Inorganica Chimica Acta, 49 (1981) 205–208
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Manganese(II) and Manganese(III) Complexes of Linear Pentadentate Schiff Base Ligands

W. M. COLEMAN, III

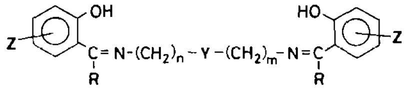
Naval Biosciences Laboratory, Naval Supply Center, Oakland, Calif. 94625, U.S.A.

Received October 22, 1980

Manganese(II) and manganese(III) complexes of linear potentially pentadentate ligands with donor sets of O_2N_2P and N_4P derived from substituted salicylaldehydes and pyridine with a polyamine have been synthesized. Characterization via elemental analysis, infrared–visible spectra and magnetic susceptibility has been accomplished. Pentacoordinate high spin complexes are produced in all cases. Reactivity with various oxidation states of dioxygen and nitric oxide is discussed.

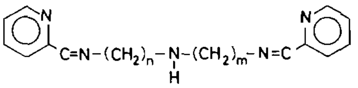
Introduction

Manganese complexes employing hexadentate, pentadentate, and quadridentate Schiff base ligands have received some study in our laboratory [1–10]. These complexes have been of the types illustrated below in Structures, I, II. The resulting Mn(II) and Mn(III) complexes were found to be of high-spin electron configuration. The electrochemical behavior and reactivity patterns with dioxygen and nitric oxide were found to be related to the Z group bound to the aromatic ring.



R	*n*	*m*	*Y*	*Name*
H	1	1	Not present	SALEN
H	2	2	N–H	ZSALDIEN
H	2	2	–S–	ZSALDAES
H	2	3	N–H	ZSALEPT
H	3	3	N–H	ZSALDPT
H	3	4	N–H	ZSALBPT
H	3	3	–O–	ZSALDAPE
C_6H_5	3	3	N–H	HBPDPT
H	2	2	$\mathrm{-\underset{H}{N}-(CH_2)_2-\underset{H}{N}-}$	Z-SAL 1,4,7,10
H	3	3	$\mathrm{-\underset{H}{N}-(CH_2)_2-\underset{H}{N}-}$	Z-SAL 1,5,8,12
H	3	3	$\mathrm{-\underset{H}{N}-(CH_2)_3-\underset{H}{N}-}$	Z-SAL 1,5,9,13

I



n	*m*	*Name*
2	3	PYEPT
3	3	PYDPT

II

Niswander and Taylor [11] have examined the chemistry of the Co complexes of the Schiff base ligand derived from the condensation of selected salicylaldehydes (Z-SAL) and bis(3-aminopropyl) methyl phosphine and found that a 5-coordinate Co(II) complex could be prepared when Z = 5–NO_2. Solutions of the complex were found to be susceptible to oxygenation but the stoichiometry was not well defined. In this report we wish to relay our findings on the chemistry of a comparable ligand system with Mn(II) and Mn(III) where R = $\mathrm{CH_2CH_2CH_2{-}\underset{Ph}{\underset{|}{P}}{-}CH_2CH_2CH_2{-}}$ as described by Structure I and II.

Experimental Section

Materials

The ligands were prepared in an alcoholic medium by condensing the substituted aldehyde with bis(3-amino propyl) phenyl phosphine. These were not isolated but deprotonated with alcoholic KOH and then complexed with a methanolic solution of manganese(II) acetate tetrahydrate. The aldehydes were obtained from Eastman Chemical Co. or Aldrich Chemical Co. Bis(3-amino propyl) phenyl phosphine (PhDAPP) was obtained from K & K Laboratories, Inc. All other chemicals were reagent grade. All sol-

TABLE I. Elemental Analyses and Magnetic Susceptibility Data on the Complexes.

Complex	%C		%H		%N		μ BM
	C	F	C	F	C	F	
$Mn^{III}(SALPhDAPP)NCS \cdot H_2O$	57.75	57.36	5.20	4.73	7.48	7.89	4.90
$Mn^{III}(5MeOSALPhDAPP)NCS \cdot \frac{1}{2}H_2O$	56.86	56.61	5.10	5.20	6.86	6.86	4.85
$Mn^{III}(5NO_2SALPhDAPP)NCS \cdot H_2O$	49.77	49.56	4.17	4.04	10.75	10.63	4.90
$Mn^{II}(PYPhDAPP)(NCS)_2 \cdot H_2O$	52.78	52.70	4.94	4.56	14.21	14.64	5.81

vents used in the preparations were deaerated with N_2.

Preparation of the Complexes

Mn(III)(Z-SALPhDAPP)NCS; Z = H, 5-CH_3O

To 0.01 *M* of Z-SAL in 15 ml of isopropyl alcohol was added 0.005 *M* of PhDAPP in 15 ml of isopropyl alcohol. The yellow solution was brought to reflux under N_2 after which 0.02 *M* of KOH in 10 ml of deaerated methanol was added. The heating was secured but the heating mantel was left around the flask. Then 0.005 *M* of $Mn(II)(OAc)_2 \cdot 4H_2O$ in 10 ml of deaerated methanol was added dropwise. An immediate precipitation of a yellow material occurred. After stirring for ½ hr the solution was filtered under N_2 into a deaerated methanol solution (15 ml) containing 0.02 *M* of NH_4NCS. After filtration was complete the filtrate was then exposed to dry air via a fritted glass bubbler. The solution changed color from reddish to dark green immediately. After 1 hr of bubbling the solution contained a dark green precipitate which was filtered washed with methanol and dried at 100 °C in vacuum.

The yellow material isolated in the filtration, presumably the Mn(II) complex, was found to discolor very rapidly even when isolated in an N_2 atmosphere.

Mn^{III}(5-NO_2SALPhDAPP)NCS

To 0.01 *M* of 5-NO_2SAL in 15 ml of warm 95% ethanol was added 0.005 *M* of PhDAPP in 15 ml of $CHCl_3$. The yellow solution was brought to reflux under N_2 for ½ hr. Then 0.03 *M* NH_4NCS in 10 ml deaerated CH_3OH was added followed by 0.005 *M* of $Mn^{III}(OAc)_3 \cdot 2H_2O$ in 15 ml of deaerated CH_3OH which was added dropwise. A precipitate formed which was filtered off and the filtrate was allowed to stand in the air for two weeks. After which time a rust brown precipitate was isolated, washed twice with 95% ethanol and dried at 100 °C in vacuum.

Mn^{II}(PyPhDAPP)(NCS)$_2$

To 0.01 *M* of PY in 15 ml of 95% ethanol was added 0.005 *M* of PhDAPP. The slight yellow solution was brought to reflux under N_2 for two hr. Then 0.005 *M* of $Mn^{II}(OAc)_2 \cdot 4H_2O$ in 15 ml of deaerated CH_3OH was added dropwise. To this orange solution was then added 0.02 *M* of NH_4NCS as a powdered solid. Halfway through the NCS addition a yellow precipitate formed which was isolated, washed with 95% ethanol and dried at 100 °C in vacuum.

Physical Measurements

Elemental analyses were performed by the Microchemical Analysis Laboratory, Department of Chemistry, University of California, Berkeley. Infrared spectra were obtained on a Beckman IR-5A recording spectrophotometer as Nujol mulls. Magnetic susceptibility data were obtained by the NMR method. Ultraviolet–visible spectra were measured with a Cary 219 recording spectrophotometer. Electrochemical results were obtained in DMSO on equipment described previously [6]. ESR spectra were obtained on a Varian Model 4500 spectrometer in DMF/Toluene (50/50 v/v).

Results and Discussion

A series of Mn(III) and Mn(II) complexes have been prepared from linear potentially pentadentate ligands containing an O_2N_2P ligand field. The analytical data, Table I, support the proposed composition, MnL, where L is the ligand. All of the complexes were isolated as hydrates. The complexes Mn^{II}(Z-SALPhDAPP) where Z = H, 5-NO_2 and 5-CH_3O are extremely susceptible to oxygenation in the solid state (*i.e.* decolorization will occur within a few hr even if prepared in an inert box) and consequently were not isolated.

The room-temperature magnetic susceptibility data, Table I, suggest high-spin electron configurations for all of the complexes. The same results were obtained in our previous reports on Mn(II) and Mn(III) complexes [1–10].

The solution visible spectra (DMSO) of Mn^{III}(Z-SALPhDAPP)NCS reveals d → d bands (shoulders) at 610 nm (Z = H) and 640 nm (Z = 5-CH_3O). The

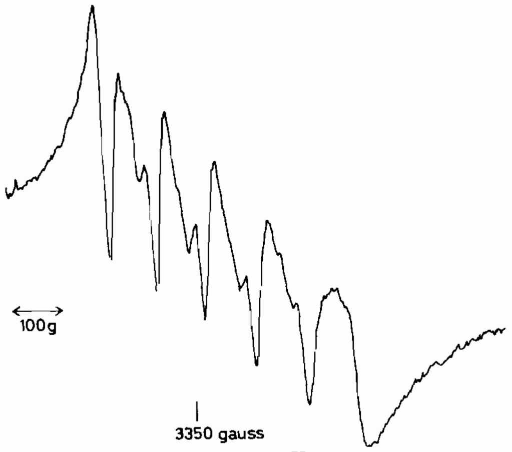


Fig. 1. ESR spectrum of Mn^{II} (PYPhDAPP)(NCS)$_2$ (10^{-2} *m*) dissolved in DMF/Toluene (50/50) at –150 °C.

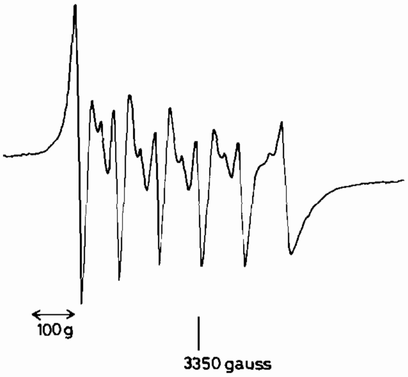


Fig. 2. ESR spectrum of Mn^{III} (SALPhDAPP) (NCS) (10^{-3} *m*) dissolved in DMF/Toluene (50/50) plus NO at –150 °C.

extinction coefficients were found to be 130 (Z = H) and 140 (Z = 5-CH$_3$O). The visible spectra suggests that the Mn(III) complexes are octahedral in solution [2], the sixth donor being the solvent DMSO. The 5-NO$_2$ derivative possesses a large charge-transfer band that obscures the less intense d → d transition.

The proposed formulation for the complexes is supported by infrared data. The complexes, formulated as hydrates, have broad bands around 3400 cm^{-1} which are assigned to OH stretching modes. The infrared of all complexes display a strong absorption band in the region 1650–1610 cm^{-1} which is assigned to a coordinated C≡N stretching mode in the Schiff base [2]. The complexes display the characteristic C≡N stretch for an N-coordinated thiocyanate ion [12] around 2050 cm^{-1}. This IR data reveals that the complexes are octahedral in the solid state with the sixth donor atom coming from the coordinated thiocyanate ion.

All of the Mn(III) complexes are ESR silent which is predicted for high spin even electron systems [2]. Mn^{II}(PYPhDAPP)(NCS)$_2$ does possess an ESR spectrum containing 6 lines (I = 5/2 for Mn) (coupling = 90 gauss). At –150 °C each of these six lines are split into three, Figure 1. This ESR behavior is identical to that found with the comparable Mn^{II}-(PYDPT)(NCS)$_2$ complexes [5] and is consistent with a high spin electron configuration.

Dioxygen Reactivity

All of the Mn(II) complexes, prepared *in situ,* with the exception of Mn^{II}(PYPhDAPP)(NCS)$_2$ react with dioxygen. If the oxygenation is carried out in the presence of excess NCS$^-$, complexes of the formula Mn^{III}(Z-SALPhDAPP)NCS (Z = H, 5-CH$_3$O) can be isolated. This reactivity pattern has been used successfully for the preparation of other Mn(III) complexes from a Mn(II) precursor [2, 9]. It seems generally accepted now that the reaction of a Mn(II) complex with dioxygen proceeds thru a Mn(III) complex which can be precipitated in the presence of excess anion.

Mn^{II}(PYPhDAPP)(NCS)$_2$ fails to react with dioxygen. This was predicted based on the results obtained on the comparable Mn^{II}(PYDPT)(NCS)$_2$ series [5]. A discussion of the structure–reactivity relationships between manganese complexes and dioxygen reveals these results to be a general phenomenon [8].

Nitric Oxide Reactivity

All of the Mn(III) complexes were found to react with NO when dissolved in DMF/Toluene (50/50). The reaction was not reversed when N$_2$ was bubbled through the solution. Dark brown–green solutions of the complexes are reduced to Mn(II) resulting in a Mn^{II}(L)(NO) complex. Figure 2 is the ESR spectrum obtained at –150 °C when Mn^{III}(SALPhDAPP)-NCS is reacted with NO in DMF/Toluene. The six groups of triplets indicate the presence of Mn(II) in a high spin electron configuration. These results parallel exactly those found with the Mn^{III}(Z-SALDPT)NCS series [3].

Mn^{II}(PYPhDAPP)(NCS)$_2$ does not react with NO. A similar pattern of reactivity was found for the comparable Mn^{II}(PYDPT)(NCS)$_2$ complex [5].

O_2^{1-} and O_2^{2-} Reactivity

All of the Mn(III) complexes reacted with O_2^{1-} and O_2^{2-} as revealed by a color change from green to yellow. The reactions have been monitored by UV–VIS spectrophotometry in the same manner as Valentine [13]. When DMSO solutions of the Mn(III) complexes were titrated with O_2^{1-} and O_2^{2-}, no isosbestic points were observed in the spectra. This result indicates that a mixture of products are formed in this reaction. However, the d → d band associated with Mn(III) is gradually erased upon addition of O_2^{1-} and O_2^{2-}. The absence of isosbestic points in the Mn^{III}(SALPhDAPP)NCS titrations is in contrast to the findings with Mn^{III}(Z-SALDPT)-NCS complexes [14] and the findings of Valentine [13]. When the Mn^{III}(Z-SALDPT)NCS complexes are titrated with O_2^{1-} and O_2^{2-} well defined isosbestic points occur at several wavelengths. This evidence was interpreted as indicating only two products in the Mn^{III}(Z-SALDPT)NCS plus O_2^{1-}/O_2^{2-} reaction, possibly a Mn^{II}(Z-SALDPT) oxygen complex [14]. These results with the Mn^{III} (Z-SALPhDAPP)NCS complexes are not as straightforward and the identity of the mixture of products is unclear.

Preliminary electrochemical investigations employing cyclic voltammetry have shown that the complexes are not well behaved based on reversible or quasi-reversible criteria. Irreversible reduction waves are obtained on every complex. This behavior is also in contrast to that displayed by the comparable Mn^{III}(Z-SALDPT)NCS complexes which possess well behaved quasi-reversible properties. Consequently, the chemistry observed with O_2^{1-}/O_2^{2-} may have some of its foundation in the nonideal electrochemical behavior of the complexes. The reason for this irreversible cyclic voltamagramic behavior is not clear.

In summary, the reactivity patterns of a set of Mn complexes containing potential pentadentate ligands O_2N_2P and N_4P with O_2, O_2^{1-}, O_2^{2-} and NO have been examined. The results indicate that the O_2N_2P and N_4P ligand field induces the Mn to react in much the same manner as other ligand fields comprised of O_2N_3, O_3N_2, O_2N_2S, and N_5. Subtle differences in O_2^{1-} and O_2^{2-} reactivity and electrochemical behavior however were demonstrated.

Acknowledgements

The author expresses thanks to Dr. R. K. Boggess (Radford University) for the preliminary electrochemical investigation. The support of the Office of Naval Research is greatly acknowledged.

References

1 W. M. Coleman and L. T. Taylor, *Inorg. Chem., 16,* 1114 (1977).
2 W. M. Coleman, R. R. Goehring and L. T. Taylor, *Syn. React. Inorg. Metal-Org. Chem., 7,* 333 (1977).
3 W. M. Coleman and L. T. Taylor, *J. Am. Chem. Soc., 100,* 1705 (1978).
4 W. M. Coleman and L. T. Taylor, *Inorg. Chim. Acta, 30,* L291 (1978).
5 W. M. Coleman and L. T. Taylor, *J. Inorg. and Nucl. Chem., 41,* 95 (1979).
6 W. M. Coleman, R. R. Goehring, L. T. Taylor, J. G. Mason and R. K. Boggess, *J. Am. Chem. Soc., 101,* 2311 (1979).
7 R. K. Boggess, J. W. Hughes, W. M. Coleman and L. T. Taylor, *Inorg. Chim. Acta, 38,* 183 (1978).
8 W. M. Coleman and L. T. Taylor, *Coord. Chem. Rev., 32,* 1 (1980).
9 W. M. Coleman and L. T. Taylor, *J. Inorg. Nucl. Chem., 42,* 683 (1980).
10 S. J. E. Titus, W. M. Barr and L. T. Taylor, *Inorg. Chim. Acta, 32,* 103 (1979).
11 R. H. Niswander and L. T. Taylor, *Inorg. Chem., 15,* 2360 (1976).
12 W. C. Fultz, J. L. Burmeister, J. J. MacDougall and J. H. Nelson, *Inorg. Chem., 19,* 1085 (1980).
13 J. S. Valentine and A. E. Quinn, *Inorg. Chem., 15,* 1997 (1976).
14 W. M. Coleman and L. T. Taylor. Manuscript in preparation.