Synthesis and Structural Investigations of $[Mn_3O_4(phen)_4(H_2O)_2](NO_3)_4\cdot 2.5H_2O$: A Water-Bound Complex Obtained by Cerium(IV) Oxidation

K. Rajender Reddy,[†] M. V. Rajasekharan,*[,†] Navamoney Arulsamy,[‡] and Derek J. Hodgson*[‡,§]

School of Chemistry, University of Hyderabad, Hyderabad 500134, India, and Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071

Received March 8, 1995[⊗]

The trinuclear manganese complex $[Mn_3O_4(phen)_4(H_2O)_2](NO_3)_4\cdot 2.5H_2O$, **1** (where, phen = 1,10-phenanthroline), has been synthesized by the Ce(IV) oxidation of a concentrated solution of manganese(II) acetate and phen in 1.6 N nitric acid. The complex crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.700(2)$ Å, $b = 12.643(3)$ Å, $c = 20.509(4)$ Å, $\alpha = 78.37(3)°$, $\beta = 83.12(3)°$, $\gamma = 82.50(3)°$, and $Z = 2$. The structure was solved by direct methods and refined by least-squares techniques to the conventional R (R_w) factors of 0.055 (0.076) based on 4609 unique reflections with $F_o \geqslant 6.0\sigma(F_o)$. The structure of the cation consists of an oxo-bridged $Mn_3O_4^{4+}$ core, with the geometry of the manganese atoms being octahedral. The coordination polyhedron of one of the manganese atoms (Mn(1)) consists of two μ oxo ligands and two pairs of nitrogen atoms of two phen moieties, whereas that of each of the remaining two manganese atoms consists of three μ-oxo ligands, two nitrogen atoms of a phen moiety, and the oxygen atom of a water molecule. The complex represents the second example for water coordination to manganese(IV) centers in complexes with a $Mn_3O_4^{4+}$ core. Optical spectra in ligand buffer (pH 4.5) reveal complete conversion of the complex into a $Mn^{III}Mn^{IV}$ species. The observed room-temperature (298 K) magnetic moment of 3.75 μ_B indicates the presence of strong antiferromagnetic coupling in the complex.

Introduction

The naturally occurring multinuclear manganese species with μ-oxo and μ-carboxylato units are known to be responsible for the diverse redox functions of enzymes such as photosystem II, Mn catalases, and Mn ribonucleotide reductase.[1−3] Apart from their involvement in the functions of the biological systems, the multinuclear manganese species, and hence, their synthetic analogues, are also of catalytic importance. Recently, it was shown that some bis(μ-oxo)dimanganese(III,IV) complexes are capable of catalyzing the oxidation of water by Ce(IV) oxidants.[4] Catalytic oxidation of alkanes[5] and catalysis of the bleaching action of H_2O_2 in detergents at low temperatures[6] by multinuclear manganese complexes have also been reported. Owing to their potential application as catalysts for the oxidation of organic substrates together with their synthetic importance, a large number of multinuclear manganese complexes of various types of ligands have been synthesized and structurally characterized.[7]

The α-diimine ligand 2,2′-bipyridyl (bpy) has been extensively used in these syntheses; as a result, mono-,[8] di-,[9] tri-,[10] tetra-,[11] and polynuclear[12] manganese complexes of this ligand are well studied. However, only few such complexes are known for the closely related ligand 1,10-phenanthroline (phen).[13]

In our continuing interest in the synthesis of high-oxidation-state manganese complexes by Ce(IV) oxidation, we have used both bpy and phen ligands and previously reported the formation of the mononuclear Mn^{III} complex $[Mn(phen)_2Cl_2]^+$ [14] and the dinuclear $Mn^{III}Mn^{IV}$ complex $\{[Mn(bpy)(H_2O)]_2(\mu\text{-}O)_2(\mu\text{-}$

[†] University of Hyderabad.

[‡] University of Wyoming.

[§] Present address: Department of Chemistry, Mississippi State University, P.O. Drawer BQ, Mississippi State, MS 39762.

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1996.

(1) (a) Renger, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 643. (b) Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 725.

(2) Pecoraro, V. L.; Baldwin, M. J.; Gelasco, A. *Chem. Rev.* **1994**, *94*, 807.

(3) (a) Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1153. (b) Christou, G. *Acc. Chem. Res.* **1989**, *22*, 328.

(4) (a) Ramaraj, R.; Kira, A.; Kaneko, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 825. (b) Swarnabala, G.; Rajasekharan, M. V. *Proc.—Indian Acad. Sci., Chem. Sci.* **1990**, *102*, 87.

(5) Menege, S.; Dunand-Sauthier, M. N.; Lambeaux, C.; Fontecave, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1885.

(6) Hage, R.; Iburg, J. E.; Kerschner, J.; Koek, J. H.; Lempers, E. L. M.; Martens, R. J.; Racherla, U. S.; Russel, S. W.; Swarthoff, J.; Van Vliet, M. R. P.; Warnaar, J. B.; van der Wolf, L.; Krijnen, B. *Nature* **1994**, *369*, 637.

(7) (a) Arulsamy, N.; Glerup, J.; Hazell, A.; Hodgson, D. J.; McKenzie, C. J.; Toftlund, H. *Inorg. Chem.* **1994**, *33*, 3023. (b) Pal, S.; Chan, M. K.; Armstrong, W. H. *J. Am. Chem. Soc.* **1992**, *114*, 6398. (c) Pal, S.; Armstrong, W. H. *Inorg. Chem.* **1992**, *31*, 5417. (d) Goodson, P. A.; Glerup, J.; Hodgson, D. J.; Michelsen, K.; Weihe, H. *Inorg. Chem.* **1991**, *30*, 4909. (e) Goodson, P. A.; Oki, A. R.; Glerup, J.; Hodgson, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 6248. (f) Oki, A. R.; Glerup, J.; Hodgson, D. J. *Inorg. Chem.* **1990**, *29*, 2435. (g) Goodson, P. A.; Glerup, J.; Hodgson, D. J.; Michelsen, K.; Pedersen, E. *Inorg. Chem.* **1990**, *29*, 503. (h) Wieghardt, K.; Bossek, U.; Ventur, D.; Weiss, J. *J. Chem. Soc., Chem. Commun.* **1985**, 347.

(8) Goodwin, H. A.; Sylva, R. N. *Aust. J. Chem.* **1967**, *20*, 629.

(9) (a) Sarneski, J. E.; Didiuk, M.; Thorp, H. H.; Crabtree, R. H.; Brudvig, G. W.; Faller, J. W.; Schulte, G. K. *Inorg. Chem.* **1991**, *30*, 2833. (b) Blackman, A. G.; Huffman, J. C.; Lobkovsky, E. B.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1991**, 989. (c) Bashkin, J. S.; Schake, A. R.; Vincent, B.; Chang, H. R.; Li, Q.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1988**, 700. (d) Menege, S.; Girerd, J. J.; Gleizes, A. *J. Chem. Soc., Chem. Commun.* **1988**, 431. (e) Cooper, S. R.; Dismukes, G. C.; Klein, M. P.; Calvin, M. *J. Am. Chem. Soc.* **1978**, *100*, 7248. (f) Unpublished structural data for $[Mn_2O(OAc)_2(H_2O)(NO_3)(bpy)_2]^+$ from K. R. Reddy and M. V. Rajasekharan.

(10) (a) Sarneski, J. E.; Thorp, H. H.; Brudvig, G. W.; Crabtree, R. H.; Schulte, G. K. *J. Am. Chem. Soc.* **1990**, *112*, 7255. (b) Auger, N.; Girerd, J. J.; Corbella, M.; Gleizes, A.; Zimmermann, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 448.

(11) (a) Vincent, J. B.; Christmas, C.; Huffman, J. C.; Christou, G.; Chang, H. R.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1987**, 236. (b) Vincent, J. B.; Christman, C.; Chang, H. R.; Li, Q.; Boyd, P. D. W.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1989**, *111*, 2086. (c) Philouze, C.; Blondin, G.; Menage, S.; Auger, N.; Girerd, J. J.; Vigner, D.; Lance, M.; Nierlich, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1629. (d) Jiang, Z. H.; Ma, S. L.; Liao, D. Z.; Yan, S. P.; Wang, G. L.; Yao, X. K.; Wang, R. L. *J. Chem. Soc., Chem. Commun.* **1993**, 745.

0020-1669/96/1335-2283$12.00/0 © 1996 American Chemical Society

OAc)}$^{3+}$.[15] In this paper, we wish to report the synthesis and studies of a novel trinuclear $\mathrm{Mn^{IV}}_3$ complex.

Experimental Section

Materials. Manganese(II) acetate tetrahydrate, ammonium ceric nitrate, and phen were reagent grade and were used as supplied. The solvents acetonitrile and dimethylformamide were distilled by standard procedures[16] and stored over molecular sieves.

Synthesis of $[\mathrm{Mn_3O_4(phen)_4(H_2O)_2](NO_3)_4{\cdot}2.5H_2O}$ (1). Phen (2.01 g, 10.16 mmol) was added to a solution of $\mathrm{Mn(OAc)_2{\cdot}4H_2O}$ (1.21 g, 4.94 mmol) in dilute nitric acid (1.6 N, 20 mL). Slow addition of an aqueous solution (2 mL) of $\mathrm{(NH_4)_2Ce(NO_3)_6}$ (3.3 g, 6.02 mmol) to the solution resulted in a brown solution, which was filtered and kept at room temperature. Dark brown crystalline material deposited in 2 days, was filtered off, and was washed with dilute nitric acid (0.2 N). Well-formed crystals suitable for X-ray diffraction were obtained by recrystallization from 1.6 N nitric acid. Yield: 1.25 g (60% based on starting manganese(II) acetate). Anal. Calcd for $\mathrm{C_{48}H_{41}N_{12}O_{20.5}Mn_3}$: C, 44.23; H, 3.23; N, 13.14. Found: C, 44.23; H, 3.36; N, 12.81. Equivalent weight: calcd, 213.1; determined by iodometry, 226.0.

Physical Measurements. Electronic spectra were recorded using a Perkin-Elmer Lambda 3B UV−vis spectrophotometer. The CHN elemental analysis was performed on a Perkin-Elmer 240C elemental analyzer. Equivalent weight was estimated by using a known procedure.[17] Excess KI (10% solution in water) and $\mathrm{H_2SO_4}$ (6 N, 2 mL) were added to the complex dissolved in water−acetonitrile (2:1) mixture. The liberated iodine was titrated with sodium thiosulfate (0.02 N), which was previously standardized with $\mathrm{KIO_3}$, using starch indicator.

EPR spectra were recorded for the complex as a powder and frozen solution on a JEOL FE-3X spectrometer. Magnetic susceptibility was measured using a Cahn 3000 microbalance at room temperature (298 K). The molar susceptibility was corrected for diamagnetism using Pascal's constants.[18]

Crystallographic Measurements. A brown rectangular prism with approximate dimensions of 0.20 × 0.38 × 0.50 mm^3 was mounted on a Nicolet R3m/V diffractometer equipped with a molybdenum tube [$\lambda(\mathrm{K}\alpha_1) = 0.709\,26$ Å; $\lambda(\mathrm{K}\alpha_2) = 0.713\,54$ Å] and a graphite monochromator for data collection at room temperature. The cell constants and orientation matrices were derived from a least-squares refinement of the setting angles of 50 reflections. The crystallographic and data collection parameters are listed in Table 1. The structure was solved in the triclinic space group $P\bar{1}$ (No. 2) by direct methods and refined by standard full-matrix least-squares techniques; programs used were from the SHELXTL system.[19]

The asymmetric unit consisted of one trinuclear cation, four nitrate anions, and 2.5 water molecules. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at calculated positions and were refined by a riding model with fixed isotropic thermal parameters. The final values of the atomic positional parameters are listed in Table 2.

Table 1. Crystallographic Data for **1**

empirical formula: $\mathrm{C_{48}H_{41}N_{12}O_{20.5}Mn_3}$	fw: 1278.7
$a = 10.700(2)$ Å	space group: $P\bar{1}$ (No. 2)
$b = 12.643(3)$ Å	$T = 25$ °C
$c = 20.509(4)$ Å	$\lambda = 0.710\,73$ Å
$\alpha = 78.37(3)°$	$\rho_{\mathrm{calcd}} = 1.584$ g cm^{-3}
$\beta = 83.12(3)°$	$\mu = 7.86$ cm^{-1}
$\gamma = 82.50(3)°$	$R^a = 0.055$
$V = 2682(1)$ Å^3	$R_w{}^b = 0.076$
$Z = 2$	

$^a\ R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b\ R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Results and Discussion

Synthesis. The Ce(IV) oxidation, as described in the Experimental Section, was necessarily done at low pH, and the resultant trinuclear manganese complex, $[\mathrm{Mn_3O_4(phen)_4(H_2O)_2}]\mathrm{(NO_3)_4{\cdot}2.5H_2O}$, **1**, was recrystallized from 1.6 N nitric acid. We previously reported the formation of $[\mathrm{Mn(phen)_2Cl_2}]^+$ and $\{[\mathrm{Mn(bpy)(H_2O)}]_2(\mu\text{-O})_2(\mu\text{-OAc})\}^{3+}$ by Ce(IV) oxidation reactions in acetic and perchloric acids, respectively.[14,15] The formation of different types of products in the above oxidation reactions suggests that the solution chemistry of the manganese−bpy and manganese−phen systems under low-pH conditions is complicated by several disproportionation equilibria. We propose that $[\mathrm{MnL_2(OH)(H_2O)}]^{2+}$ (where L = bpy or phen) is the initial species formed by the first one-electron transfer to Ce(IV) as shown in the following equation:

$$\mathrm{Mn^{II}(aq)} \xrightarrow[\mathrm{Ce(IV)}]{\mathrm{2L}} [\mathrm{MnL_2(H_2O)_2}]^{3+} \leftrightarrow [\mathrm{MnL_2(OH)(H_2O)}]^{2+} + \mathrm{H^+}$$

The $[\mathrm{MnL_2(OH)(H_2O)}]^{2+}$ species has also been suggested to be the only species present in dilute (<1 mM) solutions at low pH.[20] From our previous and present studies,[14,15] we conclude that, in concentrated solutions, disproportionation of the initially formed Mn(III)−hydroxo species followed by subsequent aggregation leads to the formation of different types of products depending on the ligand (bpy or phen) and the anions present. It may be noted that although the trinuclear manganese complex of bpy was prepared by treating $[\mathrm{Mn_2O_2(bpy)_2}]^{3+}$ with concentrated $\mathrm{HNO_3}$ acid,[10b] the complex can also be obtained directly by reacting $\mathrm{Mn(ClO_4)_2{\cdot}6H_2O}$ with bpy in the presence of Ce(IV) oxidant in perchloric acid.[21] *(Caution! Perchlorate salts could be explosive; care should be taken.)* A similar procedure, however, is not suitable for the present synthesis due to the poor solubility of $\mathrm{phen{\cdot}HClO_4}$ in perchloric acid.

Structure of $[\mathrm{Mn_3O_4(phen)_4(H_2O)_2](NO_3)_4{\cdot}2.5H_2O}$ (1). The structure consists of the trinuclear cation $[\mathrm{Mn_3O_4(phen)_4(H_2O)_2}]^{4+}$, nitrate anions, and water molecules. A view of the cation is shown in Figure 1, and selected bond distances and angles are listed in Table 3.

The three manganese atoms occupy the vertices of an isosceles triangle. One of the manganese atoms (Mn(1)) is linked to the other two manganese atoms (Mn(2) and (Mn(3)) by means of two individual μ-oxo bridges, *viz.*, O(1) and O(2), respectively. Mn(2) and Mn(3) are themselves linked to each other by two mutual μ-oxo bridges (O(3) and O(4)). The Mn−Mn distances involving Mn(1) are equal at 3.249 Å, and the distance between the doubly bridged manganese atoms, Mn(2) and Mn(3), is considerably shorter at 2.675 Å. The latter

---

(12) (a) Libby, E.; Folting, K.; Huffman, J. C.; Christou, G. *J. Am. Chem. Soc.* **1990**, *112*, 5354. (b) Perlepes, S. P.; Huffman, J. C.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1991**, 1657. (c) Schake, A. R.; Tsai, H. L.; Vries, N. D.; Webb, R. J.; Folting, K.; Hendrickson, D. N.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1992**, 181. (d) Wang, S.; Tsai, H. L.; Streib, W. E.; Christou, G.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1992**, 677. (e) Sessoli, R.; Tsai, H. L.; Schake, A. R.; Wang, S.; Vincent, J. B. *J. Am. Chem. Soc.* **1993**, *115*, 1804. (f) Cavaluzzo, M.; Chen, Q.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1993**, 131.

(13) (a) Stebler, M.; Ludi, A.; Bürgi, H. B. *Inorg. Chem.* **1986**, *25*, 4743. (b) Swarnabala, G.; Reddy, K. R.; Jyotsna, T.; Rajasekharan, M. V. *Transition Met. Chem.* **1994**, *19*, 506.

(14) Reddy, K. R.; Rajasekharan, M. V. *Polyhedron* **1994**, *13*, 765.

(15) Reddy, K. R.; Rajasekharan, M. V.; Padhye, S.; Dahan, F.; Tuchagues, J. P. *Inorg. Chem.* **1994**, *33*, 428.

(16) Furniss, B. S., Hannaford, A. J., Rogers, V., Smith, P. W. G., Tatchell, A. R., Eds. *Vogel's Text Book of Practical Organic Chemistry*; ELBS: London, 1978.

(17) Bassett, J., Denney, R. C., Jeffery, G. H., Mendham, J., Eds. *Vogel's Text Book of Qualitative Inorganic Analysis*; ELBS: London, 1978.

(18) Dutta, R. L.; Syamal, A. *Elements of Magneto Chemistry*; S. Chand & Co. Ltd.: New Delhi, 1982.

(19) Sheldrick, G. M. *SHELXTL-PLUS Crystallographic System*, Version 2; Nicolet XRD Corp.: Madison, WI, 1987.

(20) Hayword, M. P.; Wells, C. F. *Transition Met. Chem.* **1987**, *12*, 179.

(21) Reddy, K. R. Ph.D. Thesis, University of Hyderabad, 1993.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for **1**

	x	*y*	*z*	*U*(eq)[a]
Mn(1)	3604	2663	2910	34(1)
O(1)	4082(4)	3759(3)	2295(2)	40(2)
O(2)	2219(4)	3332(3)	3274(4)	35(2)
N(1)	2761(5)	2119(4)	2240(3)	37(2)
N(2)	5152(5)	1702(4)	2521(3)	41(2)
N(3)	3239(5)	1306(4)	3639(3)	41(2)
N(4)	4563(5)	2937(5)	3639(3)	40(2)
Mn(2)	1494(1)	4717(1)	3059(1)	33(1)
O(3)	2919(4)	5393(3)	2878(2)	37(2)
O(4)	1684(4)	4767(3)	2164(2)	37(2)
O(1W)	−172(4)	4079(4)	3274(2)	40(2)
N(5)	1452(5)	4960(4)	4034(3)	36(2)
N(6)	344(5)	6194(4)	3012(3)	42(2)
Mn(3)	3289(1)	5118(1)	2043(1)	37(1)
O(2W)	5010(5)	5633(4)	1910(3)	57(2)
N(7)	2679(6)	6675(5)	1586(3)	46(2)
N(8)	3411(6)	4938(5)	1046(3)	48(2)
C(1)	1561(7)	2367(6)	2115(3)	45(3)
C(2)	1123(8)	2051(7)	1566(4)	57(3)
C(3)	1940(8)	1508(7)	1163(4)	59(3)
C(4)	3219(8)	1241(6)	1281(4)	50(3)
C(5)	4169(9)	683(7)	875(4)	66(4)
C(6)	5368(9)	456(7)	1020(4)	67(4)
C(7)	5767(7)	775(6)	1585(4)	50(3)
C(8)	7030(8)	605(6)	1767(4)	59(3)
C(9)	7308(7)	972(6)	2302(4)	55(3)
C(10)	6340(7)	1529(6)	2674(4)	46(3)
C(11)	4871(7)	1337(5)	1981(3)	42(3)
C(12)	3582(7)	1549(5)	1831(3)	39(3)
C(13)	2555(7)	504(6)	3627(4)	54(3)
C(14)	2272(8)	−255(7)	4208(6)	73(4)
C(15)	2644(9)	−191(7)	4791(5)	73(4)
C(16)	3344(7)	646(7)	4832(4)	55(3)
C(17)	3765(9)	831(8)	5425(4)	73(4)
C(18)	4433(9)	1652(9)	5427(4)	75(4)
C(19)	4751(7)	2404(7)	4824(4)	55(3)
C(20)	5402(9)	3300(8)	4784(5)	73(4)
C(21)	5611(8)	3979(8)	4192(5)	68(4)
C(22)	5164(7)	3789(6)	3614(4)	50(3)
C(23)	4361(7)	2234(6)	4235(3)	43(3)
C(24)	3652(7)	1370(6)	4242(3)	44(3)
C(25)	2009(6)	4319(6)	4533(3)	41(3)
C(26)	2069(7)	4648(7)	5137(4)	51(3)
C(27)	1521(7)	5643(7)	5228(4)	52(3)
C(28)	906(7)	6342(6)	4717(4)	44(3)
C(29)	246(8)	7381(7)	4765(5)	58(3)
C(30)	−371(8)	7996(7)	4271(5)	64(4)
C(31)	−381(8)	7627(6)	3652(4)	54(3)
C(32)	−1032(9)	8182(7)	3120(5)	72(4)
C(33)	−983(8)	7747(7)	2558(5)	70(4)
C(34)	−277(7)	6746(6)	2509(4)	53(3)
C(35)	268(7)	6603(5)	3583(4)	42(3)
C(36)	900(6)	5968(5)	4122(3)	33(2)
C(37)	2382(7)	7536(6)	1867(4)	51(3)
C(38)	1895(9)	8547(7)	1499(5)	72(4)
C(39)	1675(10)	8642(7)	850(5)	75(4)
C(40)	2003(9)	7736(7)	535(5)	66(4)
C(41)	1864(11)	7747(9)	−143(5)	94(5)
C(42)	2244(12)	6857(9)	−414(5)	97(5)
C(43)	2758(9)	5863(8)	−32(4)	72(4)
C(44)	3182(11)	4882(9)	−275(4)	93(5)
C(45)	3706(11)	4009(8)	130(4)	81(4)
C(46)	3834(9)	4062(7)	805(4)	64(4)
C(47)	2892(7)	5831(6)	639(4)	51(3)
C(48)	2512(7)	6759(6)	931(4)	49(3)
N(9)	−1051(8)	1564(6)	3678(3)	57(3)
O(5)	−1145(7)	655(5)	3602(3)	92(3)
O(6)	−2009(6)	2167(5)	3843(3)	80(3)
O(7)	6(6)	1939(5)	3608(3)	72(3)
N(10)	2163(6)	5971(6)	7785(3)	55(3)
O(8)	1319(6)	6719(6)	7817(4)	94(3)
O(9)	3122(5)	5961(5)	8090(3)	73(3)
O(10)	2130(6)	5271(5)	7446(3)	74(3)
N(11)	8203(10)	8388(8)	654(5)	115(6)
O(11)	7223(11)	8217(12)	466(7)	248(11)
O(12)	8709(12)	9193(9)	385(7)	226(9)
O(13)	8640(19)	7779(14)	1132(9)	394(18)
N(12)	4188(13)	8388(11)	2968(8)	442(27)
O(14)	3828(15)	7668(16)	3414(8)	529(30)
O(15)	5295(13)	8562(17)	2894(9)	353(16)
O(16)	3439(18)	8945(11)	2603(9)	363(18)
O(3W)	6598(8)	6305(6)	3412(4)	116(4)
O(4W)	5518(10)	7572(7)	1554(8)	225(8)
O(5W)	9842(58)	5302(53)	701(32)	573(55)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

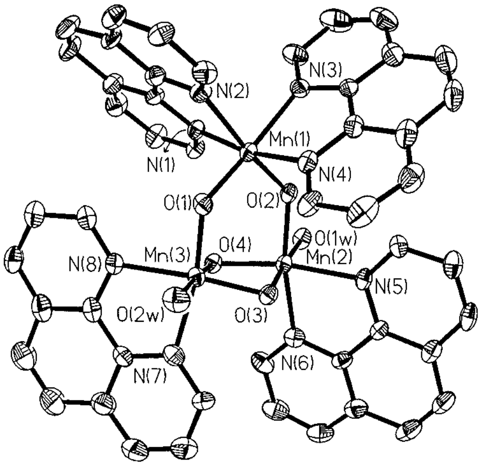

Figure 1. View of the $[Mn_3O_4(phen)_4(H_2O)_2]^{4+}$ cation in the crystals of the nitrate salt, **1**. Hydrogen atoms are omitted for clarity.

distance is characteristic of bis(μ-oxo)dimanganese units.[7d−g] The geometry of each of the manganese atoms is octahedral. The coordination octahedron of Mn(1) consists of two pairs of nitrogen atoms of two phen moieties and two μ-oxo groups, whereas that of each of Mn(2) and Mn(3) atoms consists of a pair of nitrogen atoms of a phen moiety, three μ-oxo oxygen atoms, and the oxygen atom of a water molecule. The observed average Mn−N and $Mn-O_{oxo}$ distances of 2.065 and 1.798 Å, respectively, and oxidation state analysis of the complex demonstrate that the cluster contains three Mn(IV) centers. The structural parameters associated with the Mn_3O_4 core are comparable to those of the analogous bpy complex cations, *viz.*, $[Mn_3O_4(bpy)_4(H_2O)_2]^{4+}$ (**2**) and $[Mn_3O_4(bpy)_4Cl_2]^{2+}$ (**3**).[10] However, the $Mn-O_{aqua}$ distances (average 2.01(1) Å) in **1** are shorter than those of **2** (average 2.04(1) Å), even though the coordinated water molecules in the present cation appear to participate in hydrogen bonding with lattice water molecules and nitrate anions, with the O(1W)···O(7) and O(2W)···O(4W) distances being 2.641 and 2.520 Å, respectively. The Mn−Mn distances in **1**−**3** are considerably shorter than the corresponding distances in the methoxy-bridged trimanganese cation $[Mn_3(L)_2(CH_3O)_2(CH_3OH)(C_2H_5OH)]^+$ (**4**) (where L = the trianion of bis(benzoylacetone) 1,3-diiminopropan-2-ol), reported by Mikuriya.[22] This could be explained to arise from the presence of Jahn−Teller-distorted d^4 Mn(III) centers in **4**; the manganese centers in **1**, as already mentioned, are in the +4 oxidation state.

The three manganese atoms and the two μ-oxo bridges, O(1) and O(2), in **1** are coplanar. The doubly bridged Mn_2O_2 segment is also planar, and these two planes are perpendicular to each other. A similar observation has also been made for **2**

---

[22] Mikuriya, M.; Majima, K.; Yamato, Y. *Chem. Lett.* **1992**, 1929.

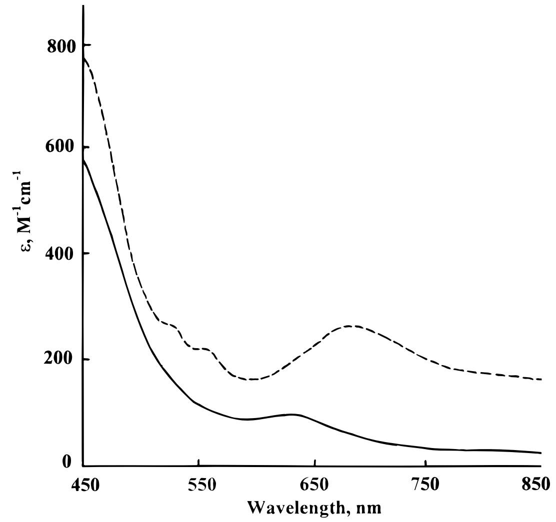

Figure 2. Electronic absorption spectra of **1** in ligand buffer at pH 4.5, measured immediately after dissolution (—) and after 48 h (- - -).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1**

Mn(1)−O(1)	1.761(4)	Mn(1)−O(2)	1.770(4)
Mn(1)−N(1)	2.004(6)	Mn(1)−N(2)	2.100(5)
Mn(1)−N(3)	2.080(5)	Mn(1)−N(4)	2.019(6)
O(1)−Mn(3)	1.819(4)	O(2)−Mn(2)	1.810(4)
Mn(2)−O(3)	1.808(5)	Mn(2)−O(4)	1.810(4)
Mn(2)−O(1W)	2.017(5)	Mn(2)−N(5)	2.079(6)
Mn(2)−N(6)	2.090(5)	O(3)−Mn(3)	1.804(5)
O(4)−Mn(3)	1.806(5)	Mn(3)−O(2W)	2.002(5)
Mn(3)−N(7)	2.061(6)	Mn(3)−N(8)	2.091(6)

O(1)−Mn(1)−O(2)	98.8(2)	O(1)−Mn(1)−N(1)	90.8(2)
O(2)−Mn(1)−N(1)	96.6(2)	O(1)−Mn(1)−N(2)	87.3(2)
O(2)−Mn(1)−N(2)	173.4(2)	N(1)−Mn(1)−N(2)	80.5(2)
O(1)−Mn(1)−N(3)	174.0(2)	O(2)−Mn(1)−N(3)	86.4(2)
N(1)−Mn(1)−N(3)	91.6(2)	N(2)−Mn(1)−N(3)	87.7(2)
O(1)−Mn(1)−N(4)	96.5(2)	O(2)−Mn(1)−N(4)	88.9(2)
N(1)−Mn(1)−N(4)	170.0(2)	N(2)−Mn(1)−N(4)	93.1(2)
N(3)−Mn(1)−N(4)	80.5(2)	Mn(1)−O(1)−Mn(3)	130.4(2)
Mn(1)−O(2)−Mn(2)	130.3(2)	O(2)−Mn(2)−O(3)	98.6(2)
O(2)−Mn(2)−O(4)	95.4(2)	O(3)−Mn(2)−O(4)	82.8(2)
O(2)−Mn(2)−O(1W)	85.8(2)	O(3)−Mn(2)−O(1W)	175.3(2)
O(4)−Mn(2)−O(1W)	98.7(2)	O(2)−Mn(2)−N(5)	92.2(2)
O(3)−Mn(2)−N(5)	86.9(2)	O(4)−Mn(2)−N(5)	168.0(2)
O(1W)−Mn(2)−N(5)	91.1(2)	O(2)−Mn(2)−N(6)	165.9(2)
O(3)−Mn(2)−N(6)	91.9(2)	O(4)−Mn(2)−N(6)	95.2(2)
O(1W)−Mn(2)−N(6)	83.5(2)	N(5)−Mn(2)−N(6)	79.0(2)
Mn(2)−O(3)−Mn(3)	95.6(2)	Mn(2)−O(4)−Mn(3)	95.4(2)
O(1)−Mn(3)−O(3)	95.7(2)	O(1)−Mn(3)−O(4)	97.7(2)
O(3)−Mn(3)−O(4)	83.0(2)	O(1)−Mn(3)−O(2W)	86.7(2)
O(3)−Mn(3)−O(2W)	95.2(2)	O(4)−Mn(3)−O(2W)	175.3(2)
O(1)−Mn(3)−N(7)	167.8(2)	O(3)−Mn(3)−N(7)	94.1(2)
O(4)−Mn(3)−N(7)	90.5(2)	O(2W)−Mn(3)−N(7)	85.3(2)
O(1)−Mn(3)−N(8)	91.9(2)	O(3)−Mn(3)−N(8)	170.2(2)
O(4)−Mn(3)−N(8)	89.8(2)	O(2W)−Mn(3)−N(8)	91.4(2)
N(7)−Mn(3)−N(8)	79.1(2)		

and **3**, while the hydroxy-bound trinuclear complex $[Mn_3O_4(bpea)_3(OH)]^{3+}$ (**5**) (where bpea = *N,N*-bis(2-pyridylmethyl)ethylamine) exhibits considerable deviation in the plane formed by the three manganese atoms and the two single μ-oxo bridges, due to hydrogen bonding between the hydrogen atom of the hydroxo group and an oxygen atom of the doubly bridged Mn_2O_2 segment.[7b]

Spectral and Magnetic Data. The Mn^{IV}_3 complex is soluble in highly polar solvents such as water, dimethylformamide, and dimethyl sulfoxide and is insoluble in moderately polar solvents such as dichloromethane, chloroform, and acetonitrile. Solutions are deep-brown and decompose over a period of time, as judged from their electronic absorption spectra, depositing a brown solid. The spectrum of the complex in acetate buffer (pH 4.5) reveals a broad absorption at 610 nm. The buffer solution, also containing excess ligand, slowly generates the spectral pattern known for the $Mn^{III}Mn^{IV}$ cation $[Mn_2O_2(phen)_4]^{3+}$, with a band at 684 nm and two shoulders at 535 and 560 nm.[9e] The spectra recorded immediately after dissolving the complex in pH 4.5 ligand buffer and after standing for 48 h are shown in Figure 2. The absorbance at 684 nm corresponds to more than 95% conversion to the $Mn^{III}Mn^{IV}$ species according to the following equation, using the ϵ value of 553 M^{-1} L^{-1} for $[Mn_2O_2(phen)_4]^{3+}$(aq) at pH 4.5.[9e]

$$2[Mn_3O_4(phen)_4(H_2O)_2]^{4+} + 4H^+ + 4phen + 3D \rightarrow 3\,[Mn_2O_2(phen)_4]^{3+} + 6H_2O + 3D^+$$

(D = donor ligand phen or water)

A similar observation has also been made from the EPR spectra of the analogous bpy complex, **2** in acetate buffer, in which ligand oxidation has been suggested to occur, since no dioxygen evolution was detected from the solutions.[10a]

The EPR spectrum of **1** in powder form at room temperature (298 K) exhibits a strong signal at $g \cong 2$. Additional low-field lines were also observed on lowering the temperature to 150 K. The frozen-solution EPR spectrum in dimethylformamide glass at 150 K exhibits the multiline pattern usually observed for $Mn^{III}Mn^{IV}$ species[7f] along with Mn^{II} signals, indicating the break up of the trinuclear core. The observed magnetic moment of 3.75 μ_B per complex molecule at room temperature for the present complex is comparable to the magnetic moment values reported for other Mn^{IV}_3 complexes[10] and can analogously be attributed to the presence of strong antiferromagnetic interaction between the metal centers in the complex.

In conclusion, the formation of the present complex with water coordination to Mn(IV) centers, at low pHs, demonstrates the stabilization of coordinated aqua molecules in the environment of high-valence manganese. The requirement of high acidic conditions for the synthesis of the complex and its disproportionation into a dinuclear $Mn^{III}Mn^{IV}$ species in pH 4.5 ligand buffer suggest that the pH of the medium has a definite influence on the nuclearity and oxidation state of the manganese species formed.

Acknowledgment. This work was supported by the National Science Foundation through Grant No. CHE-9007607 (to D.J.H.). K.R.R. thanks the CSIR (New Delhi) for financial assistance.

Supporting Information Available: Tables S1 and S2 (hydrogen atom parameters and anisotropic parameters, respectively) and Table S3 (bond lengths and angles) (11 pages). For ordering information, consult any current masthead page. Listing of observed and calculated structure amplitudes are available from D.J.H. on request.

IC9502640