Table III. Influence of Electron-Donating Substituents[a] on Pfeiffer Activity[a]

compd	α_p	compd	α_p
d-cinchonine	−0.384	*l*-strychnine	−0.210
d-quinidine[b]	−0.177	*l*-brucine[b]	−0.179
l-cinchonidine	+0.337		
l-quinine[b]	+0.140		

[a] All solutions contain 0.01 M $Zn(phen)_3Cl_2$ and 0.02 M activating agent. [b] The methoxy derivative of the pair.

pounds $Zn(phen)_3$ plus (cinchonine or quinidine), (strychnine or brucine), or (cinchonidine and quinine) there is further evidence of charge-transfer interaction. The second compound in each pair enclosed in parentheses is a ring-substituted derivative of the first with a methoxy group substituting a hydrogen. The results of Pfeiffer-activity studies are shown in Table III. When the aromatic ring on the various alkaloids is substituted with an electron-donor group, the Pfeiffer activity is markedly reduced. All of these observations are consistent with the assumption that the environmental compound is an electron acceptor. In a further attempt to support this contention we studied the UV spectrum of these systems at 0.01 M concentration and with the use of a 0.10-mm cell (since we have a presumed association, high dilutions would dissociate the complex so no results could be expected at 10^{-4} M). Unfortunately no significant change in the spectrum of the phenanthroline ligands could be obtained. This is not too surprising since the molar absorptivity of a charge-transfer band of this type is likely to be on the order of 10^2. This band will be buried in the transition within the rings with an absorptivity of more than 10^4. Thus even if binding is quantitative, the expected change in absorbance is on the order of 1% or less. The short path length also makes differential measurements rather unreliable. NMR results however support this model. Ogino and Kumagi[2b] had found that the chemical shifts of the phenanthroline protons as well as the chemical shifts of the protons on the heterocyclic base in the alkaloid were altered when the complex and the alkaloid were mixed. The protons on the aliphatic groups of the alkaloid showed a much smaller change. The observed shifts were those expected for ring currents and strongly suggested π–π interactions.

The 2 to 1 stoichiometry of the super complexes found in this study is quite striking. We have found that this stoichiometry is quite general. It is not related to the electrostatic interaction since both mono- and divalent AMP anions are bound as are positively charged alkaloid cations.[2a]

In summary we feel that Pfeiffer activity in these systems is due to the formation of a complex containing predominantly 2 mol of environmental compound/mol of tris(phenanthroline)zinc. This aggregate is held together largely by charge-transfer interactions between the phenanthroline ligand and an acceptor group on the environmental compound, this interaction being augmented by electrostatic factors. The two stabilizing forces have different steric requirements, and thus a complex Pfeiffer activity results as one enhances one of these forces.

Acknowledgment. The authors wish to thank the Rutgers University Research Council and Biomedical Grant Program for support of this work. This work was part of the Ph.D. thesis of C.C.-Y.L.

Registry No. $Zn(phen)_3^{2+}$, 28293-61-0; NaAMP, 132-00-3.

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Triboluminescence, Single-Crystal Polarized Absorption and Photoluminescence, and High-Pressure Studies of Linear-Chain Manganese(II) Compounds

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Received August 9, 1979

$((CH_3)_3NH)_3Mn_2Cl_7$, a linear-chain manganese(II) compound which contains both six-coordinate and four-coordinate manganese sites, is brightly triboluminescent. Both the triboluminescence and the photoluminescence spectra exhibit simultaneous emissions from both sites. The emission and d–d absorption spectra are assigned by using single-crystal polarization techniques. The triboluminescence is assigned to the $^4E \rightarrow {}^6A$ transition from the six-coordinate manganese ion and the $^4T_1 \rightarrow {}^6A$ transition from the four-coordinate manganese ion. A comparison of the emission intensities shows that the triboluminescence is equivalent to the high-pressure photoluminescence with $P < 2 \pm 1$ kbar. The relationship between the pressure and the mechanism of the triboluminescence excitation is discussed.

Triboluminescence (TL), the emission of light caused by the application of mechanical stress on crystals, occurs from a large number of compounds.[2,3] The best studied of these are aromatic compounds.[2,4] Triboluminescence from metal complexes is less common.[5] The TL of uranyl salts,[6] europium complexes,[4,7] and tetrahedral manganese salts[8] has been spectroscopically studied. In addition, TL from tetracyanoplatinate crystals has been observed.[5,9]

Crystals of $((CH_3)_3NH)_3Mn_2Cl_7$,[10] which contain chains of face-sharing $MnCl_6$ octahedra and discrete $MnCl_4^{2-}$ ions in the crystal lattice, triboluminesce brightly in the red region of the visible spectrum.[11] A similar salt, $(CH_3)_4NMnCl_3$,[12]

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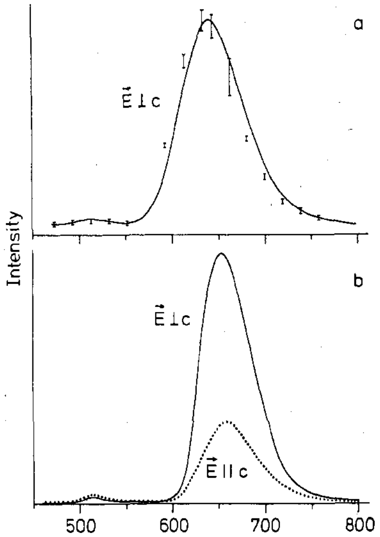

Figure 1. Luminescence spectra of $((CH_3)_3NH)_3Mn_2Cl_7$: (a) triboluminescence spectrum superimposed on the unpolarized photoluminescence spectrum; (b) single-crystal polarized luminescence spectra.

which also contains chains of face-sharing octahedra and which is also photoluminescent, is not TL active. In the course of preliminary spectroscopic investigations of the former compound, it was found that two different luminescences simultaneously occur, the most intense in the red and the other in the green region of the spectrum. The pressure dependence of the intensities and wavelengths of these luminescences offered a new method of relating the pressure values under which the luminescent centers emit in the TL experiment and in the hydrostatic high-pressure photoluminescence experiment. We report here the results of our studies of the triboluminescence, single-crystal polarized luminescence and absorbance, and high-pressure spectroscopic studies of linear-chain manganese complexes.

Experimental Section

$((CH_3)_3NH)_3Mn_2Cl_7$[8] and $(CH_3)_4NMnCl_3$[12] were prepared by using literature methods. Crystals having dimensions of approximately 2 mm × 2 mm × 3 cm were grown from aqueous solution. Domains of these crystals which were clear and exhibited complete extinction under a polarizing microscope were used for the polarized spectroscopic studies.

The instruments used in the spectroscopic studies of the triboluminescence,[8] single-crystal polarized absorbance,[13] single-crystal polarized luminescence,[14] and high-pressure polarized luminescence[15] have all been described previously. In all of the luminescence studies, the crystals were mounted with the crystallographic c axis parallel to the direction of polarization of the laser beam. The triboluminescence spectra are unpolarized.

Results

1. Triboluminescence and Photoluminescence. The triboluminescence spectrum of crystals of $((CH_3)_3NH)_3Mn_2Cl_7$ is shown superimposed on the unpolarized photoluminescence spectrum of the same compound in Figure 1a. This compound is relatively strongly triboluminescent in both its crystalline and powder (microcrystalline) forms. The spectrum of this compound, whose photo- and triboluminescences appear red to the eye, clearly shows a weak emission maximum in the green region of the spectrum at 513 nm. The similar linear-chain compound $(CH_3)_4NMnCl_3$ is not triboluminescent although the photoluminescence spectrum at room temperature is similar to that of the triboluminescent compound.

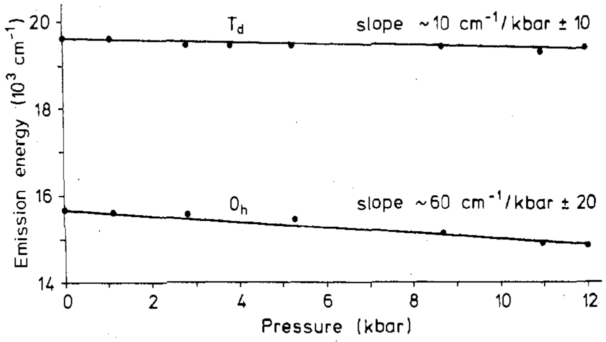

Figure 2. Shift of the emission energy as a function of hydrostatic pressure.

The polarized luminescence spectrum of single crystals of $((CH_3)_3NH)_3Mn_2Cl_7$ is shown at the bottom of Figure 1. The emission maximum at 656 nm is about 3 times more intense in perpendicular polarization than in parallel polarization. The maximum at 513 nm is not polarized within the experimental uncertainty. The ratios of the intensities of the 656:513-nm band are about 11:1 in parallel polarization and about 40:1 in perpendicular polarization. They remain unchanged within experimental error at liquid-nitrogen temperature. These ratios are sensitive to the alignment of the crystals and thus represent lower limits.

2. Pressure Dependence of the Photoluminescence. The emission maxima of $((CH_3)_3NH)_3Mn_2Cl_7$ at 656 and 513 nm both shift to longer wavelengths with increasing hydrostatic pressure. A plot of the energies of the emission maxima as a function of pressure is shown in Figure 2. The pressure dependence of the two emission bands is different. The 656-nm band decreases 60 ± 20 cm^{-1}/kbar while the 513-nm band shifts by only 10 ± 10 cm^{-1}/kbar. The energy shift is linear with pressure over the pressure range studied.

The polarization of the emission in the high-pressure measurements does not change significantly as a function of pressure. For example, the perpendicular to parallel intensity ratio was about 3:1 for the 656-nm emission and 0.81 with a standard deviation of 0.12 for the 513-nm emission band. The constancy was unexpected in view of the experimental difficulties in maintaining a constant crystal orientation as the pressure is changed.

The intensity of the 513-nm emission band relative to that of the 656-nm emission changed dramatically as a function of pressure. Qualitatively, the intensity of the 656-nm band changes only slightly but that of the 513-nm band decreases drastically. At atmospheric pressure in the pressure cell, the ratio of the intensities was 15 ± 3 under parallel polarization and 60 ± 6 under perpendicular polarization. These ratios respectively increased to 200 ± 40 and 650 ± 130 at a pressure of 2 ± 1 kbar. As the pressure further increased, the ratios also increased. In addition, the experimental uncertainties also sharply increased because of the difficulty in accurately measuring the intensity of the very weak 513-nm emission band.

3. Single-Crystal Polarized Absorption Spectroscopy. The single-crystal absorption spectra of $((CH_3)_3NH)_3Mn_2Cl_7$ under parallel and perpendicular polarization at 80 K are shown in Figure 3a. The energies of the absorption bands are given in Table I together with their polarizations and assignments (vide infra). For assistance in the assignment of the above compound's spectrum, the 80 K single-crystal polarized absorption spectrum of $(CH_3)_4NMnCl_3$ was also measured. The spectra are shown in Figure 3b, and energies of the absorption bands of this compound are given in Table II.[16]

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Table I. Assignment of the Single-Crystal Polarized Absorption Spectrum of $((CH_3)_3NH)_3Mn_2Cl_7$

band energy, $cm^{-1} \times 10^3$	obsd polarizn[a]	C_{3v} (six-coordinate)	"T_d" (four-coordinate)
18.6	⊥	$^4E(^4T_{1g})$	$^4T_1$
22.08	s/⊥		
22.26	∥, ⊥		
22.35	∥, ⊥		
(22.5)[b]	(∥, ⊥)	$^4A_1(^4T_{2g}) + {}^4E(^4T_{2g})$	
23.09	∥, ⊥		^4E
23.18	∥, ⊥		
(23.1)[b]	*b*	$^4E(^4E_g)$	
23.33	∥, ⊥	$^4A_1(^4A_{1g})$	$^4A_1$
23.55	∥		
23.77	∥		
26.10	s/⊥		$^4T_2$
26.37	s/⊥		
26.55	⊥	$^4E(^4T_{2g})$	
26.70	⊥		
27.08	∥	$^4A_1(^4T_{2g})$	
27.87	∥, ⊥		^4E
28.08	⊥	$^4E(^4E_g)$	
c			

[a] Polarization symbols: ∥, polarized parallel to the chain axis; ⊥, polarized perpendicular to the chain axis; s/⊥, observed polarization at the border of the experimental uncertainty. [b] Broad bands partially obscured by other, sharper bands. [c] Higher energy absorptions were observed as shoulders on charge-transfer bands.

Table II. Assignment of the Single-Crystal Polarized Absorption and Emission Spectra of $(CH_3)_4NMnCl_3$

band energy, $cm^{-1} \times 10^3$	obsd polarizn[a]	assignt (C_{3v})
18.6	⊥	$^4E(^4T_{1g})$
22.5	∥, ⊥	$^4A_1(^4T_{2g}) + {}^4E(^4T_{2g})$
23.1	⊥	$^4E(^4E_g)$
23.7[b]	∥	$^4A_1(^4A_{1g})$
26.6[c]	⊥	$^4E(^4T_{2g})$
27.2	∥	$^4A_1(^4T_{2g})$
28.2	⊥	$^4E(^4E_g)$
d		
15.2 (emission)	⊥	$^4E(^4T_{1g})$

[a] Polarization symbols: ∥, polarized parallel to the chain axis; ⊥, polarized perpendicular to the chain axis. [b] Lowest energy band of a doublet with energy separation 200 cm⁻¹ ± 20%. [c] Lowest energy band of a doublet with energy separation 250 cm⁻¹ + 20%. [d] Higher energy absorptions were observed as shoulders on charge-transfer bands.

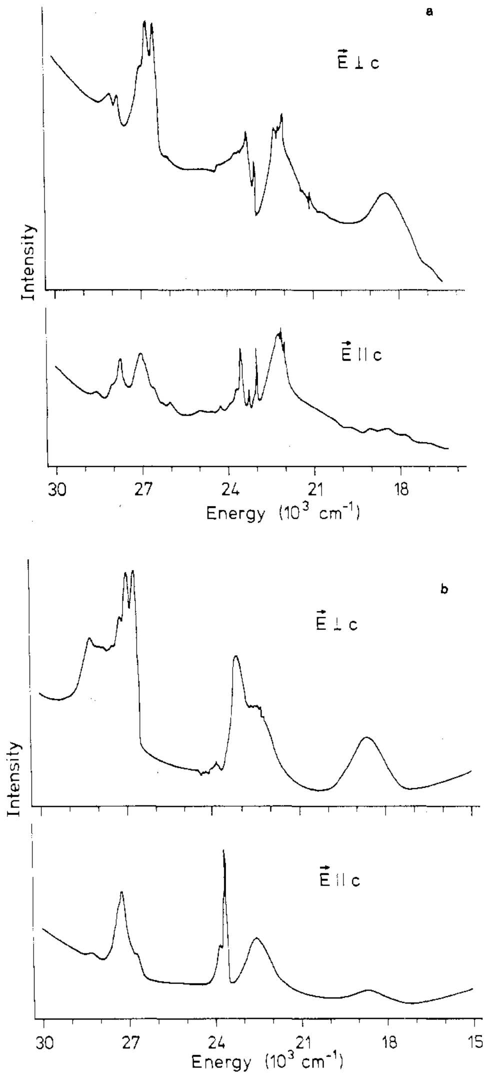

Figure 3. Single-crystal polarized 77 K absorption spectra of (a) $((CH_3)_3NH)_2Mn_2Cl_7$ and (b) $(CH_3)_4NMnCl_3$.

Discussion

1. Emitting Excited States. The two emission bands in the luminescence spectrum of $((CH_3)_3NH)_3Mn_2Cl_7$ originate from the luminescences from the four- and six-coordinate Mn complexes in the molecular crystal. The red luminescence with a maximum at 656 nm originates from the six-coordinate manganese centers having C_{3v} symmetry. A red luminescence (at 665 nm) is also observed from $(CH_3)_4NMnCl_3$ which contains only six-coordinate manganese ions in C_{3v} symmetry. The green luminescence which is observed from $((CH_3)_3NH)_3Mn_2Cl_7$ (but not from $(CH_3)_4NMnCl_3$) originates from the four-coordinate manganese centers in the molecular crystal. The wavelength of the maximum of this luminescence is almost identical with that observed from crystals of tetrahedral $MnCl_4^{2-}$ salts.[8]

The crystal and molecular structures of the above compounds are known.[10,12] In $((CH_3)_3NH)_3Mn_2Cl_7$, chains of face-sharing $MnCl_6$ octahedra run parallel to the *c* direction of the hexagonal lattice. Discrete $MnCl_4^{2-}$ ions are located between the chains. The crystallographic symmetry of the chains is C_{3v}. The $MnCl_4^{2-}$ anions are located in sites of C_{3v} symmetry with significant distortion from T_d symmetry. In $(CH_3)_4NMnCl_3$ only the chains of $MnCl_6$ octahedra exist. The distortion from octahedral symmetry in this compound is larger than that in the former compound.

The single-crystal emission spectra of the above compounds show that the 656-nm emission is strongly polarized in the direction perpendicular to the chain axis. In C_{3v} symmetry, this polarization requires that the transition be from an excited state of E symmetry to the ground state having A symmetry. This assignment is consistent with the predictions of ligand field theory and with the ordering of states observed in the absorption spectra (vide infra).

The emission from the four-coordinate site surprisingly is not strongly polarized. The state giving rise to the 513-nm emission maximum cannot be assigned on the basis of the emission spectrum alone.

2. Polarized Absorption Spectroscopy. The assignment of the absorption spectrum of $((CH_3)_3NH)_3Mn_2Cl_7$ is simplified by comparing it to the spectra of other crystals containing only six-coordinate manganese ions in a linear chain and of crystals containing only four-coordinate manganese ions. The spectrum of the compound containing both the six- and four-coordinate sites is virtually a superposition of the spectra of the purely six-coordinate compound and that of the purely four-coordinate

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compound. Further aids in assigning the spectrum are the strong polarizations of absorption from the six-coordinate sites, the virtually nonpolarized nature of the absorptions from the four-coordinate sites, and the very different band widths.

The absorption energy maxima, the observed polarizations, and the assignments of the bands of $(CH_3)_4NMnCl_3$ are given in Table II. Several aspects are of interest. First, the lowest energy absorption band is strongly polarized perpendicular to the crystal axis. The assignment of this band to $^4E(^4T_{1g})$ is consistent with the emission results discussed above. The ^4E state also is expected to be lowest in energy for a D_3 elongation along the chain axis (i.e., when $Dt > 0$).[17] Second, the half widths of the bands are related to the slopes $d(\Delta E)/d(Dq)$ of the state energies in the energy level diagrams.[18] Note that the transitions to $^4E(^4E_g)$ and $^4A(^4A_g)$ are very sharp while those to the components of the first $^4T_{1g}$, for example, are relatively broad.[19] Finally, note that in two of the absorption bands in Table II fine structure is observed. This structure probably is caused by vibronic coupling and represents a small distortion of the molecular geometry in those excited states relative to that of the ground state.

The absorption energy maxima, the observed polarizations, and the assignments of the bands of $((CH_3)_3NH)_3Mn_2Cl_7$ are given in Table I. Note that bands with very similar energies, identical polarizations, and similar fine structure to those observed in the spectrum of $(CH_3)_4NMnCl_3$ are also observed here. These bands are readily assigned to absorptions arising from the six-coordinate sites in the crystal. The remaining bands, most of which are not significantly polarized within the experimental error of these measurements, are assigned to absorptions of the four-coordinate manganese sites. The energies of the four-coordinate absorptions are very similar to those reported for $MnCl_4^{2-}$ ions in solution[20] but are much more highly resolved. It is of interest that many of the bands from the four-coordinate sites exhibit splitting. For example, the lowest energy four-coordinate absorption appears as two bands at 22.08×10^3 and 22.26×10^3 cm^{-1}. The $^4T_1$ state of tetrahedral symmetry is expected to split into ^4E and $^4A_2$ in C_{3v} symmetry. The former state will be allowed in perpendicular polarization, the latter will be forbidden. A slight perpendicular polarization was observed for the 22.08×10^3 cm^{-1} absorption but its magnitude was within the limits of the experimental uncertainty. Thus, although it is tempting to assign it to the ^4E state, such an assignment cannot be made with certainty. In all of the cases where splitting is observed, the magnitude is on the order of several hundred reciprocal centimeters. Thus the splitting could possibly be the result of vibronic fine structure. Measurements at temperatures lower than 80 K are needed to clarify the assignments. In Table I, the peaks are assigned to the parent state in T_d symmetry.

3. Triboluminescence. (a) Assignment. The triboluminescence spectrum of $((CH_3)_3NH)_3Mn_2Cl_7$ is shown superimposed on the unpolarized photoluminescence spectrum in Figure 1a. The emitting excited states in triboluminescence can readily be assigned to the ^4E state of the six-coordinate manganese and the $^4T_1$ state of the "T_d" four-coordinate manganese ions. No emission from molecular nitrogen[2,21] was observed in the 300–400-nm region of the triboluminescence spectrum.

(b) Pressure Conditions. The pressure at the emitting triboluminescent crystal sites when the TL occurs is unknown for every crystal studied to date. Generally, internal pressures on the order of several kilobars may be attained before fracture of the crystal relieves the strain. Local pressures at the tips of moving cracks may be significantly higher.[22]

Two observables from the high-pressure luminescence spectroscopic study can be used to determine the pressure at triboluminescent sites: the shift of the wavelength of the emission maximum with pressure and the changes in the relative intensities of the emissions from the two different manganese complexes. The former observable is relatively insensitive to pressure in the present compound while the latter provides the first sensitive quantitive method of determining the pressure.

The shift of the emission maximum is 60 ± 20 cm^{-1}/kbar for the six-coordinate site and 10 ± 10 cm^{-1}/kbar for the four-coordinate site. The experimental uncertainty in measuring the TL maximum is on the order of 250 cm^{-1}. With the use of these values and the data from Figure 1, the pressure at the six-coordinate site during its triboluminescence is between 0 and 6 kbars and that at the four-coordinate site is between 0 and 15 kbars. Although the expected values lie within these calculated ranges, the uncertainties are too large to make them useful.

The change in the relative *intensities* of the two emission maxima as a function of pressure provides a more sensitive method of calculating the pressure during triboluminescence. The ratio of the intensity of the six-coordinate emission to that of the four-coordinate emission increases by a factor of one order of magnitude when the pressure is increased from atmospheric pressure to 2 ± 1 kbar. The intensity ratio observed in the triboluminescence spectrum is within experimental error of the intensity ratio observed in the pressure experiment at atmospheric pressure. Thus, the pressure at the emitting sites during triboluminescence is less than 2 ± 1 kbar.

(c) Mechanistic Considerations. According to the recently developed theory of triboluminescence excitation, TL can occur when a crack moves through a crystal having a polar space group.[23] The dynamics of TL have been quantitatively related to the dynamics of crystal fracture.[23] In addition, a large body of evidence has been accumulated which shows a very strong correlation between triboluminescence activity and polar space groups and the corresponding absence of TL activity in crystals having nonpolar space groups.[24,25] The proposed excitation mechanism involves charge production on the newly created surfaces of the moving crack followed by electron-impact excitation, charge–hole recombination excitation, or some other form of molecular excitation by the charges produced during fracture.

The observations on the manganese complexes support both aspects of the theory. The triboluminescent $((CH_3)_3NH)_3Mn_2Cl_7$ has a polar space group $P6_3mc$ and the nontriboluminescent $(CH_3)_4NMnCl_3$ has a nonpolar centrosymmetric $P6_3/m$ space group. In the series of tetrahedral manganese compounds previously reported, the above correlation between space group and TL activity was also observed. Most importantly, the calculated pressure of the emitting molecules in the TL experiment is consistent with the proposal that excitation and emission take place on the surface of a crack. Under these conditions, the effective pressure surrounding the emitting molecule should be small (near atmospheric pressure). The calculated upper limit of the pressure on the emitting

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manganese centers calculated in this work is 2 ± 1 kbar. Finally, the small change of the emission energy as a function of pressure strongly argues against a mechanism involving thermal population of excited states under high pressure. An internal pressure of the order of several hundred kilobar would be required in order for the ground and ^4E excited states to be separated by an energy of the order of kT at room temperature.

Acknowledgment. J.I.Z. gratefully acknowledges the Army Research Office (Durham) for the support of this work, the Alexander von Humboldt Society for a fellowship at the Universität Regensburg, and the Camille and Henry Dreyfus Teacher-Scholar Award.

Registry No. $((CH_3)_3NH)_3Mn_2Cl_7$, 58150-41-7; $(CH_3)_4NMnCl_3$, 31826-81-0.

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Electrochemical and Spectroscopic Studies of Tris(3,5-di-*tert*-butylcatecholato)manganese(IV) and Its Dioxygen Adduct

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Received May 14, 1979

Tris(3,5-di-*tert*-butylcatechol) anion (DTBC) complexes of manganese(II), -(III), and -(IV) have been studied in aprotic solvents by electrochemical, spectroscopic, and magnetic methods. The blue $[Mn^{IV}(DTBC^{2-})_3]^{2-}$ complex reversibly binds oxygen at room temperature to form a red-brown complex $[Mn^{IV}(DTBC^{2-})_2(SQ^{-}\cdot)(O_2^{-}\cdot)]^{2-}$ (SQ = semiquinone) with an apparent formation constant of 2.9 atm^{-1} at 25 °C.

Manganese is an essential element in a number of biological systems.[1] In two of these, photosystem II in green plant photosynthesis[2-5] and certain superoxide dismutases,[6] manganese appears to serve as an electron-transfer agent in reactions that involve molecular oxygen and its reduced states. This has prompted interest in the interactions of molecular oxygen with manganese(II), -(III), and -(IV) complexes which may serve as biological model systems. The manganese complexes that are formed by polyhydroxy ligands are attractive model systems because of their ability to stabilize and solubilize the +3 and +4 oxidation states and to resist irreversible oxidation.[7-11] Several of these complexes react reversibly with molecular oxygen and peroxide ion.[7-9,11]

Although several manganese–catechol complexes have been reported,[12-20] most of the studies have been concerned with the comparison of metal–catechol formation constants[14,16,17,20] and metal-catalyzed autoxidations of catechol.[15,18] The aqueous chemistry of tris(catecholato) complexes of manganese(II) and -(III) has been described as well as the reversible oxidation of tris(3,5-di-*tert*-butylcatecholato)manganese(III) ($[Mn^{III}(DTBC)_3]^{3-}$) to form a unique tris(semiquinonato)manganese(III) complex.[10] A recent communication[21] has reported that the oxidation product of $Mn^{III}(DTBC)_3{}^{3-}$ reversibly binds molecular oxygen in dimethyl sulfoxide at room temperature.

The present paper summarizes the electrochemical, spectroscopic, and magnetic characterization of the oxygen-binding species $Mn^{IV}(DTBC)_3{}^{2-}$ and its O_2 adduct in aprotic solvents. Related studies of the DTBC complexes of manganese(II) and -(III) also are discussed. The $Mn^{IV}(DTBC)_3{}^{2-}$ complex appears to be the first example of a reversible oxygen-binding metal center that is complexed by catecholate ligands.[22-26] The only other example is the $V^{IV}(DTBC)_2$ complex,[27,28] which binds oxygen with a 1:2 O_2:metal ratio.

Experimental Section

Equipment. Cyclic voltammetry measurements were made with a three-electrode potentiostat based on the use of solid-state operational amplifiers.[29] A Princeton Applied Research Model 173 Potentiostat/Galvanostat with the Model 175 universal programmer and Model 179 digital coulometer also was used for cyclic voltammetry and controlled potential electrolysis. Cyclic voltammograms were recorded on Houston Instrument Series 2000 and Hewlett-Packard Model 7030A X-Y recorders.

The Leeds and Northrup electrochemical cell has been described by Sawyer and Roberts[30] and was equipped with a Beckman platinum-inlay working electrode (area 0.23 cm^2), a platinum-flag auxiliary

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