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Pulsed Nuclear Magnetic Resonance Study of the Molecular Dynamics of Fluxional Organometallic Molecules in the Solid State. 2. Complexes Containing η^1 (σ-Bonded) Cyclopentadienyl Rings

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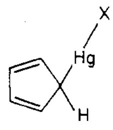
Motion of the organic moiety of fluxional organometallic compounds of the series $(\eta^1\text{-C}_5\text{H}_5)\text{HgX}$ (X = η^1-C$_5$H$_5$, Cl, Br, I) in the solid state is confirmed by the temperature dependence of T_1, the spin–lattice relaxation time, and $T_{1\rho}$ the spin–lattice relaxation time in the rotating frame, and values for the activation energy for this process are obtained. The results are discussed in relation to the molecular structure of the compounds and to the results of high-resolution (solution) NMR as well as to the results from continuous-wave (CW) solid-state NMR.

Introduction

It has been shown in the previous article[2] that pulsed NMR studies of fluxional cyclooctatetraene complexes can be very useful in investigating motion in the solid state. In the cyclooctatetraene complexes, the bonding between the metal atoms and the cyclooctatetraene ring is similar to that observed in metal–butadiene complexes, i.e., delocalized over several carbon atoms. In some fluxional organometallic molecules the localization of bonding is extreme, the static structure containing a metal–carbon σ bond. The series of compounds chosen for study were $(\eta^1\text{-C}_5\text{H}_5)\text{HgX}$ (**1**) where X = Cl, Br, I, and $(\eta^1\text{-C}_5\text{H}_5)$. These compounds have been extensively investigated.[3-14] Although preliminary results on $(\eta^1\text{-C}_5\text{H}_5)_2$Hg generally favored η^1, one group proposed a η^5 (π-bonded) structure **2**,[5,9,10] while another proposed a di(η^3), di(π-allyl) bonding to mercury[6] (structure **3**).



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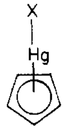

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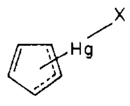

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Recent solution NMR results[12] have conclusively shown that the cyclopentadienylmercury halides are indeed η^1, the chloride ($(\eta^1\text{-C}_5\text{H}_5)\text{HgCl}$) showing a completely resolved spectrum at low temperatures. It was also suggested that the cyclopentadienyl rings in bis(cyclopentadienyl)mercury were η^1 since broadening of the single resonance occurred below 173 K. More recently, Campbell and Green[13] have studied the spectrum of bis(methylcyclopentadienyl)mercury and have shown unambiguously that the rings in this compound are η^1. Both 1,2 and 1,3 shifts have been proposed[3,11] as possible rearrangement pathways in solution. Calculations by Su[15] employing modified Woodward–Hoffmann rules predict a 1,2 rearrangement pathway.

The compounds in this series $(\eta^1\text{-C}_5\text{H}_5)\text{HgX}$ have recently been investigated by continuous-wave (wide-line) solid-state NMR.[16] It was shown that the cyclopentadienyl rings in each of the compounds in this series possess considerable motional freedom in the solid state at room temperature.

The purpose of the present work was first to substantiate the occurrence of motion and second to obtain better values for the activation energies involved for the reorientation processes in these compounds by measurement of the temperature dependence of T_1 (the spin–lattice relaxation time) and $T_{1\rho}$ (the spin–lattice relaxation time in the rotating frame) by pulse NMR techniques.

Experimental Section

The pulse spectrometer and temperature variation were identical with those described in the previous article.[2] The frequency was maintained at 14 MHz for all measurements on these compounds.

The temperature range over which the compounds were studied was different for each compound. The upper limit was the temperature at which the compound started to decompose, and the lower limit was the temperature at which, by a combination of short T_2 and dead time of the pulse spectrometer, the signal to noise ratio became too small for meaningful results to be obtained.

The compounds were prepared using the procedures outlined in ref 16.

Results

$(\eta^1\text{-C}_5\text{H}_5)_2$Hg. T_1 and $T_{1\rho}$ were measured over the temperature ranges 304–185 and 270–185 K, respectively. The value of T_1 was found to pass through a minimum at about 244 K. Figure 1 shows a computer fit to the experimental results; the values for E_a the activation energy, τ_∞ the correlation time at infinite temperatures, and the constant C are given in Table I. The value of $T_{1\rho}$ was not observed to pass through a minimum before the signal to noise ratio became too great. A computer calculation was performed to find the value of E_a (Table I) from the experimental $T_{1\rho}$ data; in this calculation the values for τ_∞ and C obtained from the T_1 experiment were used and kept constant. The calculated dependence of $T_{1\rho}$ on temperature is shown together with the experimentally determined values in Figure 1, the calculated position of the minimum value for $T_{1\rho}$ being 180 K. The values for the activation energy obtained from T_1 and $T_{1\rho}$ experiments are in reasonable agreement, the mean value being 6.15 kcal/mol.

$(\eta^1\text{-C}_5\text{H}_5)$HgCl. T_1 and $T_{1\rho}$ were measured over the temperature range 330–268 K. The value of T_1 was found to be decreasing as temperature increased; however T_1 was not observed to pass through a minimum at temperatures below 330 K (decomposition of the compound was found to increase markedly with time above this temperature). The value of $T_{1\rho}$ was found to pass through a minimum value of 300 K and a good fit to the experimental $T_{1\rho}$ results was obtained. The values for E_a, τ_∞, and C thus obtained are given in Table I.

A calculation was then performed to find a value of E_a from the T_1 data; in this calculation the values obtained for τ_∞ and C from $T_{1\rho}$ were used and kept constant. The calculated dependence of T_1 on temperature is shown, together with the experimentally determined values, in Figure 2 (upper curve).

The values obtained for the activation energy from T_1 and $T_{1\rho}$ experiments are in reasonable agreement, the mean value being 9.85 kcal/mol.

Table I. Values for the Activation Energy, E_a, Together with the Values for the Constants τ_∞ Used in Eq 2 of Ref 2 and the Constant C Used in Eq 1 and 3 of Ref 2

			Activation energy, kcal mol^{-1}			
Compd	τ_∞, s	$10^{-9}C$, s^{-2}	T_1[a]	$T_{1\rho}$[b]	BPP[c]	Waugh[d]
$(\eta^1\text{-}C_5H_5)_2Hg$	7.81×10^{-14} [a]	1.05[a]	5.65	6.26	2.5	5.7
$(\eta^1\text{-}C_5H_5)HgCl$	5.94×10^{-14} [b]	1.37[b]	9.50	10.2	14.0	9.8
$(\eta^1\text{-}C_5H_5)HgBr$	1.43×10^{-13} [b]	1.63[b]	8.05	8.36	8.5	8.9
$(\eta^1\text{-}C_5H_5)HgI$	1.34×10^{-14} [b]	2.38[b]	9.93	10.3	11.4	8.6

[a] Values obtained from T_1 measurements. [b] Values obtained from $T_{1\rho}$ measurements. [c] Values obtained using the procedure of ref 18, 19. [d] Values obtained using the procedure of ref 20.

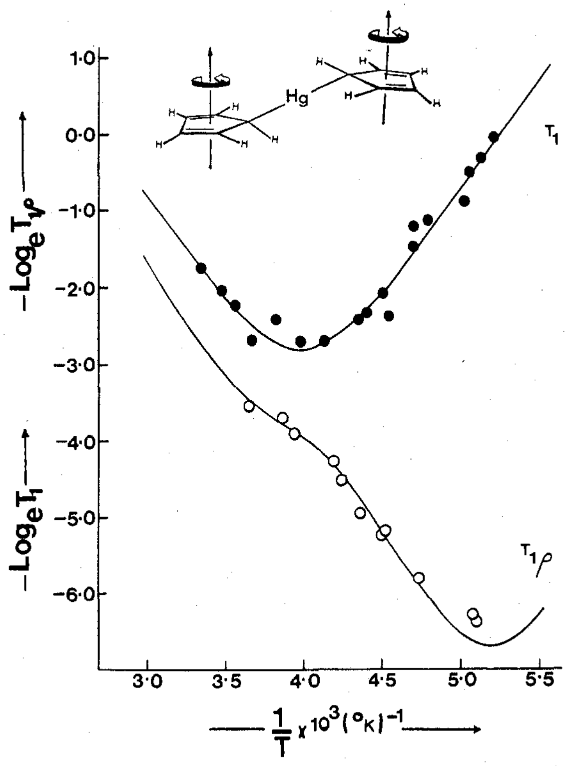

Figure 1. Variation of ln T_1 (T_1 in seconds) and ln $T_{1\rho}$ ($T_{1\rho}$ in seconds) against the reciprocal of absolute temperature for $(\eta^1\text{-}C_5H_5)_2Hg$ in the solid state. The filled circles represent the experimental T_1 data and the open circles represent the experimental $T_{1\rho}$ data, both sets of data were collected at 14 MHz. The continuous curves represent the theoretical relationships obtained using the constants given in Table I. In this case a least-squares fit to the experimental T_1 data yielded values of τ_∞, C, and E_a. These values were then used to fit the experimental $T_{1\rho}$ data, the values of τ_∞ and C being kept constant and only E_a being allowed to vary.

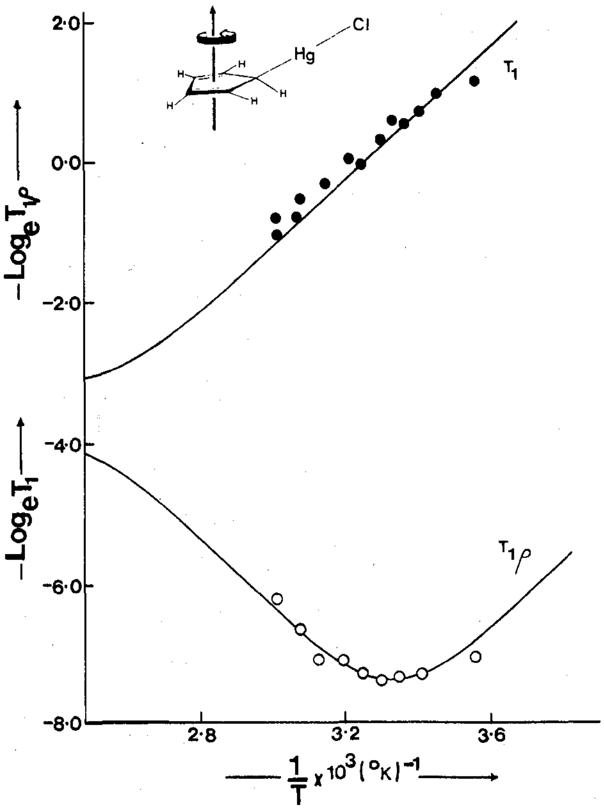

Figure 2. Variation of ln T_1 (T_1 in seconds) and ln $T_{1\rho}$ ($T_{1\rho}$ in seconds) against the reciprocal of absolute temperature for $(\eta^1\text{-}C_5H_5)HgCl$ in the solid state. The filled circles represent the experimental T_1 data and the open circles represent the experimental $T_{1\rho}$ data; both sets of data were collected at 14 MHz. The continuous curves represent the theoretical relationships obtained using the constants given in Table I. In this case a least-squares fit to the experimental $T_{1\rho}$ data yielded values of τ_∞, C, and E_a. These values were then used to fit the experimental T_1 data, the values of τ_∞ and C being kept constant and only E_a being allowed to vary.

$(\eta^1\text{-}C_5H_5)HgBr$. Results very similar to those of $(\eta^1\text{-}C_5H_5)HgCl$ were obtained; i.e., no minimum for T_1 was observed but $T_{1\rho}$ was observed to pass through a minimum. A computer fit to the experimental $T_{1\rho}$ data yielded values for E_a, τ_∞, and C (Table I). The values of τ_∞ and C were then used and kept constant to calculate a value for E_a (Table I) from the T_1 data. The mean value for E_a from the T_1 and $T_{1\rho}$ experiments is 8.21 kcal/mol. The calculated curves for T_1 (upper curve) and $T_{1\rho}$ (lower curve) are shown, together with the experimentally obtained values, in Figure 3.

$(\eta^1\text{-}C_5H_5)HgI$. The results for this compound were similar to those of $(\eta^1\text{-}C_5H_5)HgCl$ and $(\eta^1\text{-}C_5H_5)HgBr$ (Figure 4). The values of E_a, τ_∞, and C were obtained from the $T_{1\rho}$ results (Table I). The values of τ_∞ and C thus obtained were used to calculate a value of E_a from the T_1 results. The mean value for E_a was found to be 10.1 kcal/mol.

Discussion

Motion of the cyclopentadienyl moiety in the solid state for this series of compounds may now be considered firmly established. The results of the pulse NMR experiments are in complete accord with the earlier CW results, the most probable motion being a series of 1,2 shifts of the ring relative to the mercury atom, with the simultaneous rotation of the cyclopentadienyl ring together with the "breaking" and "re-forming" of the carbon–mercury σ bond.[17] The activation parameters in each case are approximately equal to, or less than, 10 kcal/mol, which is consistent with motion occurring (on an NMR time scale) in the solid state at room temperature.

The values for the activation energy for rotation to occur in this series are in the order I ~ Cl > Br > $\eta^1\text{-}C_5H_5$. If the activation energy was dependent soley on intramolecular forces, one would expect the order of activation energies to be Cl > Br > I > $\eta^1\text{-}C_5H_5$; i.e., as the electronegativity of X decreases, so does the value of the activation energy,[17] which is different from that found in the present work. The change in order

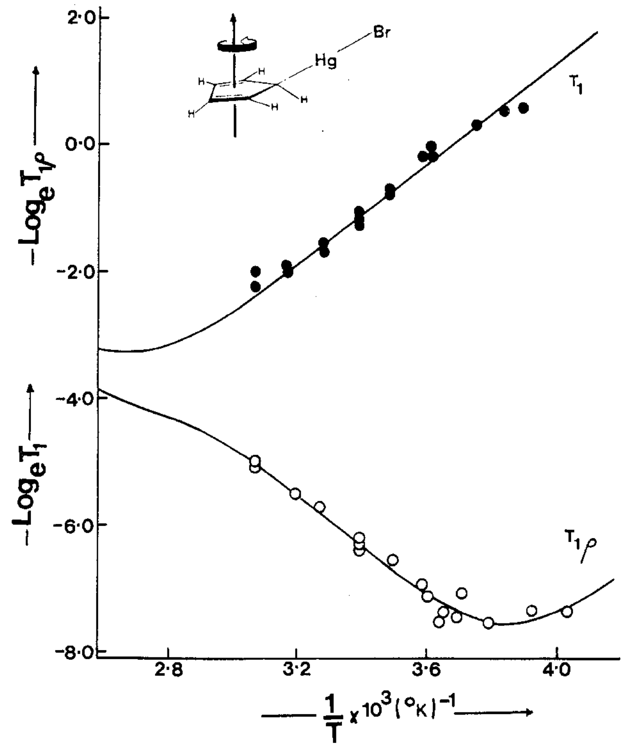

Figure 3. Variation of ln T_1 (T_1 in seconds) and ln $T_{1\rho}$ ($T_{1\rho}$ in seconds) against the reciprocal of absolute temperature for $(\eta^1\text{-C}_5\text{H}_5)\text{HgBr}$ in the solid state. The filled circles represent the experimental T_1 data and the open circles represent the experimental $T_{1\rho}$ data; both sets of data were collected at 14 MHz. The continuous curves represent the theoretical relationships obtained using the constants given in Table I. In this case, a least-squares fit to the experimental $T_{1\rho}$ data yielded values of τ_∞, C, and E_a. These values were then used to fit the experimental T_1 data, the values of τ_∞ and C being kept constant and only E_a being allowed to vary.

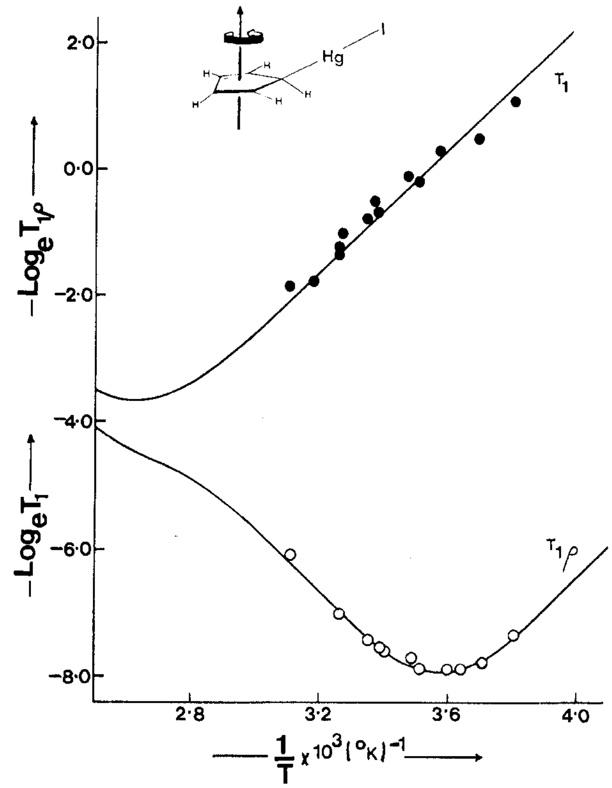

Figure 4. Variation of ln T_1 (T_1 in seconds) and ln $T_{1\rho}$ ($T_{1\rho}$ in seconds) against the reciprocal of absolute temperature for $(\eta^1\text{-C}_5\text{H}_5)\text{HgI}$ in the solid state. The filled circles represent the experimental T_1 data and the open circles represent the experimental $T_{1\rho}$ data; both sets of data were collected at 14 MHz. The continuous curves represent the theoretical relationships obtained using the constants given in Table I. In this case a least-squares fit to the experimental $T_{1\rho}$ data yielded values of τ_∞, C, and E_a. These values were then used to fit the experimental T_1 data, the values of τ_∞ and C being kept constant and only E_a being allowed to vary.

could well be caused by different intermolecular forces present in the lattice due to a different packing arrangement and/or by the larger size of the iodide ligand. Nonetheless the intramolecular contribution is considerable, as the values of the activation energies of the complexes with halide ligands are much larger than that of the bis(cyclopentadienyl)mercury complex.

Comparison of the mean values of activation energy from these experiments with those obtained from the CW solid-state experiments (Table I) shows that the same order of the activation energies was obtained using the empirical procedure of Bloembergen, Purcell, and Pound[18] as modified by Smith;[19] however, closer numerical values were obtained by using the very empirical method of Waugh,[20] although the value for the activation energy for the $(\eta^1\text{-C}_5\text{H}_5)\text{HgBr}$ was slightly larger than that of $(\eta^1\text{-C}_5\text{H}_5)\text{HgI}$.

In the case of the compounds with X = Cl, Br, and I it would be of interest to compare the results with those from high-resolution NMR studies in solution. Unfortunately, complete line shape analyses have not been done. However, from the temperature ranges over which the changes occur in solution, the activation energies can be estimated to be smaller, but of the same order of magnitude as those obtained in the solid state. This again shows that intramolecular forces in the solid state do not lead to "locked or instantaneous structures".[21] However, these forces could well be sufficient to interchange the expected order of the activation energies.

Taken together with the previous results on the motion of cyclooctatetraene ligands in solid organometallic complexes, the results indicate that many fluxional organometallic compounds are quite mobile in the solid state as well as in solution, at least in cases where the organic ligands are unsubstituted, and that in these cases the bonding does not produce rigid molecules in the solid. Pulsed NMR measurements in the solid state yield accurate values for the barriers to rotation which can be related at least qualitatively to the molecular structures and to NMR measurements in solution. In specific cases, where the barrier to reorientation is small, for example, $(\text{COT})\text{Fe}_2(\text{CO})_5$ or $(\eta^1\text{-C}_5\text{H}_5)_2\text{Hg}$, information may be obtained concerning the motion which is difficult or impossible to obtain in solution because of the very low temperatures that would have to be used.

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Registry No. $(\eta^1\text{-C}_5\text{H}_5)_2\text{Hg}$, 18263-08-6; $(\eta^1\text{-C}_5\text{H}_5)\text{HgCl}$, 12071-53-3; $(\eta^1\text{-C}_5\text{H}_5)\text{HgBr}$, 1003-25-4; $(\eta^1\text{-C}_5\text{H}_5)\text{HgI}$, 24414-35-5.

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Manganese(II) Complexes of Selected N_4 Tetradentate Ligands

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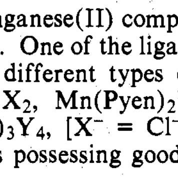
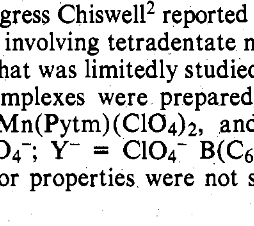
Manganese(II) complexes of the neutral Schiff base ligand (Pytm) derived from 2-pyridinecarboxaldehyde and trimethylenediamine have been synthesized. Complexes of general formula $Mn(Pytm)X_2 \cdot nH_2O$ were formed where X^- may be Cl^-, Br^-, I^-, NO_2^-, or NCS^- and n is 0 or 1. Two additional materials 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%.