(8) E. Maslowsky, Jr., and K. Nakamoto, *Inorg. Chem.*, **8**, 1108 (1969).
(9) G. G. Dvoryantseva, K. F. Turchin, R. B. Materikova, Yu. N. Sheinker, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, **166**, 868 (1966).
(10) A. N. Mesmeyanov, L. A. Fedorov, R. B. Materikova, E. I. Fedin, and N. A. Kochetkova, *Chem. Commun.*, 105 (1969).
(11) W. Kitching and B. F. Hagarty, *J. Organomet. Chem.*, **16**, 39 (1969).
(12) P. West, M. C. Woodville, and M. D. Rausch, *J. Am. Chem. Soc.*, **91**, 5649 (1969).
(13) C. H. Campbell and M. L. H. Green, *J. Chem. Soc. A*, 3282 (1971).
(14) J. Mink, L. Burscis, and G. Vegh, *J. Organomet. Chem.*, **34**, C4 (1972).
(15) C. C. Su, *J. Am. Chem. Soc.*, **93**, 5653 (1971).
(16) A. J. Campbell, C. A. Fyfe, R. G. Goel, E. Maslowsky, and C. V. Senoff, *J. Am. Chem. Soc.*, **94**, 8387 (1972).
(17) The activation energy will be less than the energy of the Hg–C σ bond.
(18) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).
(19) G. W. Smith, *J. Chem. Phys.*, **50**, 3595 (1969).
(20) J. S. Waugh and E. I. Fedin, *Sov. Phys.—Solid State (Engl. Transl.)*, **4**, 1633 (1963).
(21) V. W. Egger and T. L. James, *J. Organomet. Chem.*, **26**, 335 (1971).

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Manganese(II) Complexes of Selected N_4 Tetradentate Ligands

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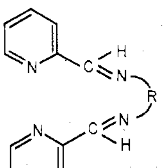
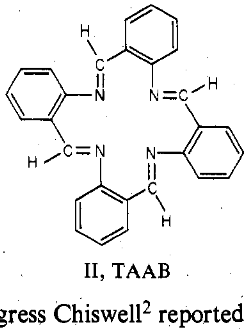
Manganese(II) complexes of the neutral Schiff base ligand (Pytm) derived from 2-pyridinecarboxaldehyde and trimethylenediamine have been synthesized. Complexes of general formula $Mn(Pytm)X_2{\cdot}nH_2O$ were formed where X^- may be Cl^-, Br^-, I^-, NO_2^-, or NCS^- and n is 0 or 1. Two additional materials were isolated: $Mn(Pytm)(Cl)(PF_6)$ and $Mn_2(Pytm)(N_3)_4$. Infrared studies suggest the nitrite ion is O bonded and the thiocyanate ion is N bonded. High-spin magnetic behavior is observed for all derivatives except azide which has an anomalous moment. Gross geometrical features of the complexes have been ascertained from ESR spectra in the solid state. The axial distortion parameter, D, correlates inversely with the donor strength of the axial coordinating ability of the anion.

Introduction

A useful model complex for studying the role of manganese in photosynthetic oxygen evolution is not available. The ubiquity of N_4 macrocyclic ligands in nature has led Calvin and co-workers[1] to suggest that perhaps manganese is bound to a "porphyrin- or corrin-like" ring in the chloroplasts. Consequently we have undertaken a study to synthesize and characterize a series of potentially model manganese complexes which employ relatively simple N_4 tetradentate ligands. This report describes (1) the preparation and properties of manganese(II) complexes of the neutral Schiff base ligands derived from ethylenediamine or trimethylenediamine and 2-pyridinecarboxaldehyde, I, and (2) the self-condensation reaction of *o*-aminobenzaldehyde in the presence of various manganese salts. The latter study was envisioned to yield manganese complexes of tetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecine, II, hereafter referred to as TAAB.



Ia, Pyen, R = C_2H_4
b, Pytm, R = C_3H_6



II, TAAB

While this work was in progress Chiswell[2] reported a series of manganese(II) complexes involving tetradentate nitrogen donors. One of the ligands that was limitedly studied was I. Three different types of complexes were prepared: $Mn(Pyen)X_2$, $Mn(Pyen)_2Y_2$, $Mn(Pytm)(ClO_4)_2$, and $Mn_2(Pytm)_3Y_4$, [X^- = Cl^-, ClO_4^-; Y^- = ClO_4^- $B(C_6H_5)_4^-$]. Anions possessing good donor properties were not studied.

Experimental Section

Materials. 2-Pyridinecarboxaldehyde (Py) and 1,3-diaminopropane (tm) were obtained from Aldrich Chemical Co., Milwaukee, Wis. 1,2-Diaminoethane (en) was obtained from Fisher Scientific, Fairlawn, N. J. Before use, the 2-pyridinecarboxaldehyde was distilled, in vacuo, collecting the fraction which boiled at 40–41 °C at 5 mmHg. *o*-Aminobenzaldehyde (AB) was prepared by the method of Smith and Opie.[3] The preparation of the bisanhydro trimer (2,4:2′,*N*-(*o*-aminobenzo)-1,3:α,2″-(α-hydroxytoluo)-1,2,3,4-tetrahydroquinazoline) followed the method described by Albert and Yamamoto.[4] All other chemicals and solvents were reagent grade or equivalent. In some cases, the absolute ethanol was passed through a column containing 3-Å molecular sieves to ensure dryness.

Preparation of $Mn(Pytm)Cl_2{\cdot}H_2O$. To a stirred solution of freshly distilled 2-pyridinecarboxaldehyde (2.14 g, 0.02 mol) dissolved in 50 ml of dried ethanol was added under nitrogen 1,3-diaminopropane (tm) (0.75 g, 0.01 mol). The solution was heated to reflux for ca. 15 min, while the color turned from a very pale yellow to a deeper yellow. To this hot solution was added dropwise a solution of $MnCl_2{\cdot}4H_2O$ (1.98 g, 0.01 mol) prepared by dissolving the salt in 40 ml of absolute ethanol. The solution immediately became a darker yellow than previously noted, and the color further intensified upon heating for an additional 30 min. Upon cooling overnight, a finely divided yellow precipitate formed which was isolated in a water-free atmosphere, yield 85%. Only partial success was achieved in recrystallization from either absolute ethanol or an ethanol–methanol mixture. The yellow precipitate was washed several times with absolute ethanol and then dried in vacuo at 100 °C for 12 h.

Preparation of $Mn(Pytm)I_2$. This compound was prepared and isolated as described above with the exception that $MnI_2{\cdot}4H_2O$ was substituted for $MnCl_2{\cdot}4H_2O$. A yellow-orange material was produced; yield 90%.

Preparation of $Mn(Pytm)(NCS)_2$. The quadridentate Schiff base ligand was prepared, in situ, as described previously. To the resulting pale yellow solution was added dropwise a solution of $MnCl_2{\cdot}4H_2O$ prepared by dissolving the salt (1.98 g, 0.01 mol) in 60 ml of absolute ethanol. The solution immediately became a darker yellow than previously noted. The mixture was stirred for an additional 30 min after which solid NaSCN (3.24 g, 0.04 mol) was added and dissolved upon stirring. After dissolution a yellow product precipitated which was isolated in a water-free atmosphere, recrystallized from absolute ethanol, and dried as previously described; yield 93%.

Preparation of $Mn(Pytm)(Cl)(PF_6)$. This material was prepared as described above with the exception that a saturated ethanol solution of NH_4PF_6 (6.5 g, 0.04 mol) was added in place of solid NaSCN. A yellow-green material was isolated; yield 88%.

Preparation of $Mn(Pytm)Br_2{\cdot}H_2O$. The quadridentate Schiff base ligand was prepared, in situ, as described previously. To the hot yellow solution was added dropwise a solution of $Mn(OAc)_2{\cdot}4H_2O$ (2.45 g, 0.01 mol) in 50 ml of absolute ethanol. The resulting mixture was allowed to heat for 10 min after which 60 ml of a saturated solution of ethanolic LiBr was added. Yellow-orange crystals were isolated after the volume of solution had been reduced by one-third. The complex was washed and dried as described previously; yield 90%.

Preparation of Mn(Pytm)$(NO_2)_2$. Preparation and isolation of this yellow complex were carried out in the manner described above with the exception that a saturated ethanol solution of $NaNO_2$ (2.8 g, 0.04 mol) was added in place of LiBr; yield 75%.

Preparation of Mn_2(Pytm)$(N_3)_4$. This yellow precipitate was prepared as previously described except that a solution of NaN_3 (0.04 mol, 30 ml of methanol) was substituted for $NaNO_2$; yield 60%.

Attempted Self-Condensation of *o*-Aminobenzaldehyde in the Presence of Manganese(II). To 1.21 g (0.01 mol) of *o*-aminobenzaldehyde dissolved in 40 ml of absolute ethanol was added under nitrogen 1 ml of concentrated HNO_3. To this hot refluxing solution was added 0.0025 mol of either aqueous $Mn(NO_3)_2$ or ethanolic solutions of $MnSO_4{\cdot}4H_2O$, $MnCl_2{\cdot}4H_2O$, $MnI_2{\cdot}4H_2O$, or $(Et_4N)_2MnCl_4$. The resulting mixture in each case was heated for several hours, and upon cooling and the addition of water, a cream-colored precipitate formed each time which did not contain manganese.

Rearrangement of the Bisanhydro Trimer of *o*-Aminobenzaldehyde in the Presence of Manganese. To 1.64 g (0.005 mol) of bisanhydro trimer dissolved in 100 ml of absolute EtOH was added a 50% aqueous solution of $Mn(NO_3)_2$ which was equivalent to 1.8 g (0.005 mol) of metal ion. The solution was heated to reflux for several hours after which only a slight yellow coloration was produced. The solution was concentrated and a white precipitate was isolated which was characterized by infrared and elemental analysis to be unreacted bisanhydro trimer. This procedure was repeated employing $MnCl_2{\cdot}4H_2O$ in ethanol as well as in acetonitrile; the results were identical with those described above.

Physical Measurements. Infrared absorption spectra in the region 4000–250 cm^{-1} were determined employing Nujol mulls or, in certain cases, KBr pellets with a Beckman IR-20A recording spectrophotometer. Magnetic susceptibility data were obtained at room temperature by the Faraday method using mercury(II) tetrathiocyanatocobaltate(II) as the calibrant. Diamagnetic corrections were made employing Pascal's constants. Molar conductances were measured using a Barnstead Model PM-70CB conductivity bridge and a cell with a constant of 1.48 cm^{-1}. The distilled water and methanol used for these measurements had specific conductances of less than 10^{-6} ohm^{-1}. Thermal gravimetric analysis (tga) in the temperature range 25–200 °C was performed using a Stone Model 5 instrument. Samples were run at atmospheric pressure with a temperature programing rate of 5 °C/min with weight losses being detected by a Cahn RG electrobalance. Elemental analyses were performed by the Analytical Services Division of the Chemistry Department of Virginia Polytechnic Institute and State University on a Perkin-Elmer 240 carbon–hydrogen–nitrogen analyzer. The electron spin resonance data on polycrystalline material were obtained on a Varian E-12 ESR instrument which contained an X-band E-101 microwave bridge with either a Varian E-231 or E-234-2 cavity. The magnetic field was controlled by a Hall-effect sensor probe, and 1% pitch in KBr was used as a calibrant. Ultraviolet–visible–near-infrared spectra at room temperature were obtained using a Cary 14 recording spectrophotometer. Solution spectra were taken utilizing spectroquality solvents in matched solution cells. Diffuse transmittance spectra were obtained using Nujol mulls supported on Whatman No. 1 filter paper.

Results and Discussion

Manganese(II) complexes were prepared by the addition of an alcoholic solution containing the metal ion to another alcoholic solution of preformed ligand. The desired product could be obtained either by cooling this solution or by adding the appropriate ammonium, sodium, or lithium salt and then cooling. Better preparative results were obtained when the reactions were run under an inert atmosphere and in dried solvents. Complexes of the general formula Mn(Pytm)$X_2{\cdot}nH_2O$ were formed where X^- may be Cl^-, Br^-, I^-, NO_2^-, or NCS^- and n equals 0 or 1, Table I. Two additional materials were isolated which are formulated Mn(Pytm)(Cl)(PF_6) and Mn_2(Pytm)$(N_3)_4$. Concerning the ethylenediamine-derived ligand only one complex, Mn(Pyen)$(SCN)_2$, could be isolated from solution. The known hydrolytic instability associated with the 5-5-5 membered rings of Pyen in the presence of other divalent metal ions no doubt accounts for the finding.[5] Complexes of trivalent rare earth ions with Pyen, however, have been shown to be hydrolytically stable for several days in an aqueous medium.[6] The bright yellow Mn(Pyen)$(SCN)_2$ was not extensively characterized in this study.

Table I. Analytical Data for the Manganese(II) Complexes

Compd	% C		% H		% N		μ_{eff}, μ_B
	Calcd	Found	Calcd	Found	Calcd	Found	
Mn(Pytm)-$(NCS)_2$	48.23	47.99	3.78	3.96	19.86	19.41	5.92
Mn(Pytm)-I_2	32.14	32.28	2.85	2.84	10.00	10.09	5.92
Mn(Pytm)-$Cl_2{\cdot}H_2O$	45.25	45.68	4.52	5.04	14.07	14.07	5.76
Mn(Pytm)-(PF_6)(Cl)	36.95	36.88	3.28	3.29	11.48	11.29	5.95
Mn(Pytm)-$Br_2{\cdot}H_2O$	37.15	37.84	3.71	3.61	11.56	11.48	5.92
Mn(Pytm)-$(ONO)_2$	45.14	45.07	4.01	4.26	21.06	20.71	6.03
Mn_2(Pytm)-$(N_3)_4$	33.96	34.45	3.02	3.14	42.26	41.88	5.47

The resulting Mn–Pytm complexes are highly crystalline and ranged in color from greenish yellow to bright yellow. All compounds are very soluble in water but decompose after several hours in solution as evidenced by the formation of an insoluble brown precipitate which we have attributed to some oxidized manganese-containing species. All compounds are slightly soluble in methanol and acetone, but none of the materials were soluble in nitromethane, chloroform, or benzene. They all dissolve in pyridine but produce white precipitates a few minutes after dissolution. Elemental analyses and infrared spectra of these white materials supported the formation of $Mn(py)_2X_2$ with liberation of the quadridentate ligand Pytm.

The compounds are thermally stable, melting above 180 °C with decomposition. None of the complexes isolated were sensitive to oxygen in the solid state or in solution. Various oxidants such as I_2, $NOPF_6$, and H_2O_2 were used in an attempt to isolate Mn(III) complexes, but none were successful. In each instance, there appeared to be decomposition of the ligand as indicated by the infrared spectrum, instead of metal oxidation.

Infrared vibrational modes associated with Pytm are in excellent agreement with those recently reported for Ni(Pytm)X_2.[7] Bands assignable to pyridine include four ring stretching vibrations in the range 1600–1430 cm^{-1}, a ring breathing vibration around 1000 cm^{-1}, and a ring C–H out-of-plane deformation around 780 cm^{-1}. Ordinarily, the C=N stretching frequency for the free base would be expected to occur at somewhat higher energy than the C=N stretching mode for the metal complex. However, in Pytm and Pyen the lowering of the Schiff base stretching frequency upon complexation (5–10 cm^{-1}) is not as large as expected (25–50 cm^{-1}). The acyclic C=N group in Pyen and Pytm is conjugated to the π-electron system of the pyridine ring thereby lowering the free-ligand C=N stretching frequency.[8] Upon coordination to manganese(II), this π-electron interaction is expected to diminish. The shifts and the lack of splitting in the ring stretching modes, are taken as an indication that both types of nitrogen are coordinated. The absence of N—H or C=O stretching modes and the presence of strong Schiff base absorptions indicate that the anticipated ligand is not partially hydrolyzed in the complex.

The nitrite group of Mn(Pytm)$(NO_2)_2$ exhibits asymmetric (1395 cm^{-1}) and symmetric (1195 cm^{-1}) stretching vibrational modes and a deformation (825 cm^{-1}) mode. A comparison of our data with the extensive literature[9] values available strongly suggests that the nitrite group is coordinated through the oxygen. It was interesting to note that, over a period of several weeks, the nitrito complex absorbed water and broad peaks around 1335 and 1260 cm^{-1} appeared in the ir spectrum. It was concluded that water was displacing ONO^- as a coordinating group, thus giving rise to ionic absorptions for nitrite.

In the case of Mn(Pytm)$(NCS)_2$, the strong broad peak at 2068 cm^{-1} for the C═N stretch, the shoulder at 803 cm^{-1} attributable to a C—S stretch, and the NCS bend at 472 cm^{-1} are all indicative of coordination through the nitrogen atom.[10] Our observed absorptions at 2106 and 2068 cm^{-1} for ν_{as}, 1306 cm^{-1} for ν_s, and a deformation at 610 cm^{-1} suggest that all azide groups are coordinated to the metal ion.[11] The hexafluorophosphate anion in Mn(Pytm)(PF_6)(Cl) shows a broad absorption from 857 to 827 cm^{-1}, which is assignable to a noncoordinated PF_6^- group.[11]

The compounds listed as monohydrates show the characteristic water absorption as a rather sharp band at 3363 cm^{-1} for the bromide complex and a broad absorption around 3430 cm^{-1} for the chloride complex.[12] The water of the chloride complex is probably lattice water and that of the bromide is coordinated as evidenced by the fact that the chloride complex can be dehydrated at 100 °C, in vacuo, whereas, the coordinated water of the bromide cannot be removed at higher temperatures.

Molar conductances for Mn(Pytm)$X_2 \cdot nH_2O$ complexes have been measured. Insolubility of the complexes limited the solvent choices to water and methanol. Since the complexes decompose in water after several hours as evidenced by the appearance of an insoluble brown precipitate, all materials were measured immediately after dissolution. The data indicate that each complex is a 1:2 electrolyte in water. In methanol, the complexes are only partially solvolyzed. All of the materials except the iodide derivative were shown to be 1:1 electrolytes in 0.001 M solutions. Mn(Pytm)I_2 behaved similarly in both methanol and water. Upon dilution, the conductivity data of many of the complexes in methanol supported a 1:2 electrolyte. The azide complex, which has been tentatively formulated as Mn_2(Pytm)$(N_3)_4$, behaved differently from the other manganese complexes in water, in that the complex is a 1:3 electrolyte. In methanol, however, the complex behaved as a 1:1 electrolyte. These data suggest that the azide complex is best formulated as a dinuclear species rather than as $[Mn(Pytm)]^{2+}[Mn(N_3)_4]^{2-}$.

The literature values for magnetic moments of manganese(II) complexes range from 5.65 to 6.10 μ_B.[13] From Table I, the compounds listed have μ_{eff} = 5.7–6.1 μ_B. The only compound which does not fall within the range expected for high-spin systems is the Mn_2(Pytm)$(N_3)_4$. This abnormally low magnetic moment can possibly be explained by spin exchange between the two manganese atoms.

Electron spin resonance spectroscopy of high-spin Mn(II) has been demonstrated to be very useful in determining complex geometry and metal ion symmetry.[14,15] Table II shows the data acquired from X-band ESR spectra on polycrystalline Mn(Pytm)X_2 complexes at room temperature. The estimation of D and λ values was made by comparing the data in Table II with electron spin resonance transition probability plots.[16,17] These plots show the probability of an ESR transition as a function of axial distortion (D) vs magnetic field with the λ parameter (E/D) being held constant where E is a measure of rhombic distortion. The work by Dowsing and Gibson[17] on the γ-picoline complexes of manganese(II) gave ESR spectra very similar to those of the Mn(Pytm)X_2 complexes.

The ESR spectra of both Mn(Pytm)$Cl_2 \cdot H_2O$ and Mn(Pytm)(PF_6)(Cl) show a single broad absorption of 3010 and 3170 G, respectively (Figure 1A and B). It is obvious that the metal atom cannot be in a regular cubic environment in the solid state since it is surrounded by four nitrogen donors and two anions. The ESR spectra are nevertheless very similar to those of manganese complexes in a regular cubic environment such as $Mn(H_2O)_6^{2+}$. It has been observed by several workers[14,18] that presumably double-chloro-bridged polymeric species of manganese complexes show this same type of ESR spectrum. A polymeric structure in the solid state can be envisioned where chloride ions bridge pairs of $Mn(Pytm)^{2+}$ centers. The g_{eff} values are 2.262 and 2.095, respectively, for Mn(Pytm)$Cl_2 \cdot H_2O$ and Mn(Pytm)(PF_6)(Cl). If the Mn(II) had been in a pure $^6S_{5/2}$ state with no zero-field splitting, its g value would have been 2.0023, the value for the free electron. Any crystal field splitting on this S state would have produced a different g value; however, it is usually lowered when compared to the value for the free electron. It has been proposed by Fidone and Stevens[19] that when low-lying ligand states are mixed into manganese d states, a positive contribution to the g value occurs. Thus, the covalent nature of a ligand to metal bond may cause this increase in the g value.

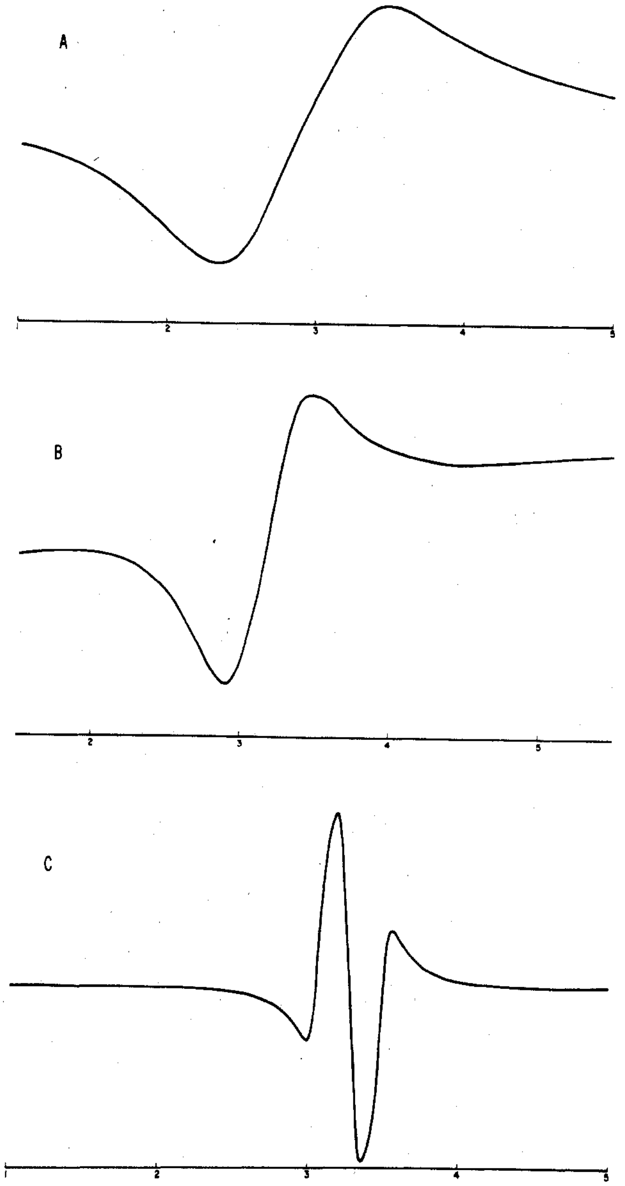


Figure 1. Room-temperature solid-state ESR spectra of (A) Mn(Pytm)$Cl_2 \cdot H_2O$, (B) Mn(Pytm)(Cl)(PF_6), and (C) Mn_2(Pytm)$(N_3)_4$; field in kG.

The strongest transitions are found at 1175 and 1160 G (g_{eff} $\simeq$ 6) for Mn(Pytm)$Br_2 \cdot H_2O$ and Mn(Pytm)I_2, respectively (Figure 2C and D). These transitions, along with another line around g_{eff} = 2, are typical of nearly axial symmetry (λ

Table II. ESR Absorptions of Mn(II) Complexes[a]

Compd	Absorptions, G	g_{eff}	Axial distortion, cm^{-1}
$Mn(Pytm)Cl_2 \cdot H_2O$	3010	2.262	
$Mn(Pytm)(PF_6)(Cl)$	3170	2.095	
$Mn(Pytm)Br_2 \cdot H_2O$	1175	5.498	0.58–0.62
	4750		
	6750		
$Mn(Pytm)I_2$	1160	5.743	0.48–0.52
	3500		
	6200		
	9000		
$Mn(Pytm)(NCS)_2$	3365	2.002	0.075
	2660		
	2050		
$Mn(Pytm)(ONO)_2$	480	2.0	0.05
	1280		
	2225		
	3000		
	4480		
	5680		
$Mn_2(Pytm)(N_3)_4$	2990	2.029	<0.05
	3278		
	3560		

[a] All complexes are believed to be six-coordinate in the solid state.

close to zero) with tetragonal distortion of D greater than 0.02 cm^{-1}. The strong absorption is an indication of the geometry, lines of medium intensity at higher fields are an indication of the axial distortion parameter, D, and the separations between the lines are indications of the magnitude of λ. Absolute zero-field parameters were not assigned because these ESR spectra were run only on polycrystalline materials. A more detailed assignment would involve isomorphic dilution, single-crystal studies, and also Q-band ESR. In these complexes, the λ value was found to be very low (i.e., between 0.0 and 0.1 cm^{-1}). The axial distortion parameter was found to be between 0.48 and 0.50 cm^{-1} for the bromide and 0.58–0.62 cm^{-1} for the iodide.

$Mn(Pytm)(ONO)_2$ and $Mn(Pytm)(NCS)_2$ both have low λ values in the range 0.0–0.01 cm^{-1} as would be expected for the assignment of the previous compounds. The isothiocyanate has its strongest line at 3365 G which gives $g_{\text{eff}} = 2.002$, very close to the free-electron value (Figure 2A). From the remaining lines, the axial distortion, D, could be assigned as 0.075 cm^{-1}. The nitrito complex showed a much broader spectrum than the preceding complex with its strongest lines at 2225 and 4480 G (Figure 2B). The shoulder at 480 G was assigned to a pair of Kramers doublets which were of the order of $h\nu$. The lines at 1280, 3000, and 5680 G indicated an axially distorted complex with λ on the order of 0.0–0.01 cm^{-1} and D close to 0.05 cm^{-1}.

Additional studies were made to see if water of hydration would effect the ESR spectrum by displacement of the anionic coordinated group. The anhydrous vs. hydrated spectrum of the isothiocyanate showed no shifts; however, the hydrated species of the nitrito complex showed a definite shift which was consistent with the previous infrared interpretation where water was shown to displace the ONO^- to form ionic NO_2^-.

Figure 1C shows the ESR spectra of the $Mn_2(Pytm)(N_3)_4$. No estimation of λ is possible due to the closeness of the lines and lack of absorptions at higher fields for this polycrystalline material. The axial splitting parameter, D, must be greater than 0.05 cm^{-1}, since the strongest absorption at $g_{\text{eff}} = 2.03$ is split slightly at higher and lower fields.

It can be seen from Table II that the ESR spectrum of these type of complexes is a function of the coordinating ability of the anion and, thus, should correlate inversely with the spectrochemical series. This trend has been observed to a limited extent in other distorted octahedral complexes.[20] It seems as if the nitrito anion is a better coordinating group than the isothiocyanate anion for Mn(II) in these complexes as judged by comparing their D values. These two anions are close together in the spectrochemical series, and a reversal of their order might be expected since Mn(II) is a hard acid and the oxygen of the nitrito group is a harder base than the nitrogen of the isothiocyanato group.

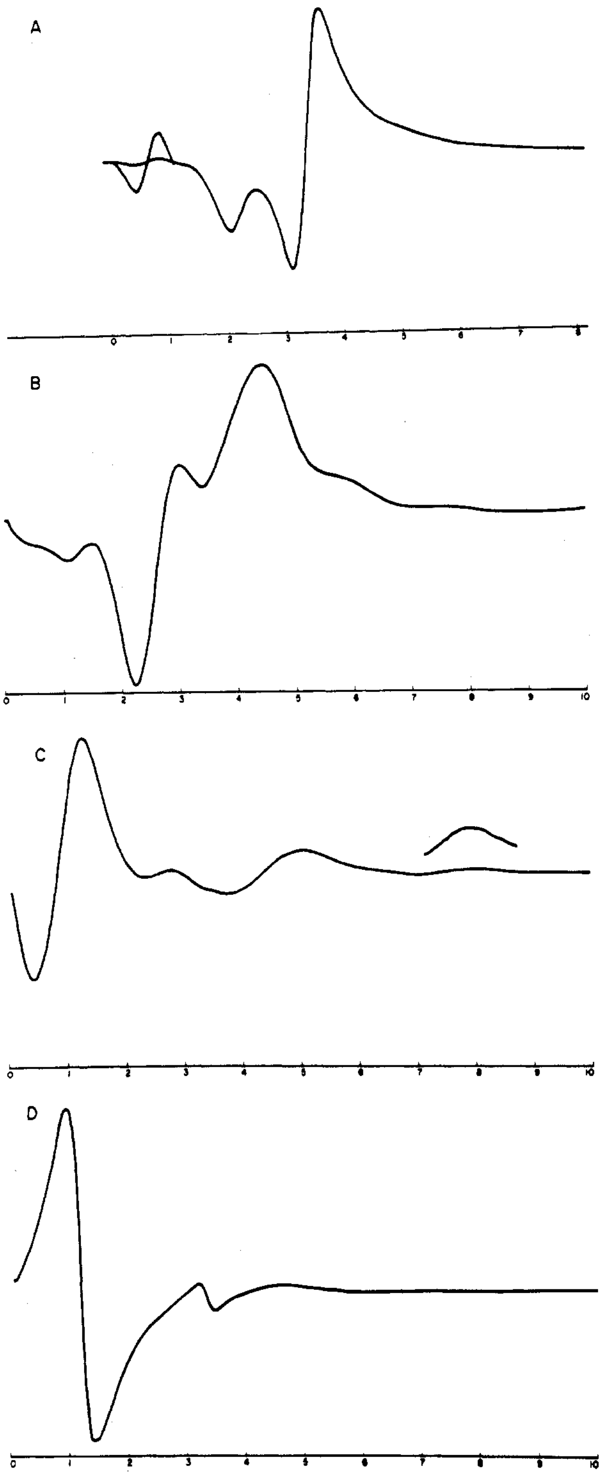


Figure 2. Room-temperature solid-state ESR spectra of (A) $Mn(Pytm)(NCS)_2$, (B) $Mn(Pytm)(ONO)_2$, (C) $Mn(Pytm)Br_2 \cdot H_2O$, and (D) $Mn(Pytm)I_2$; field in kG.

Self-Condensation of *o*-Aminobenzaldehyde in the Presence of Manganese(II). It was shown as early as 1927 by Seidel and Dick[21] that *o*-aminobenzaldehyde (AB) undergoes self-condensation, forming two main products: a bisanhydro trimer and a trisanhydro tetramer. In the presence of certain transition metal ions, two different condensation products are obtained.[22] One is a tridentate macrocyclic ligand, tribenzo[*b,f,j*][1,5,9]triazacycloduodecine which is abbreviated TRI. A second product is a cyclic tetradentate ligand, tetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecine, TAAB. These macrocyclic Schiff bases are isolable only as their metal complexes.

Numerous reactions of AB have been run using various first-row transition metal(II) nitrates.[23] In each case, either TRI and/or TAAB complexes have been observed. Several reactions involving AB and various manganese salts have been run. Both $Mn(NO_3)_2 \cdot nH_2O$ and $MnCl_2 \cdot 4H_2O$ give, upon reaction with AB, the bisanhydro trimer which did not contain any metal ion. These results were verified by infrared and mass spectra. The ir spectrum of this material was identical with that of the same compound prepared independently by a different method and showed a broad NH and OH stretch around 3270 cm^{-1}. The mass spectrum showed a peak at m/e 327 corresponding to the bisanhydro trimer, but the parent peak appeared at m/e 356, corresponding to the ethyl ether of the bisanhydro trimer. Under certain reaction conditions, it was noted by McGeachin[24] that the hydroxy group of the bisanhydro trimer underwent a dehydration with the alcoholic solvent producing the corresponding ether of the bisanhydro trimer.

In several other reactions involving *o*-aminobenzaldehyde, $MnI_2 \cdot 4H_2O$ and $(Et_4N)_2MnCl_4$ gave different results. In these cases, a red precipitate formed which lacked metal ion and decomposed around 220 °C. It was first thought that the trisanhydro tetramer had been formed; however, both elemental analyses and mass spectra proved that assumption to be incorrect. These findings concerning the self-condensation of AB in the presence of manganese(II) reaffirm earlier conclusions reached by Eichhorn and Latif.[25]

Additional studies were made on reactions of the bisanhydro trimer with $MnCl_2 \cdot 4H_2O$ in different solvents. No ligand rearrangement was noted, and only unreacted bisanhydro trimer without any metal ion was isolated. This product again was verified by infrared spectrum and elemental analysis. These observations differ from results with other first-row transition metal ions.[26]

An explanation for the nonincorporation of manganese into this macrocyclic system is not straightforward, especially in light of the fact that Fe–Zn readily coordinate TAAB. A factor which may be considered is the larger size of Mn(II) as compared to the other metals incorporated into the macrocyclic ligand. A physical limitation of the "hole" size of the macrocyclic unit may limit the formation of either $[Mn(TRI)]^{2+}$ or $[Mn(TAAB)]^{2+}$ complexes.

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Registry No. $Mn(Pytm)(NCS)_2$, 58919-16-7; $Mn(Pytm)I_2$, 58976-80-0; $Mn(Pytm)Cl_2$, 58919-55-4; $Mn(Pytm)(PF_6)(Cl)$, 58919-53-2; $Mn(Pytm)Br_2 \cdot H_2O$, 58919-17-8; $Mn(Pytm)(ONO)_2$, 58919-18-9; $Mn_2(Pytm)(N_3)_4$, 58933-77-0; 2-pyridinecarboxaldehyde, 1121-60-4; 1,3-diaminopropane, 109-76-2.

References and Notes

(1) M. Calvin, *Rev. Pure Appl. Chem.*, **15**, 1 (1965).
(2) B. Chiswell, *Inorg. Chim. Acta*, **12**, 195 (1975).
(3) L. I. Smith and J. W. Opie, "Organic Synthesis", Collect. Vol. III, Wiley, New York, N. Y., 1955, p 56.
(4) A. Albert and H. Yamamoto, *J. Chem. Soc.*, 956 (1966).
(5) D. H. Busch and J. C. Bailar, *J. Am. Chem. Soc.*, **78**, 1137 (1956); C. M. Harris and E. D McKenzie, *J. Chem. Soc. A*, 746 (1969); E. Hoyer and B. Lorenz, *Z. Anorg. Allg. Chem.*, **350**, 160 (1967).
(6) D. A. Durham and F. A. Hart, *J. Inorg. Nucl. Chem.*, **31**, 145 (1969).
(7) T. G. Campbell and F. L. Urbach, *Inorg. Chem.*, **12**, 1836 (1973).
(8) P. E. Figgis and D. H. Busch, *J. Chem. Soc.*, 4590 (1961).
(9) K. Nakamoto, "Infrared Spectra of Inorganic and Coordinated Compounds", Wiley, New York, N. Y., 1963.
(10) L. T. Taylor, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, **7**, 785 (1968).
(11) K. Nakamoto, "Coordination Chemistry", Vol. 1, Van Nostrand-Reinhold, New York, N. Y., 1971.
(12) K. Burger, "Coordination Chemistry Experimental Methods", CRC Press, Cleveland, Ohio, 1973.
(13) J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry", Interscience, New York, N. Y., 1960.
(14) R. D. Dowsing, J. F. Gibson, D. M. L. Goodgame, M. Goodgame, and P. J. Hayward, *Nature (London)*, **219**, 1037 (1968).
(15) W. E. Bloomberg, "Magnetic Resonance in Biological Systems", A. Ehrenberg, B. E. Malstrom, and T. Vangard Ed., Pergamon Press, Elmsford, N. Y., 1967.
(16) R. D. Dowsing, J. F. Gibson, M. Goodgame, and P. J. Hayward, *J. Chem. Soc. A*, 1242 (1969).
(17) R. D. Dowsing and J. F. Gibson, *J. Chem. Phys.*, **50**, 294 (1969).
(18) R. D. Dowsing, J. F. Gibson, M. Goodgame, and P. J. Hayward, *J. Chem. Soc. A*, 187 (1969).
(19) I. Fidone and K. W. H. Stevens, *Proc. Phys. Soc., London*, **73**, 116 (1959).
(20) P. S. Bryan and J. C. Dabrowiak, *Inorg. Chem.*, **14**, 296 (1975).
(21) F. Seidel and W. Dick, *Ber. Dtsch. Chem. Ges.*, **60**, 2018 (1927).
(22) G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, **87**, 1706 (1965).
(23) L. F. Lindoy and D. H. Busch, *Prep. Inorg. React.*, **6**, 1 (1971).
(24) S. G. McGeachin, *Can. J. Chem.*, **44**, 2323 (1966).
(25) G. L. Eichhorn and R. A. Latif, *J. Am. Chem. Soc.*, **76**, 5180 (1954).
(26) L. T. Taylor, S. C. Vergez, and D. H. Busch, *J. Am. Chem. Soc.*, **88**, 3170 (1966).