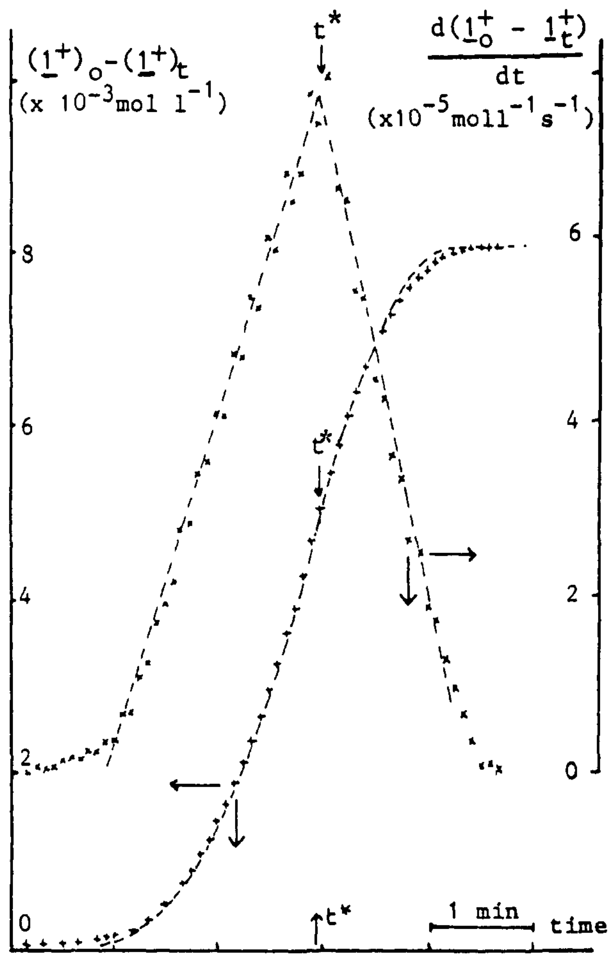

Figure 2. Experimental (+,×) and simulated (···) thermograms of reaction 1 catalyzed by electron transfer and their derivative curves with the electrolysis current switched off at time t^* (8×10^{-3} mol·L^{-1}, of **1a**$^+$(PF_6^-); 48×10^{-3} mol·L^{-1} of $P(OMe)_3$ in CH_3CN - 0.1 M $Bu_4N^+BF_4^-$).

react with dioxygen[13] or slowly with water.[14] The irreversible voltammetric behavior of **1**$^+$ and **2**$^+$ in acetonitrile shows that **2**$^\bullet$ and **3**$^\bullet$ decay, leading to ferrocene and unknown decomposition products.[8b] The few amounts of side products formed during the catalysis of reaction 1 do not allow us to establish the true deactivation reactions. However that may be, a zero order is uncommon and may be explained by one of the following hypotheses. (i) In reaction Scheme I, we have considered a steady state for the intermediates **2**$^\bullet$ and **3**$^\bullet$, so their concentrations are lower than the deactivating substrate ones (oxidizing impurities, water, etc.). If **2**$^\bullet$ or **3**$^\bullet$ deactivates according to a pseudo-first-order kinetic, the overall observed deactivation is equivalent to a zero order with respect **1**$^\bullet$. (ii) Another hypothesis may be a fast reaction of **1**$^\bullet$ with an impurity continuously introduced in the solution. This impurity should be the dioxygen present at 5 ppm in the dinitrogen used for the deoxygenation of the solution. We have already noted that dioxygen deactivated the reaction during the induction period.

Taking into account a zero order for the deactivation reactions (rate constant k_d), the thermal effect $Q(t)$ and its derivative dQ/dt versus time are expressed by the new relationships 9-12.

during the electrolysis

$$Q(t) = [0.5k(K - k_d)t^2 + (K - k_d)t]V\Delta H \qquad (9)$$

$$dQ/dt = (k(K - k_d)t + K - k_d)V\Delta H \qquad (10)$$

after switching off the current ($t > t^*$)

$$Q(t) = [-0.5kk_d(t - t^*)^2 + (k(K - k_d)t^* - k_d)(t - t^*) + (1^+)_0 - (1^+)_{t^*}]V\Delta H \qquad (11)$$

$$dQ/dt = [-kk_d(t - t^*) + k(K - k_d)t^* - k_d]V\Delta H \qquad (12)$$

Relations 10 and 12 allow access to the rate constants k and k_d from derivative curve slopes for two electrolyses carried out with different current intensities or from one experiment with the current switched off. The values of k and k_d are given in Table I ($k^\S$, $k_d^\S$).

The rate constant $k^\S$ of reaction 1, corrected for the deactivation reactions, is arene ligand dependent. The rate decreases following the sequence **1b**$^+$ > **1a**$^+$ > **1d**$^+$ > **1c**$^+$. This order agrees with stability of the corresponding paramagnetic species **1**$^\bullet$ in acetonitrile without $P(OMe)_3$, as shown by voltammetric studies.[8b] Owing to uncertainties about the nature of deactivation reactions occurring during reaction 1, we cannot discuss the values of k_d.

As a concluding remark, we could emphasize that the reaction investigated in this paper shows, for the first time, that electron-transfer catalysis allows new ways for thermochemical investigations of chemical reactions.[15,16] From an experimental point of view, a chemical reaction may be easily carried out by means of chemical redox reagents, and in such conditions, the heat dissipation may be a useful indicator of the course of the reaction. The enthalpy change ΔH of reaction 1 does not seem to be influenced by the arene ligands. It is likely that the substituents of substrates **1**$^+$ do not significantly modify the energy of the iron-arene bond. Unfortunately, because of the ionic nature of starting and final compounds (**1**$^+$, **2**$^+$), we have not been able to link the enthalpy change and bond energy with more accuracy.

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Contribution from the Department of Chemistry
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Complete Carboxylate Removal from $Mn_{12}O_{12}(OAc)_{16}(H_2O)_4 \cdot 2HOAc \cdot 4H_2O$ with Me_3SiCl: Synthesis and Characterization of Polymeric $[MnCl_3(bpy)]_n$ and an Improved Synthesis of $(NEt_4)_2MnCl_5$

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and George Christou*

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Introduction

The red-brown air-stable Mn^{III} compounds of empirical formula $MnCl_3L$ (L = bpy, phen) have been known since 1965 when Goodwin and Sylva isolated them from the reaction of L with the purple ether extract of the black solid obtained from reduction of MnO_2 with dry HCl in CCl_4.[1] The same compounds were later obtained independently by Funk and Kreis using a similar method.[2] Earlier, Gill had obtained green $(NEt_4)_2MnCl_5$ from this ether extract by treatment with an ethanolic solution of NEt_4Cl.[3] Similarly, $(NEt_4)_2MnCl_5$ was obtained by addition of NEt_4Cl to the purple solution obtained from reaction of CH_3COCl with

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MnO_2 in ether.[4] The apparently five-coordinate bpy and phen complexes were subsequently formulated as either dimeric $[MnCl_3L]_2$, containing two cis bridging chlorides, or polymeric $[MnCl_3L]_n$, with two trans bridging chlorides, on the basis of magnetic measurements which showed the complexes to have abnormally low room-temperature magnetic moments and to exhibit antiferromagnetic coupling.[5] Thermal decomposition of $(LH_2)[MnCl_5]$ has also been reported to yield solids of empirical formula $MnCl_3L$, and these were suggested to be polymeric on the basis of X-ray powder diffraction data.[6] As part of a continuing investigation into the reactivity of multinuclear Mn carboxylate clusters with various ratios of Me_3SiCl, we have discovered that excess Me_3SiCl provides convenient and high-yield syntheses of both $(NEt_4)_2MnCl_5$ and $[MnCl_3(bpy)]_n$ starting from $Mn_{12}O_{12}(OAc)_{16}(H_2O)_4{\cdot}2HOAc{\cdot}4H_2O$ (**1**). In this paper we report the preparation of these compounds, which represent rare and useful starting points for Mn^{III} chemistry. We have also taken the opportunity to finally determine the structure of $[MnCl_3(bpy)]_n$ at both −130 °C and room temperature. The results unequivocally show this compound to be polymeric in the solid state.

Experimental Section

All preparations were carried out under aerobic conditions. Acetonitrile and ether were distilled before use. All other chemicals were used as received. $[Mn_4O_2(OAc)_7(bpy)_2]ClO_4$ was available from previous work[7] and $Mn_{12}O_{12}(OAc)_{16}(H_2O)_4{\cdot}2HOAc{\cdot}4H_2O$ (**1**) was prepared by the method of Lis.[8] Infrared spectra (KBr disks) were recorded on a Nicolet 510P Fourier transform instrument. UV/vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer.

Syntheses. $[MnCl_3(bpy)]_n$. Method A. To a stirred suspension of complex **1** (0.20 g, 0.097 mmol) in MeCN (50 mL) was added Me_3SiCl (0.44 mL, 3.5 mmol). The resulting dark purple solution was filtered, and to the filtrate was added solid bpy (0.183 g, 1.2 mmol). The product crystallizes within minutes as a red-brown microcrystalline solid. This was collected by filtration, washed with MeCN (2 × 5 mL), and dried in air. Yield: 0.30 g, 81%, based on total available Mn. IR data (KBr): 1604 (m), 1595 (s), 1576 (m), 1564 (m), 1491 (w), 1475 (m), 1441 (s), 1317 (m), 1246 (w), 1170 (m), 1157 (m), 1111 (w), 1055 (w), 1016 (s), 774 (s), 737 (s), 650 (m), 626 (w), 415 (m) cm^{-1}. Electronic spectrum (MeCN) [λ_{max}, nm (ϵ_M, L mol^{-1} cm^{-1})]: 572 (464), 390 (1153). Anal. Calcd (found) for $MnC_{10}H_8N_2Cl_3$: C, 37.8 (38.2); H, 2.5 (2.5); N, 8.8 (8.7); Cl, 33.5 (32.8); Mn, 17.3 (17.8).

Method B. To a stirred solution of $[Mn_4O_2(OAc)_7(bpy)_2](ClO_4){\cdot}3H_2O$ (0.57 g, 0.50 mmol) in MeCN (70 mL) was added Me_3SiCl (0.64 mL, 5.0 mmol). After 2 days, the resulting impure black precipitate was collected by filtration, washed with Et_2O, and dried in air. Yield: 0.28 g, 44%, based on Mn. A recrystallized sample suitable for crystallography was obtained by dissolving 0.10 g of this material in ~30 mL of hot (70 °C) MeCN. The resulting dark green solution was filtered and left to cool slowly in a Dewar flask. After 3 days, large black crystals of $[MnCl_3(bpy)]_n$ were formed.

$(NEt_4)_2MnCl_5$. This light-sensitive complex was prepared in the dark. To a stirred suspension of complex **1** (0.20 g, 0.097 mmol) in Et_2O (20 mL) was added Me_3SiCl (0.74 mL, 5.8 mmol). This was stirred in the dark for 10 min and then filtered. To the dark purple filtrate was added a 0.60 M solution of NEt_4Cl (3 mL, 1.8 mmol) in EtOH. The green precipitate which rapidly formed was collected by filtration, washed with Et_2O (2 × 5 mL), and dried in air. Yield: 0.40 g, 70%. IR data (Nujol, CsI): ν_{Mn-Cl} 330 (s), 250 (s), 280 (m) cm^{-1}. Electronic spectrum (acetone) (λ_{max}, nm): 582, 422. Extinction coefficients could not be obtained owing to steady decomposition of the complex in solution in the cell.

Table I. Crystallographic Data for $[MnCl_3(bpy)]_n$

$MnC_{10}H_8N_2Cl_3$	low-temp form	room-temp form
M_r	317.48	317.48
space group	*Cc*	*Cc*
a/Å	8.122 (1)	8.170 (4)
b/Å	16.162. (3)	16.177 (12)
c/Å	9.584 (1)	9.660 (5)
β/deg	109.46 (1)	109.55 (1)
Z	4	4
V/Å^3	1186.23	1203.11
ρ_{calcd}/g·cm^{-3}	1.778	1.753
μ/cm^{-1}	17.234	16.992
T/°C	−130	25
λ/Å	0.710 69	0.710 69
range/deg	$6 \le 2\theta \le 45$	$6 \le 2\theta \le 45$
no. of obsd data; $F > 2.33\sigma(F)$	776	788
R %	1.74	1.95
R_w %	2.03	2.02

Table II. Fractional Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10) for $[MnCl_3(bpy)]_n$[a]

atom	x	y	z	B_{iso}
		(a) Low Temperature		
Mn1	7755*	180.9 (4)	7259*	10
Cl2	7719 (2)	617 (1)	9763 (1)	13
Cl3	6181 (2)	1249 (1)	6012 (1)	16
Cl4	10305 (2)	791 (1)	7448 (1)	15
N5	5593 (5)	−541 (2)	7014 (4)	12
C6	3943 (6)	−273 (3)	6532 (5)	14
C7	2543 (7)	−812 (3)	6249 (6)	18
C8	2871 (7)	−1643 (3)	6482 (5)	17
C9	4575 (7)	−1916 (3)	7037 (5)	17
C10	5918 (6)	−1351 (3)	7306 (5)	12
C11	7785 (6)	−1574 (3)	7935 (5)	13
C12	8401 (7)	−2370 (3)	8286 (5)	17
C13	10171 (7)	−2506 (3)	8911 (6)	19
C14	11286 (7)	−1832 (3)	9213 (5)	20
C15	10620 (6)	−1054 (3)	8812 (5)	16
N16	8903 (5)	−918 (2)	8156 (4)	11
		(b) Room Temperature		
Mn1	7755*	186.4 (4)	7259*	21
Cl2	7739 (2)	626 (1)	9739 (1)	28
Cl3	6205 (2)	1247 (1)	6008 (2)	33
Cl4	10296 (2)	793 (1)	7431 (2)	31
N5	5632 (5)	−541 (2)	7001 (4)	22
C6	3983 (7)	−279 (4)	6522 (6)	31
C7	2603 (8)	−814 (4)	6240 (6)	34
C8	2930 (7)	−1630 (4)	6481 (6)	35
C9	4619 (7)	−1907 (3)	7038 (6)	31
C10	5964 (6)	−1347 (3)	7298 (5)	23
C11	7812 (6)	−1563 (3)	7921 (5)	23
C12	8431 (8)	−2362 (4)	8275 (6)	34
C13	10176 (8)	−2495 (4)	8892 (6)	36
C14	11281 (8)	−1830 (4)	9183 (6)	36
C15	10633 (6)	−1050 (4)	8785 (5)	29
N16	8916 (5)	−917 (2)	8141 (4)	22

[a] Values marked with an asterisk were not varied.

X-ray Crystallography and Structure Solution. Data were collected on a Picker four-circle diffractometer at both room temperature and at −130 °C; details of the diffractometry, low-temperature facilities, and computational procedures employed by the Molecular Structure Center are available elsewhere.[9] Data collection parameters are summarized in Table I. Data were initially collected at low temperature. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to one of the monoclinic space groups *C*2/*c* or *Cc*. Subsequent solution and refinement of the structure confirmed the noncentrosymmetric choice *Cc*. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. All non-hydrogen atoms were readily located and all hydrogen atoms were clearly visible in a difference Fourier synthesis based on the non-hydrogen parameters. All hydrogen atoms were refined isotropically and non-hydrogen atoms anisotropically in the final cycles. Data were then collected from the same crystal at room temperature where it exhibits a different color. Starting coordinates were taken from the above structure. The structure solution proceeded similarly. Final Fourier difference maps for both structures were essentially featureless and no absorption correction was performed. Final discrepancy indices are included in Table I.

Results

Treatment of complex **1** with sufficient Me_3SiCl to abstract all carboxylate groups leads to formation of a dark purple solution.

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Table III. Selected Bond Distances (Å) and Angles (deg) for the Low- and Room-Temperature Forms of $[MnCl_3(bpy)]_n$

	low temp	room temp
Mn1-Cl2	2.510 (2)	2.504 (2)
Mn1-Cl2′	2.710 (2)	2.762 (2)
Mn1-Cl3	2.242 (2)	2.252 (2)
Mn1-Cl4	2.246 (2)	2.232 (2)
Mn1-N5	2.055 (4)	2.066 (4)
Mn1-N16	2.056 (4)	2.041 (4)
Cl2-Mn1-Cl2′	167.83 (3)	168.08 (3)
Cl2-Mn1-Cl3	93.42 (5)	96.06 (6)
Cl2′-Mn1-Cl3	96.14 (5)	90.28 (6)
Cl2-Mn1-Cl4	91.08 (4)	93.10 (7)
Cl2′-Mn1-Cl4	95.93 (4)	96.67 (6)
Cl2-Mn1-N5	82.60 (10)	89.96 (11)
Cl2′-Mn1-N5	89.28 (10)	79.56 (11)
Cl2-Mn1-N16	80.07 (10)	82.21 (12)
Cl2′-Mn1-N16	89.51 (10)	90.26 (11)
Cl3-Mn1-Cl4	92.95 (5)	92.70 (7)
Cl3-Mn1-N5	93.59 (11)	93.49 (12)
Cl3-Mn1-N16	170.64 (11)	170.09 (11)
Cl4-Mn1-N5	171.16 (11)	170.40 (11)
Cl4-Mn1-N16	93.88 (11)	94.14 (12)
N5-Mn1-N16	78.99 (15)	78.85 (16)
Mn1-Cl2-Mn1′	135.23 (5)	135.08 (6)

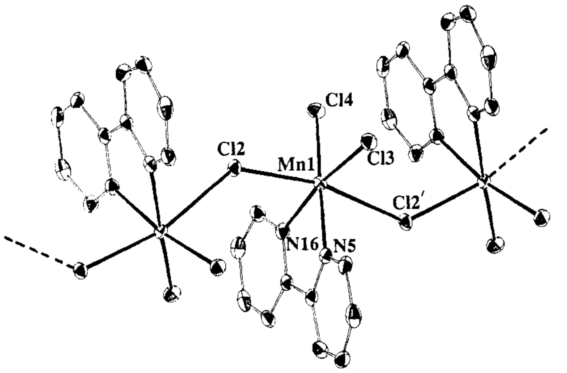

Figure 1. ORTEP representation of $[MnCl_3(bpy)]_n$ (low-temperature form) showing three repeating units of the 1-D polymer.

Addition of bpy to this solution leads to rapid crystallization of $[MnCl_3(bpy)]_n$ whereas addition of NEt_4Cl yields microcrystalline $(NEt_4)_2MnCl_5$, the identity of which was confirmed by comparison with previously reported IR and UV/vis spectral data.[10] The crystal structure of $[MnCl_3(bpy)]_n$ has been determined at both −130 °C and room temperature. Crystallographic data are listed in Table I. Fractional coordinates and selected bond distances and angles are collected in Tables II and III, respectively. An ORTEP representation is shown in Figure 1, and the structure will be described below.

Discussion

We are currently directing efforts toward the development of Mn carboxylate chemistry, seeking species of various nuclearities and oxidation levels.[11] One synthetic approach that has proven fruitful is carboxylate abstraction with Me_3SiCl[12] from smaller nuclearity Mn/RCO_2^- species. In many cases, we have found that this triggers a structural and nuclearity change. For example, we have already reported the Me_3SiCl-mediated conversions of $[Mn_3O(OAc)_6(py)_3](ClO_4)$ to $Mn_4O_3Cl_4(OAc)_3(py)_3$[13] and $(NBu^n_4)[Mn_4O_2(OAc)_7(pic)_2]$ to $Mn_8O_4(OAc)_{12}(pic)_4$ ($picH_2$ = picolinic acid).[14] We have since added Me_3SiCl to a number of Mn carboxylate species of various nuclearities. The influence of the Me_3SiCl:Mn ratio has also been explored. The present results stem from the reaction of Me_3SiCl with $Mn_{12}O_{12}(OAc)_{16}(H_2O)_4 \cdot 2HOAc \cdot 4H_2O$ (**1**) in a ratio sufficient to abstract all carboxylate groups (≥34 equiv). It was felt important to determine the products from what represents the limiting situation in the study of the influence of the Me_3SiCl:Mn ratio.

Treatment of complex **1** suspended in MeCN with 36 equiv of Me_3SiCl gave a purple-black solution. Addition of 12 equiv of bpy initially gave a green solution followed by rapid formation of red-brown microcrystalline $[MnCl_3(bpy)]_n$ in good (81%) yield. The product can be recrystallized without change from hot (70 °C) MeCN. The same compound can also be obtained from the reaction of $[Mn_4O_2(OAc)_7(bpy)_2](ClO_4)$ with 10 equiv of Me_3SiCl followed by recrystallization from hot MeCN. During cooling to −130 °C for X-ray data collection, the crystal changed color from nearly black to bright red. This was found to be reversible, and the crystal reverted to the dark color on rewarming to room temperature. To probe any structural consequence of this change, data were collected on the same crystal at both −130 °C and room temperature.

It was suspected that the purple-black solution formed on addition of Me_3SiCl to the MeCN solution of complex **1** might contain "$MnCl_3$", an ethereal solution of which Gill had used to prepare $(NEt_4)_2MnCl_5$ by addition of an ethanolic solution of NEt_4Cl.[3] In agreement with the above, we have found that $(NEt_4)_2MnCl_5$ can be prepared directly from $Mn_{12}O_{12}(OAc)_{16}(H_2O)_4 \cdot 2HOAc \cdot 4H_2O$ on sequential treatment with Me_3SiCl and NEt_4Cl in Et_2O. Thus, addition of Me_3SiCl to an ether suspension of complex **1** gave an intense purple solution, which, on addition of an ethanolic solution of NEt_4Cl, gave a green microcrystalline precipitate of $(NEt_4)_2MnCl_5$. The same reaction carried out in MeCN gave only a green solution, $(NEt_4)_2MnCl_5$ being too soluble in this solvent to crystallize. The original preparation of this complex required reduction of MnO_2 with dry HCl in CCl_4 to give an unidentified black solid, the purple ether extract of which gave $(NEt_4)_2MnCl_5$ on treatment with NEt_4Cl. This purple ether extract appears analogous to the purple solution obtained in our work, addition of NEt_4Cl to both giving $(NEt_4)_2MnCl_5$. Reaction of Me_3SiCl with the easily prepared $Mn_{12}O_{12}(OAc)_{16}(H_2O)_4 \cdot 2HOAc \cdot 4H_2O$ is thus a simple method of preparing the "purple preparative solution" described by Goodwin and Sylva,[1] from which may be prepared in high yield $(NEt_4)_2MnCl_5$, $[MnCl_3(bpy)]_n$, and many other pentachloromanganate(III) salts[10] and amine adducts of $MnCl_3$.[2,15]

X-ray structural analysis of both the low- and room-temperature forms of $[MnCl_3(bpy)]_n$ show this compound to be polymeric. Figure 1 shows part of the structure of the low-temperature form of $[MnCl_3(bpy)]_n$. It consists of an infinite chain of $MnCl_2(bpy)$ units joined by asymmetrically bridging Cl^- ions. The geometry around each Mn is distorted octahedral. The expected Jahn–Teller distortions about the high-spin d^4 Mn^{III} ion are evident along the Cl2–Mn–Cl2′ axis. These bond lengths of 2.51 and 2.71 Å are significantly longer than the terminal Mn1–Cl3 and Mn1–Cl4 lengths of ~2.24 Å. "Long" Mn^{III}–Cl bonds have previously been observed in $Mn_2O(OAc)_2(bpy)_2Cl_2$ (2.61 Å, Jahn–Teller elongated terminal)[16] and $Mn_4O_3Cl_4(OAc)_3(py)_3$ (2.67 Å, μ_3-bridging)[13] and in a Schiff base Mn^{II}–Mn^{III} dimer (2.77 Å, μ_2-bridging).[17] However, the distances of 2.71 Å in the low-temperature form and 2.76 Å in the room-temperature form of the polymer are unprecedented for a solely Mn^{III} system. This may be of some relevance to the photosynthetic water oxidation center, given that Cl^- is an essential cofactor in photosynthetic oxygen evolution.[18] EXAFS studies of the native system have attempted to address

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the question of whether chloride is bound to the manganese cluster.[19,20] It now seems certain that EXAFS alone will be unable to provide a definite answer, as any Mn–Cl interactions at the extremely long distance of 2.7 Å will be obscured by the strong feature due to the Mn–Mn separation of ~2.7 Å. Indeed, any Mn–Cl distances of ~2.7 Å at the biological site may lead to an erroneous estimate of the number of Mn···Mn separations at ~2.7 Å.

Somewhat to our surprise, the structure of the room-temperature form of $[MnCl_3(bpy)]_n$ is very similar to that of the low-temperature form, with only a few small differences in bond lengths and angles. Comparisons of these are given in Table III. We had wondered whether at higher temperature the bridging Cl^- ions would be found more symmetrically located between the Mn centers. In fact, the opposite was observed; the major difference between the structures is that the low-temperature 2.710 (2) Å Mn–Cl bond is further elongated to 2.762 (2) Å at room temperature.

We believe that the presence of labile Cl^- ligands in $[MnCl_3(bpy)]_n$ and $(NEt_4)_2MnCl_5$ makes these materials extremely useful (and rare) starting materials for Mn^{III} chemistry. Their previous preparations were rather inconvenient, but their facile preparation from readily available complex **1** provides large quantities from simple reagents. We are currently investigating their utility for the synthesis of a variety of Mn complexes of various nuclearities.

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Supplementary Material Available: Complete listings of atomic coordinates, isotropic and anisotropic thermal parameters, and bond lengths and angles (6 pages); lists of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page. Complete MSC structure reports (No. 89281, low temperature; No. 89481, room temperature) are available on request from the Indiana University Chemistry Library.

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Role of Osmium in the Reaction of the Hydrazinium Cation with Chlorate in Acid Solution[1]

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In their 1944 monograph, Yost and Russell noted in passing the autocatalytic nature of the osmium-catalyzed reaction of the hydrazinium cation with chlorate.[2] This reaction appears to have been discovered some 30 years earlier by Hofmann who found that although the oxidation of the hydrazinium cation by chlorate in acidic solution is imperceptibly slow, it is catalyzed by osmium tetroxide.[3] Bromate[4] and iodate,[5] however, react readily with the hydrazinium cation without requiring a catalyst.

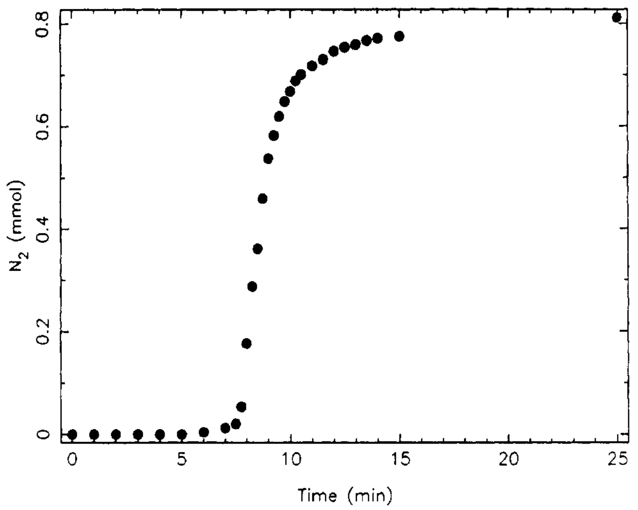

Figure 1. Time course of nitrogen gas evolution for reaction 1. Initial concentrations: $[N_2H_5^+] = 4.4 \times 10^{-2}$ M; $[ClO_3^-] = 4.1 \times 10^{-1}$ M; $[OsO_4] = 1.6 \times 10^{-3}$ M. Total solution volume = 20.0 mL.

In the presence of an osmium tetroxide catalyst and excess chlorate, the hydrazinium cation[6] is quantitatively oxidized to nitrogen.[3] The purpose of this work was to ascertain whether, in fact, reaction 1 is autocatalytic and, if so, to identify the autocatalytic species and formulate a satisfactory mechanism.

$$3N_2H_5^+ + 2ClO_3^- \xrightarrow{OsO_4} 3N_2 + 2Cl^- + 6H_2O + 3H^+ \qquad (1)$$

Experimental Section

Hydrazinium sulfate (Eastman Kodak) and sodium chlorate (Fisher) solutions were prepared with reagent grade chemicals and deionized water. Osmium tetroxide crystals (Aldrich) were dissolved in water, and the solution was stored in the dark to retard decomposition.

All experiments were carried out in vigorously stirred solutions at ambient temperatures, approximately 23 °C. The progress of the catalyzed reaction was followed by measuring the amount of nitrogen evolved as a function of time with a gas buret. The potential of a platinum redox electrode versus a reference electrode and a combination pH electrode can also be used to monitor the reaction; the response of a chloride electrode is distorted by the presence of the hydrazinium cation. Light scattering by colloidal osmium dioxide formed during the reaction, as well as gas evolution, interferes with spectroscopic absorbance measurements, particularly in the ultraviolet region.

Results

The Hydrazinium Cation–Chlorate–Osmium Tetroxide System. The catalyzed reaction, carried out in the presence of excess chlorate, was initiated by addition of the osmium tetroxide solution. After an initial phase, during which no gas evolution is detected, nitrogen is produced rapidly until all the hydrazinium cation is consumed; the pH declines simultaneously from 1.82 to 1.45. (The pH is determined by the bisulfate concentration; solutions were unbuffered.) Figure 1 illustrates a typical time course for nitrogen evolution. The induction period is shortened by increasing the concentration of the osmium tetroxide catalyst as well as that of chlorate, while increasing the concentration of the hydrazinium cation has the opposite effect.

To determine whether reaction 1 is autocatalytic, a 2.5-mL aliquot of the chlorate–hydrazinium cation–osmium tetroxide

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(6) Under the acidic conditions of this report, pH 1–2, the dominant form of hydrazine is the hydrazinium cation: $pK_{a1} = 6.07$, $pK_{a2} = 15.05$ at 25 °C.

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