$CO$_2$)$_2$ at room temperature.

Figure 2 and the data are presented in Table II. Dowsing and Gibson[12] have demonstrated that esr spectra of high-spin d^5 metal ions can be very useful in determining complex geometry and site symmetry. Their approach was successfully applied[13] to a series of tetragonally distorted MnL$_4$X$_2$ complexes where L is a substituted pyridine and X$^-$ = Cl$^-$, Br$^-$, I$^-$, NCS$^-$. These D_{4h} systems exhibited large zero field splittings with D values of 0.035–0.87 cm^{-1} and small but finite rhombic distortions with λ = 0.01–0.1. Although a detailed analysis of the observed and calculated band positions has not been done for the manganese–macrocycle complexes, a few semiquantitative statements can be made about the relative field strengths of the axial ligands and the magnitude of λ and D.

Blumberg[14] has shown that a completely rhombic system has λ, the ratio of E and D, equal to $^1/_3$ and esr signals near g_{eff} = 4.3. The number and position of the esr absorptions observed for the macrocyclic complexes suggest that λ is small or zero. The observation of a weak signal for Mn^{II}[14]aneN$_4$(SO$_3$CF$_3$)$_2$ at g_{eff} = 2.0 is particularly helpful in this regard since increasing amounts of rhombic distortion cause this signal to shift to lower field. Assuming that the macrocyclic ligand will not easily distort and thus vary the in-plane site symmetry about the metal ion, both complexes probably have similar λ values.

The main feature in the X-band spectra of the CH$_3$CO$_2^-$ and CF$_3$SO$_3^-$ complexes is a strong absorption at g_{eff} = 4.0 (1650 G) and g_{eff} = 4.77 (1400 G), respectively. The lower field absorption for CF$_3$SO$_3^-$ indicates that it is a weaker ligand than CH$_3$CO$_2^-$. It has been shown that a decrease in the crystal field on the z axis away from O_h site symmetry will cause this intense absorption to shift toward g_{eff} = 6 (1100 G). The number and position of the transitions for both derivatives indicates that D is small and on the order of 0.1–0.2 cm^{-1}. The D value for the manganese(II)–protoporphyrin IX–diaquo complex is 0.5 cm^{-1} with λ being very small.[15] However, direct comparison of the field strength of the porphyrin and [14]aneN$_4$ is not possible because of dissimilar ligands bonded on the z axis in the two systems.

Manganese(III) Complexes. The manganese(II) complexes are sensitive to oxidants and can be readily oxidized to Mn(III). Chlorine, bromine, oxygen, and hydrogen peroxide are all effective in this regard but nitrosonium salts yield the cleanest products. The most efficient route involves making the bis(acetato)manganese(II) complex followed by oxidation with NOBF$_4$ or PF$_6^-$ and finally addition of HX to give [Mn^{III}[14]aneN$_4$(X)$_2$]BF$_4$ or PF$_6^-$ where X$^-$ = Cl$^-$, Br$^-$. Direct synthesis of the Mn(III) macrocyclic complexes from the few available and stable sources of Mn(III), as has been done for certain porphyrin complexes,[16] met with little success. Reactions of [14]aneN$_4$ with Mn^{III}(CH$_3$CO$_2$)$_3$, Mn^{III}(acac)$_2$X, and Mn^{III}(acac)$_3$ either gave no color change or yielded macrocyclic manganese(III) complexes which were difficult to purify.

Table III. Absorption Spectra of [Mn^{III}[14]aneN$_4$(X)$_2$]$^+$

Axial ligand X$^-$	Solvent	Absorption
Cl$^-$ [a]	CH$_3$CN	10.9 (19), 24.1 sh, 26.5 sh, 31.2 sh, 35.9 (9500)
	SS[b]	12.9, 25.0 sh, 27.0 sh
Br$^-$ [a]	CH$_3$CN	11.7 (15), 23.2 sh, 27.0 sh, 30.8 sh, 34.4 (7800)
	SS[b]	12.8, 25.0 sh
NCS$^-$ [c]	SS[b]	12.0, 23.8 sh, 28.6 sh

[a] PF$_6^-$ salt. [b] Solid-state spectrum run at 77°K. [c] Solution stability was not sufficient for a reliable recording of the spectrum.

The manganese(III) complexes have greater resistance to pH extremes than the divalent complexes. Dilute water, ethanol, and acetonitrile solutions of the dichloro and dibromo complexes are stable to strong mineral acids. No change in visible absorption spectra obtained on these solutions was noted after 2 days of exposure to HCl, HBr, or HClO$_4$. Introduction of small amounts of hydroxide ion on the other hand causes a dark coloration and ultimately the formation of a dark insoluble material.

The electrochemistry of the new macrocyclic complexes is ill defined. Irreversible one-electron reductions are observed for [Mn^{III}([14]aneN$_4$)Cl$_2$]$^+$ and [Mn^{III}([14]aneN$_4$)Br$_2$]$^+$ at +0.20 and +0.37 V, respectively. The cyclic voltammetric (CV) curves for these cations show peak potential separations of about 110 mV. Varying the CV scan rate has no apparent effect on this separation.

The electrochemical behavior of the Mn(II) complexes in acetonitrile is complicated by solvation. The acetate derivative shows one irreversible oxidation at ∼− 0.1 V while the CF$_3$SO$_3^-$ salt exhibits a complicated multiple-wave pattern.

The redox behavior of the Mn–[14]aneN$_4$ complexes differs from that of the known manganese–porphyrin complexes. Mn(III) → Mn(II) couples for the latter generally occur in the range −0.45 to −0.23 V making them more difficult to reduce than the Mn^{III}–[14]aneN$_4$ complexes.[17] Chemically, the Mn^{III}–[14]aneN$_4$ complexes are unstable toward reduction and are immediately reduced to Mn(II) species by nitrite ion while the porphyrin complexes are not. Furthermore acetonitrile solutions of [Mn^{III}[14]aneN$_4$(Br)$_2$]$^+$ slowly darken over a period of weeks probably due to the production of bromine. This behavior has been previously noted for other cationic manganese(III) species[18] but is not common to manganese porphyrin chemistry.[19] Manganese(III) will also likely oxidize $^-$NCS since the characteristic color of [Mn^{III}[14]aneN$_4$(NCS)$_2$]$^+$ in solution fades in about 1 day.

In general manganese(III)–porphyrin complexes are susceptible to oxidation but the Mn^{III}–[14]aneN$_4$ complexes are not. Exposure of [Mn^{III}[14]aneN$_4$(Cl)$_2$]$^+$ to strong oxidants such as chlorine, persulfate, and nitrosonium ions has given no evidence of oxidations states beyond Mn(III).

All of the manganese(III) complexes are colored and have electronic spectra that are consistent with a d^4 metal ion in a tetragonally distorted environment. Table III summarizes the absorption data for all of the compounds examined. Assuming that $Dq_{xy} > Dq_z$, the expected crystal field transitions in order of increasing energy are $^5B_{1g} \rightarrow {}^5A_{1g}$, $^5B_{1g} \rightarrow {}^5B_{2g}$, $^5B_{1g} \rightarrow {}^5B_g$. The lowest energy d–d transition for all of the complexes occurs in the near-infrared region around 11 kK. The position of this band appears to be sensitive to complex environment and in acetonitrile solution it shifts to lower energy relative to the solid-state transmission spectra. This is accompanied by a noticeable change in the color of the complexes in the solid state from green or red to yellow in solution. Substitution of axial ligands by solvent can be discounted on the basis of conductance measurements (Table I). Fackler, *et al.*,[20] have studied a series of octahedral Mn(III) complexes and have noted the same type of behavior for the lowest energy band. Since the d^4 system is subject to significant Jahn–Teller effects, they assumed a tetragonal distortion and assigned the lowest energy band to the $^5B_{1g} \rightarrow {}^5A_{1g}$ electronic transition. The same assignment is probably applicable to the near-infrared band of the Mn(III) macrocyclic complexes. In support of this assignment the energy of the $^5B_{1g} \rightarrow {}^5A_{1g}$ transition ($4Ds + 5Dt$) is observed to decrease with increasing axial ligand field strength.

The remaining d–d transitions appear as shoulders on an intense band (probably a charge-transfer transition) and thus are poorly resolved. Low-temperature mull spectra (77°K) showed only a slight enhancement in the resolution of these bands. However, circular dichroism studies on a series of optically active manganese(III) complexes[21] have provided additional insight as to the number, position, and probable assignment of these higher energy transitions.

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Registry No. [Mn^{II}[14]ane$N_4(CF_3SO_3)_2$], 53198-10-0; [Mn^{II}-[14]ane$N_4(CH_3CO_2)_2$], 53166-18-0; [Mn^{III}[14]ane$N_4(NCS)_2$]NCS, 53166-20-4; [Mn^{III}[14]ane$N_4(Cl)_2$]BF_4, 53166-22-6; [Mn^{III}[14]-ane$N_4(Cl)_2$]Cl, 53166-23-7; [Mn^{III}[14]ane$N_4(Br)_2$]PF_6, 53166-25-9; [Mn^{III}[14]ane$N_4(Cl)_2$]PF_6, 53166-26-0.

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Transition Metal Complexes Containing an Optically Active Macrocyclic Ligand. Manganese(III), Nickel(II), and Copper(II)

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The synthetic macrocyclic ligand *rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (*rac*-5,14-[14]aneN_4) has been resolved *via* its nickel(II) complex. The optically active ligand has been removed from Ni(II) and transferred to copper(II) and manganese(III). A circular dichroism analysis of (+)[Mn((−)5,14-[14]aneN_4)X_2]PF_6, where X^- is Cl^- or Br^-, has been very useful in interpreting the electronic spectrum of this tetragonally distorted high-spin d^4 system. The macrocyclic crystal field ($10Dq$) for Mn(III) as measured by the position of the $^5B_{1g} \rightarrow {}^5B_{2g}$ electronic transition was found to be about 23 kK.

Introduction

As part of an effort to explore the physical and chemical properties of manganese complexes incorporating synthetic macrocyclic ligands we have synthesized a number of high-spin six-coordinate manganese(III) complexes.[2] The compounds with the cyclic secondary amine *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (*ms*-[14]aneN_4),[3] Figure 1a, are pale and give electronic transitions which are likely of d–d origin. Although the electronic spectrum of Mn(III) has been examined by a number of workers,[4-6] the transition assignments and, in particular, a frequently observed low-energy absorption have caused some difficulty. We wish to report the resolution of *rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (*rac*-5,14-[14]aneN_4),[3] Figure 1b, *via* its nickel(II) complex. It has been shown that the coordination geometry of this macrocycle is very similar to that of the more commonly encountered *ms*-[14]aneN_4 ligand[7,8] and as such the spectral results of the two systems should be related. The optically active ligand has been removed from the nickel(II) ion and incorporated into two manganese(III) complexes and one electronically related copper(II) compound. The narrow circular dichroism (CD) absorption has greatly facilitated the detection of transitions not readily observable in the absorption spectra of the complexes.

Experimental Section

Reagents and Equipment. All of the solvents used were reagent grade unless otherwise noted. The CD spectra of the complexes from 220 to 700 nm were recorded in Spectroquality acetonitrile using a Durrum-Jasco spectropolarimeter (Model J-20). The recording of the near-infrared CD spectrum (700–1150 nm) was done using a homemade device similar to that described by Schnepp, *et al.*[9] Generation of the circularly polarized light was accomplished using a quarter-wave plate supplied by Morvue Electronic Systems, Tigard, Oreg. Cary spectrophotometers, Models 14 and 118C, were used for the absorption and first-derivative spectra. Solid-state mull spectra (4.5–30 kK) were done in the manner previously described.[3]

Conductivities at room temperature on 10^{-3}–10^{-4} M solutions were obtained using a Yellow Springs Instrument Co. Model 31 conductivity bridge. Conductances consistent with other 1:1 electrolytes in