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Articles

Experimental and Theoretical Investigations of Condensation and Disproportionation of $Mn(bpy)Cl_3(H_2O)$ in Aqueous Solution

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$Mn^{III}(bpy)Cl_3H_2O$ (Goodwin, H. A.; Sylva, R. N. *Aust. J. Chem.* **1965**, *18*, 1743) crystallizes in the triclinic space group $P\bar{1}$, with $a = 6.627(1)$ Å, $b = 9.991(7)$ Å, $c = 10.116(4)$ Å, $\alpha = 84.38(4)°$, $\beta = 73.47(3)°$, $\gamma = 78.48(3)°$, $V = 629$ Å,[3] and $Z = 4$. The Mn^{III} ion has an octahedral surrounding distorted by a strong Jahn−Teller effect. Two chloride ions and the water molecule are involved into a network of hydrogen bonds. A careful study of aqueous solutions of $Mn^{III}LCl_3H_2O$ (L = bipyridine or phenanthroline) at different pH demonstrated the formation by condensation and disproportionation of $[L_2Mn^{III}O_2Mn^{IV}L_2](ClO_4)_3$ (Cooper, S. R.; Calvin, M. *J. Am. Chem. Soc.* **1977**, *99*, 6623), $[Mn^{IV}{}_3O_4L_4(H_2O)_2](ClO_4)_4$ (Sarneski, J. E.; et al. *J. Am. Chem. Soc.* **1990**, *112*, 7255) and $[Mn_4O_6(bpy)_6](ClO_4)_4$ (Philouze, C.; et al. *J. Am. Chem. Soc.* **1994**, *116*, 8557). Condensation of $MnLCl_3H_2O$ has been studied theoretically using partial charge models. It was possible to identify the mononuclear Mn^{III} and Mn^{IV} species which are able to condense through oxolation into polynuclear Mn^{IV} or mixed-valence $Mn^{III}-Mn^{IV}$ complexes. It is then shown that direct electron transfer between Mn^{III} species is either assisted by the solvent or associated with the transfer of a bpy ligand from Mn^{II} toward Mn^{IV}. Formation of chainlike tetramers is thermodynamically unfavorable and has to be assisted by the solvent to occur. The greater hydrophobicity of phenanthroline in comparison with bipyridine explains why the chainlike tetramer is not obtained in the case of phenanthroline. Substitution of an oxo bridge by two carboxylato bridges appears to be the key point for the stabilization of a chainlike tetramer similar to that proposed from EXAFS to exist in the plant oxygen evolving complex.

Introduction

The oxygen evolving complex (OEC) in plants uses a polynuclear manganese-oxo complex to extract four electrons and four protons from two water molecules, dioxygen being formed in the process.[2] This natural complex is still the object of numerous works by biochemists and biophysicists. Such use by nature of a manganese polynuclear complex has stimulated chemists to study analogous artificial systems.[3−10]

It has been shown[11] that polynuclear oxo and/or hydroxo complexes are easily obtained through polycondensation of mononuclear aquo or oxo complexes. This method has been previously used to produce the trinuclear $[Mn_3O_4L_4(H_2O)_2](ClO_4)_4$[12] with L = 2,2′-bipyridyl (bpy) or phenanthroline (phen) complexes and the tetranuclear $[Mn_4O_6(bpy)_6](ClO_4)_4$[13] complex. This way to obtain these polynuclear compounds is simple and efficient. The trinuclear Mn^{IV} species can also be obtained by acidification of the mixed-valence dimer $[(bpy)_2Mn^{III}O_2Mn^{IV}(bpy)_2]^{3+}$[7] or oxidation of Mn^{II} by permanganate.[14] The phen trinuclear analogue has been obtained.[8] The tetranuclear species $[Mn^{IV}{}_4O_6(bpy)_6]^{4+}$ has also been obtained by oxidation of Mn^{II} by permanganate followed by an additional oxidation by

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Table 1. Crystallographic Data for $Mn(bpy)Cl_3(H_2O)$

empirical formula	$C_{10}H_{10}Cl_3MnN_2O$
fw	335.50
radiation	Mo Kα
temp, K	298
space group	$P\bar{1}$
a, Å	6.627(1)
b, Å	9.991(7)
c, Å	10.116(4)
α, deg	84.38(4)
β, deg	73.47(3)
γ, deg	78.48(3)
V, Å^3	629
Z	2
N_{meas}	1651
R	3.1
R_w	3.8

dichromate.[9] It may also be obtained by electrolytic oxidation of the mixed valence dimer mentionned above.[15]

The aim of this paper is to study the condensation reactions of a mononuclear complex $Mn^{III}LCl_3(H_2O)$ with L = bpy or phen. Experimental results will be analyzed using partial charge-based models, which have been proven to be useful for understanding the first condensation steps of inorganic complexes in aqueous solutions.[11,16] This has been done using a two-step approach. Structure-independent partial charges are first computed to understand the various chemical changes occurring after dissolution of the complex at a given pH.[11] The detailed chemical structure of plausible aqueous species is then taken into account[16] to understand more subtle changes such as isomerization and/or disproportionation[7,10,17,18]

Experimental Section

All the pH measurements were made using a Tacussel PHN 81 pH-meter. The software WinPacha used for calculations and running under Windows was developed by M. Henry.

Syntheses. The mononuclear complexes were prepared as described by Goodwin and Sylva.[19]

Crystallization of $Mn(bpy)Cl_3(H_2O)$. 500 mg of $Mn(bpy)Cl_3(H_2O)$ were added to a stirred solution of HCl (10 N). To this solution were added 5 mL of Goodwin and Sylva so-called "brown solution".[19] Finally the solution was diluted with 15 mL of distilled water to obtain a red color. The solution was stored at −5 °C. After 24 h red crystals appeared.

Condensation and Disproportionation Experiments. $MnLCl_3(H_2O)$ (0.2 g) (L = phen or bpy) was dissolved in small portions and under stirring in 15 mL of a nitric acid solution at a chosen pH. The pH is controlled with a pH-meter during the addition and maintained at the chosen value by addition of a sodium hydroxide solution (5 M). After the addition, the solution is centrifuged and filtered. Sodium perchlorate[20] (0.146 g) is added with stirring to the filtrate, and the solution is set to crystallize. Within a few days crystals appeared and their nature was studied by X-ray diffraction.

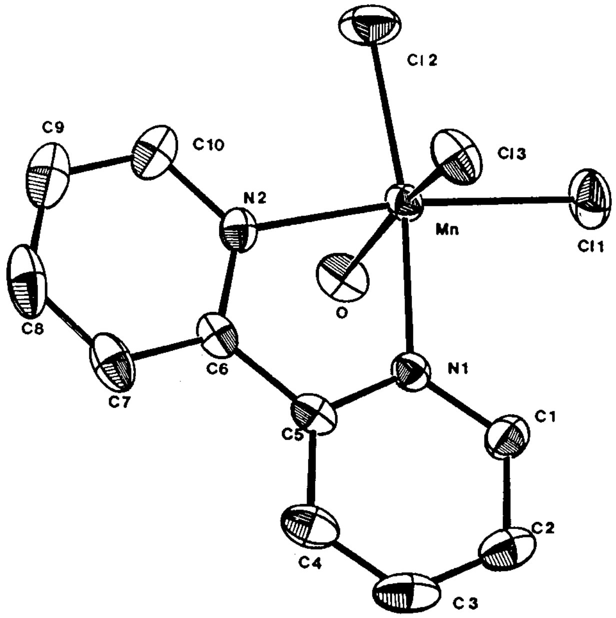

Figure 1. ORTEP drawing showing the molecular structure of $Mn(bpy)Cl_3(H_2O)$ complex.

Crystallographic Data Collection and Refinement of the Structure. A crystal was mounted on a Enraf-Nonius CAD4 automatic diffractometer using graphite monochromated Mo Kα radiation. The main crystallographic data are gathered in Table 1. Data collection was performed in the range $1° < \theta < 25°$. 1651 reflections with $I > 3\sigma(I)$ were used after Lorentz-polarization and intensity decay corrections (15% after 35 h, linearly corrected). The structure was solved by the heavy-atom method and refined by full-matrix least-squares with all non H atoms refined anisotropically. The H atoms of the water molecule were located and introduced in idealized positions and constrained to ride on their parent carbon atoms. Analytical scattering factors for neutral atoms were corrected for f' and f''.

Creation of the Data Files for Modelization. Files were created using, when possible, X-ray data. For minor transformations (i.e. atom exchanges or abstractions) X-ray data files were slightly modified. For major transformations (i.e. geometrical variations due to changes in oxidation degree, coupling of different molecular units, addition of ligands, etc.) files were created using internal coordinates (bond lengths, bond angles, and dihedral angles). For that purpose X-ray diffraction data were transformed into internal coordinates using the WinPacha software. Mononuclear Mn^{II}, Mn^{III}, and Mn^{IV} complexes with one or two bipyridine molecules were then created. These "basic units" can be combined in order to form the desired molecule. All the necessary structural data needed for this study are gathered in Table 2. For aquo ligands, the M−O and O−H bonds were supposed to lie in the same plane.

Results and Discussion.

Description of the Structure. The structure of the mononuclear $Mn(bpy)Cl_3(H_2O)$ complex is represented in Figure 1. It consists of a Mn^{III} ion coordinated to three chloride ions, a water molecule, and a bipyridine ligand. Hydrogen atoms from the water molecule are involved into hydrogen bonding. A few Mn^{III}-aquo species are known,[21−23] The ligands around the Manganese atom form a strongly distorted octahedron as expected for a Mn^{III} d^4 ion (Jahn−Teller effect). The effect of the nature of the ligands upon the hydrogen bonding network should also be considered. The chlorine atom Cl_3 situated in trans position of the water molecule displays a distance which is significantly longer than the other Mn−Cl distances (Table

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(20) Perchlorate salts of metal complexes with organic ligands are potentially explosive; only small amounts of material should be prepared, and they should be handled with great caution (cf. *J. Chem. Educ.* **1973**, *50*, A335; *Chem. Eng. News* **1983**, 61 (Dec. 5), 4; **1963**, 41 (July 8), 47).

Table 2. Mn-Coordinating Atom Bond Length (pm) as a Function of Oxidation State

bond type	distance (pm) or angle (deg)
$Mn^{II}-N(O)$	220 (222)
$Mn^{II}-OH(OH_2)$	220 (220)
$Mn^{III}-N(O)$	206 (177)
$Mn^{III}-OH(H_2O)$	200 (227)
$Mn^{IV}-N(O)$	204 (180)
$Mn^{IV}-OH(H_2O)$	192 (207)
O−H	96
H−Cl	127.5
C−H	110
C−C	154
C−O	143
C═O	123
M−O−H	180
H−O−H	104

3). This chlorine atom defines the Jahn−Teller distortion axis and forms a short hydrogen bond with an hydrogen atom belonging to the water molecule of another $Mn(bpy)Cl_3(H_2O)$. The second hydrogen atom of the water molecule makes a hydrogen bond with the chlorine atom Cl_1 lying in the plane of bipyridine ligand. Owing to this hydrogen bond, the $Mn-Cl_1$ distance is slightly longer than the $Mn-Cl_2$ one. The last chlorine atom Cl_2 is not involved in any hydrogen bonding. The Mn−Cl distances found in $Mn(bpy)Cl_3(H_2O)$ are very close to that observed in $[Mn(bpy)Cl_3]_n$.[24] The observed Mn−O distance is quite similar to that found in $[(bpy)(H_2O)Mn^{III}O(AcO)_2Mn^{III}(H_2O)(bpy)]^{2+}$,[23] while the Mn−N distances are almost identical in the three structures.

Condensation and Disproportionation of $Mn(bpy)Cl_3(H_2O)$ in Aqueous Solution. Table 4 summarizes the results of our hydrolysis and condensation experiments after dissolution of the Mn^{III} complexes in water. With bipyridine we synthesized the cyclic dimer $[(bpy)_2Mn^{III}O_2Mn^{IV}(bpy)_2](ClO_4)_3$[25] for $2.5 < pH < 5$ (Figure 2b). At pH = 2.5 there is an equilibrium between the former species and $[Mn_4O_6(bpy)_6](ClO_4)_4$ (Figure 2d). This chainlike tetranuclear complex can be isolated until pH > 1.5. At pH < 1 the tricyclic trinuclear cation $[Mn_3O_4(bpy)_4(H_2O)_2]^{4+}$ (Figure 2c) crystallizes with perchlorate and nitrate anions. With phenanthroline we have isolated the cyclic dinuclear complex $[(phen)_2Mn^{III}O_2Mn^{IV}(phen)_2](ClO_4)_3$[26] at $1.4 < pH < 5$ and we obtained only the tricyclic trinuclear cation $[Mn_3O_4(phen)_4(H_2O)_2]^{4+}$ if pH < 1.4.

The main difference between phenanthroline and bipyridine then consists of the lack of the tetranuclear species with phenanthroline. Such a difference between phenanthroline and bipyridine ligands have already be noticed for dinuclear Mn complexes bridged with di-μ-oxo units.[27,28] As both ligands are structurally very similar and display very close pK_a values (5 for phen against 4.5 for bpy), this behavior is rather surprising.

Interpretation with the Structure-Independent Partial Charge Model. To understand how the previous structures can be formed from monomeric aquo-hydroxo precursors, we have attempted to use partial charge models.

Partial charge models (PCM) are generally based on Sanderson electronegativity equalization principle.[29] The simplest model neglects the molecular potential, leading to structure-independent partial charges (SIPCM). In that case for any moiety X built with n atoms having an Allred−Rochow electronegativity $\chi_k°$, it has been shown[11] that its global softness σ_i and mean electronegativity $\langle\chi_i\rangle$ can be given by

$$\sigma_i = \sum_{k=1}^{n}\sigma_k^0 \text{ and } \langle\chi_i\rangle\sigma_i = \sum_{k=1}^{n}\sigma_k^0\,\chi_k^0 \text{ with } \sigma_k^0 = \frac{1}{1.36\sqrt{\chi_k^0}} \qquad (1)$$

with the partial charge on each constituent atom k defined as $q_k = \sigma_k°(\langle\chi_i\rangle - \chi_k°)$. When m moieties X are combined to form a given chemical compound carrying a global electrical charge z, the resulting softness σ and mean electronegativity $\langle\chi\rangle$ are given by

$$\sigma = \sum_{i=1}^{m}\sigma_i \text{ and } \sigma\,\langle\chi\rangle = z + \sum_{i=1}^{m}\sigma_i\langle\chi_i\rangle \qquad (2)$$

The charge on moiety i is again computed according to $q_i = \sigma_i(\langle\chi\rangle - \chi_i)$. From these two relationships, mean electronegativities as well as associated partial charge distributions are easily obtained knowing the rough formula of the chemical compound. Table 5 gives the Allred−Rochow electronegativities used in this work. The values for C and N have been increased from their generally accepted values (2.50 and 3.07, respectively) to account for their sp^2 rather than sp^3 hybridization in the bipyridine molecule.

Three fragments interact within the complex $Mn(bpy)Cl_3(H_2O)$: $MnCl_3$, a water molecule H_2O, and a bpy molecule. Looking at Table 6 obtained by applying eqs 1 and 2 to various moieties, we see that within the $Mn(bpy)Cl_3(H_2O)$ complex electronic density should flow both from the $MnCl_3$ ($q = +0.24$) and water ($q = +0.02$) moieties toward the bpy molecule ($q = -0.26$). As a result, the aquo ligand becomes more acidic than surrounding water molecules and protonation of chloro ligands ($q = -0.14$) should be considered

$$Mn(bpy)Cl_3(H_2O) \leftrightarrows (bpy)Mn^{III}Cl_2(HCl)(OH)$$

Now $q(HCl) = +0.07$ and $q(Mn) = +0.66$, meaning that elimination of HCl molecules should readily occur

$$(bpy)Mn^{III}Cl_2(HCl)(OH) + H_2O \rightarrow (bpy)Mn^{III}Cl_2(H_2O)(OH) + HCl$$

The same situation is encountered in $(bpy)Mn^{III}Cl_2(H_2O)(OH)$ and $(bpy)Mn^{III}Cl(H_2O)(OH)_2$ complexes obtained by successive removal of HCl molecule. The final stage of these hydrolysis reactions should then be the $(bpy)Mn^{III}(H_2O)(OH)_3$ complex. However, in aqueous solutions the HCl molecules should be completely dissociated according to: $HCl + H_2O \rightarrow H_3O^+ + Cl^-$, allowing protonation of the negatively charged OH groups ($q = -0.18$):

$$(bpy)Mn^{III}(H_2O)(OH)_3 + xH_3O^+ \leftrightarrows [(bpy)Mn^{III}(H_2O)_{x+1}(OH)_{3-x}]^{x+} + xH_2O$$

The equilibrium x value can be estimated from our measured pH value, as it has been shown that the mean electronegativity

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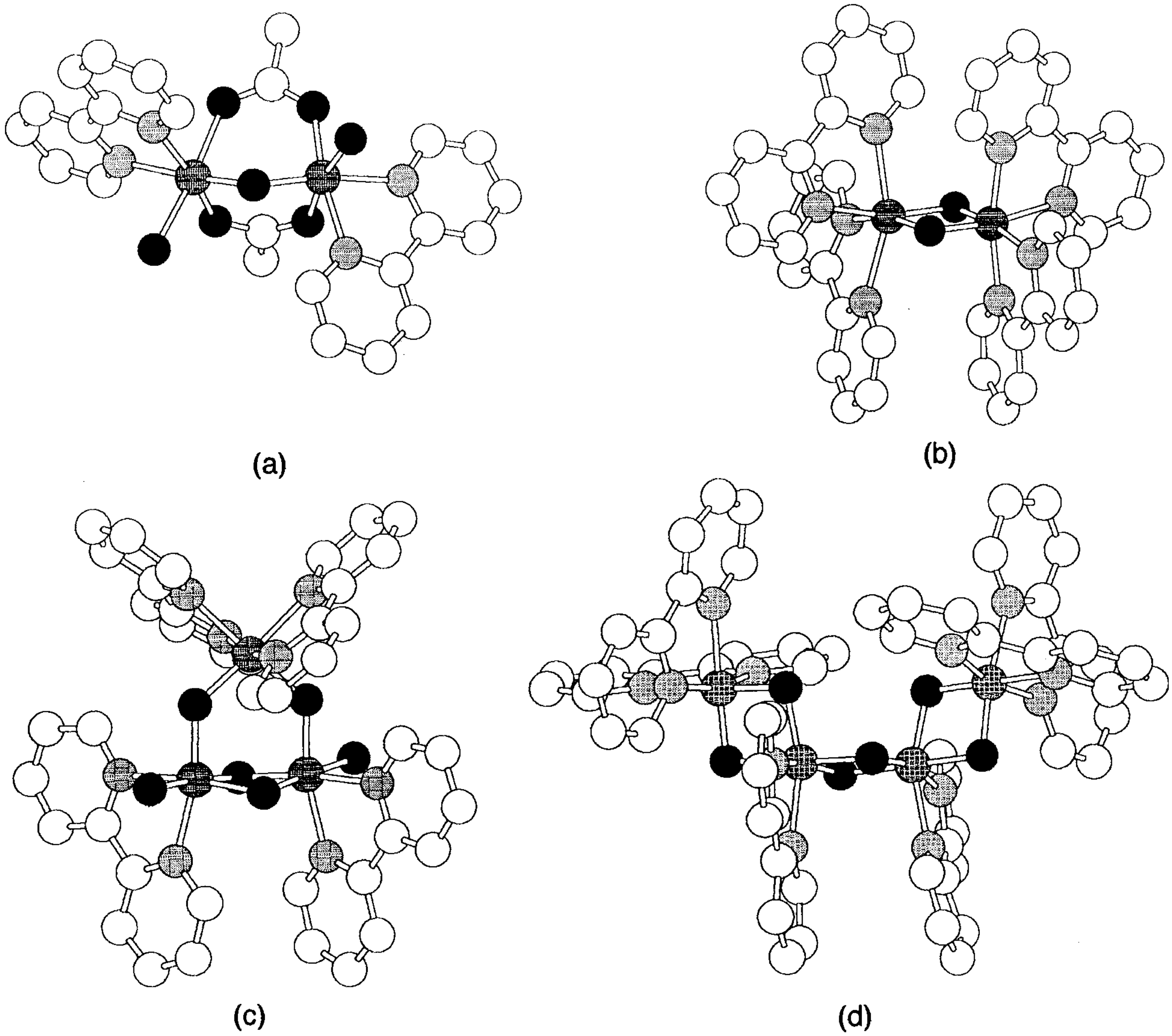

Figure 2. Molecular structures of (a) $[(bpy)(H_2O)MnO(AcO)_2Mn(H_2O)(bpy)]^{2+}$, (b) $[(bpy)_2MnO_2Mn(bpy)_2]^{3+}$, (c) $[Mn_3O_4(bpy)_4(H_2O)_2]^{4+}$, and (d) $[Mn_4O_6(bpy)_6]^{4+}$.

Table 3. Selected Bond Lengths (pm) and Angles (deg) for $Mn(bpy)Cl_3(H_2O)$

	Bond Lengths (pm)		
Mn−O	227.9(3)	Mn−Cl1	225.6(1)
Mn−N1	206.3(4)	Mn−Cl2	220.9(1)
Mn−N2	206.4(4)	Mn−Cl3	250.8(1)
	Bond Angles (deg)		
O−Mn−Cl1	90.1(1)	O−Mn−N1	83.1(1)
O−Mn−Cl2	92.2(1)	O−Mn−N2	85.0(1)
O−Mn−Cl3	168.41(9)		

of the aqueous solvent changes with pH according to $\langle\chi_{aq}\rangle = 2.732-0.035$ pH.[11] With pH ∼ 1.4, $\langle\chi_{aq}\rangle$ should be close to 2.68. For a $[(bpy)Mn^{III}(H_2O)_{x+1}(OH)_{3-x}]^{x+}$ complex $\sigma = 13.911 + 0.507x$ and $\sigma\langle\chi\rangle = 35.215 + 2.067x$. To reach $\langle\chi\rangle \sim 2.68$, we must then have $x \sim 3$. This means that the most abundant Mn^{III} species at pH ∼ 1.4 should be the aquo complex $[(bpy)Mn^{III}(H_2O)_4]^{3+}$. Such a complex lacking OH groups is unable to condense. It can however undergo a disproportionation reaction owing to the instability of aqueous Mn^{III} complexes at low pH:

$$2[(bpy)Mn^{III}(H_2O)_4]^{3+} \rightarrow [(bpy)Mn^{II}(H_2O)_4]^{2+} + [(bpy)Mn^{IV}(H_2O)_4]^{4+}$$

Table 4. Results of Condensation of $Mn(bpy)Cl_3(H_2O)$ and $Mn(phen)Cl_3(H_2O)$ Complexes as a Function of the Solution pH

	species	
pH	bipyridine	phenanthroline
0	trinuclear complex	trinuclear complex
1		
1.4		
1.5		
2	tetranuclear complex	
2.5	−	dinuclear mixed-valent complex
3	dinuclear mixed-valent complex	
4		
5		
6		
7	Mn(II) complexes and hydrated oxides	Mn(II) complexes and hydrated oxides
8		

Due to the low pH the $[(bpy)Mn^{II}(H_2O)_4]^{2+}$ complex would not be hydrolyzed, but rather transformed according to

$$[(bpy)Mn^{II}(H_2O)_4]^{2+} + 2H_2O \rightarrow [Mn^{II}(H_2O)_6]^{2+} + bpy$$

because of the repulsive interaction between the bpy and Mn moieties: $q(bpy) = +0.64$ and $q(Mn) = +0.72$. The other complex $[(bpy)Mn^{IV}(H_2O)_4]^{4+}$ should behave quite differently, as it is more electronegative than the solvent ($\chi_{aq} \sim 2.68$). With

Table 5. Allred−Rochow, Mulliken Electronegativities, and Atomic Radii Used in This Work for Computing Partial Charge Distributions

atom	H	C	N	O	Cl	Mn
Allred−Rochow electronegativity	2.10	2.75	3.60	3.50	2.83	1.43
atomic radius (pm)	37	77	75	73	99	117
Mulliken electronegativity $e\chi_i°$ (eV)	7.180	8.148	9.992	12.563	10.95	4.79

Table 6. Softnesses σ and Mean Electronegativities $\langle\chi\rangle$ of Various Moieties Used in This Work

moiety	σ	$\langle\chi\rangle$
$MnCl_3$	1.926	2.383
H_2O	1.408	2.491
bpy = $C_{10}H_8N_2$	9.268	2.536
$MnCl_3(bpy)(H_2O)$	12.602	2.508
HCl	0.944	2.438
OH	0.900	2.711
$MnCl_2$	1.489	2.251
$MnCl_2(bpy)(OH)(H_2O)$	13.065	2.511
MnCl	1.052	2.012
$MnCl(bpy)(OH)2(H_2O)$	13.528	2.514
$Mn(bpy)(OH)_3(H_2O)$	13.991	2.517
$[Mn(bpy)(H_2O)_4]^{3+}$	15.515	2.605
$[Mn(bpy)(H_2O)_4]^{4+}$	15.515	2.734

$\sigma = 15.515 - 0.507x$ and $\sigma\langle\chi\rangle = 42.412 - 2.067x$, two forms should be in equilibrium:

$$[(bpy)Mn^{IV}(H_2O)_3(OH)]^{3+} + H_2O \leftrightarrows [(bpy)Mn^{IV}(H_2O)_2(OH)_2]^{2+} + H_3O^+$$

With $q(OH) = -0.02$ and $q(Mn) = +0.77$ for the left species and $q(OH) = -0.13$ and $q(Mn) = +0.70$ for the right species, condensation reactions are expected.[11] Assuming that the most stable dimers are made of edge-sharing octahedra, it can be seen that the $x = 1$ complex should condense through olation and the $x = 2$ through oxolation:

$$2[(bpy)Mn^{IV}(H_2O)_3(OH)]^{3+} \rightarrow [(bpy)(H_2O)_2Mn^{IV}(OH)_2Mn^{IV}(H_2O)_2(bpy)]^{6+} + 2H_2O$$

$$2[(bpy)Mn^{IV}(H_2O)_2(OH)_2]^{2+} \rightarrow [(bpy)(H_2O)_2Mn^{IV}O_2Mn^{IV}(H_2O)_2(bpy)]^{4+} + 2H_2O$$

The complex having a mean electronegativity closest that of the solvent (2.68) is the di-μ-oxo complex (2.66 against 2.71 for the di-μ-hydroxo); thus, this should be the preferred form.

If our model favors the di-μ-oxo edge-sharing dimer it cannot explain why bpy ligands are not substituted by water molecules. As with the $[(bpy)Mn^{II}(H_2O)_4]^{2+}$ complex a strong repulsive interaction between bpy ligands and manganese atoms is anticipated [$q(bpy) = +1.11$ versus $q(Mn) = +0.75$]. The retention of bpy ligands with Mn^{IV} but not with Mn^{II} may then be attributed to the difference in electronic configurations. Mn^{IV} species ($3d^3$) are strongly stabilized in an octahedral ligand-field whereas this stabilization does not exist for Mn^{II} species ($3d^5$). This analysis suggests another pathway for disproportionation:

$$2[(bpy)Mn^{III}(H_2O)_4]^{3+} \rightarrow [Mn^{II}(H_2O)_6]^{2+} + [(bpy)_2Mn^{IV}(H_2O)_2]^{4+}$$

This disubstituted Mn^{IV} complex has a mean electronegativity $\langle c\rangle = 2.681$ which is very close to that of the solvent and should then also be present in solution.

According to this analysis the most probable species which can be found in aqueous solutions after disproportionation at pH ~ 1.4 are a monosubstituted di-μ-oxo dimer $[(bpy)(H_2O)_2Mn^{IV}O_2Mn^{IV}(H_2O)_2(bpy)]^{4+}$ and a disubstituted monomer $[(bpy)_2Mn^{IV}(H_2O)_2]^{4+}$. It is then rather satisfactory to see that these two complexes are just the building units of the two polynuclear complexes isolated from these aqueous solutions. The chainlike tetranuclear $[Mn^{IV}{}_4O_6(bpy)_6]^{4+}$ and the tricyclic trinuclear $[Mn^{IV}{}_3O_4(bpy)_4(H_2O)_2]^{4+}$ may accordingly be obtained throughacid oxolation between a monosubstituted di-μ-oxo dimer and two or one disubstituted monomer:

$$2[(bpy)_2Mn^{IV}(H_2O)_2]^{4+} + [(bpy)(H_2O)_2Mn^{IV}O_2Mn^{IV}(H_2O)_2(bpy)]^{4+} \rightarrow [Mn^{IV}{}_4O_6(bpy)_6]^{4+} + 8H_3O^+$$

$$[(bpy)_2Mn^{IV}(H_2O)_2]^{4+} + [(bpy)(H_2O)_2Mn^{IV}O_2Mn^{IV}(H_2O)_2(bpy)]^{4+} \rightarrow [Mn^{IV}{}_3O_4(bpy)_4(H_2O)_2]^{4+} + 4H_3O^+$$

The fact that these complexes are not obtained at higher pH, may be rationalized in the following way. When the pH is raised the disproportionation reaction is not complete, and the free bpy molecules should bind to Mn^{III} species rather than to Mn^{IV} species which are more inert toward substitution reactions:

$$[(bpy)Mn^{III}(H_2O)_4]^{3+} + bpy \rightarrow [(bpy)_2Mn^{III}(H_2O)_2]^{3+} + 2H_2O$$

The complex $[(bpy)_2Mn^{III}(H_2O)_2]^{3+}$ has $\langle c\rangle = 2.636$, which corresponds to pH ~ 2.7 for the aqueous solution. Around and/or above this value the dimer formation should then proceed as

$$[(bpy)_2Mn^{III}(H_2O)_2]^{3+} + [(bpy)_2Mn^{IV}(H_2O)_2]^{4+} \rightarrow [(bpy)_2Mn^{III}O_2Mn^{IV}(bpy)_2]^{3+} + 4H_3O^+$$

rather than between Mn^{IV} species.

It then appears that a partial charge analysis helps to rationalize the stoichiometries and the structures of the polynuclear manganese complexes which crystallize out from aqueous solutions of varying pH. The key points appear to be the initial formation of a $[(bpy)Mn^{III}(H_2O)_4]^{3+}$ complex and its subsequent disproportionation to give $[Mn^{II}(H_2O)_6]^{2+}$ and $[(bpy)Mn^{IV}(H_2O)_4]^{4+}$ as well as $[(bpy)_2Mn^{IV}(H_2O)_2]^{4+}$ complexes. Further hydrolysis and oxolation reactions then lead to the various polynuclear manganese complexes. At this stage, a deeper understanding of the involved chemistry is not possible without taking into account the detailed molecular structure of the aqueous species. Fortunately, the computation of structure-dependent partial charges is quite easy if one rely again on the electronegativity equalization principle. The key point is to use SI units for both electronegativity and hardness instead of empirical scales. With this major modification, the molecular electrostatic potential can be taken explicitly into account allowing a straightforward estimation of the electrostatic contributions to the enthalpy content of a given molecular species.

Table 7. Ionic Hydration Enthalpies ΔH_{hydr} of Ionic Species as a Function of Their Global Charge z (Evaluated from Data Given in Ref 29)

charge z	ΔH_{hydr} (kJ mol^{-1})
−2	1200 ± 200
−1	350 ± 70
0	0
+1	460 ± 200
+2	1800 ± 300
+3	3900 ± 500
+4	6800 ± 500

Interpretation with the Structure-Dependent Partial Charge Model. The basic equations of a structure-dependent partial charge model (SDPCM) expressed in volts (with e the elementary charge and ϵ_0 the vacuum permittivity) are[11]

$$\begin{cases} \chi_i = \langle \chi \rangle = \chi_i^0 + \eta_i e q_i + \dfrac{1}{4\pi\epsilon_0} \displaystyle\sum_{j=1}^{n} \dfrac{e q_j}{R_{ij}} \ \forall\ i = 1,..., n \\ \displaystyle\sum_{i=1}^{n} q_i = z \end{cases} \tag{3}$$

All symbols have the same meaning as before except that $\chi_i°$ represents now the Mulliken electronegativity of the ith atom. The η_i parameter (VC^{-1}) is the chemical hardness defined as the reciprocal of the softness $\sigma = 1/\eta$ and R_{ij} is the distance between atom i and atom j in the structure. It has been shown[30] that the chemical hardness can be nicely approximated by $\eta_i = (4\pi\epsilon_0 r_i)^{-1}$ where r_i is the atomic radius of atom i. Knowing the detailed molecular structure and having fixed values for electronegativities $\chi_i°$ and chemical hardnesses η_i (Table 5), the n partial charges and the mean electronegativity $\langle \chi \rangle$ are easily obtained by solving the linear $(n + 1) \times (n + 1)$ system (3). Knowing the partial charge distribution and the structure, the electrostatic balance energy M is readily computed as:

$$M = \frac{e^2}{8\pi\epsilon_0} \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{R_{ij}}{q_i q_j} \tag{4}$$

The lower the M value, the higher the electrostatic stability of the investigated molecular structure. Providing that there is no coordination changes around the metal cations, it may be reasonably assumed that this parameter should well describe the enthalpy changes involved when the chemical nature of the ligands around the metal atom is changing. Besides this intrinsic stability of a given molecular structure measured by our M value, we have also to consider the ionic hydration enthalpies of the complexes. Taking into account the existence of a solvation shell around the complexes in eq 3 is straightforward from a theoretical point of view. From a practical point of view this is merely impossible, owing to the lack of detailed structural data on these solvation shells. We have then to rely on empirical data in order to get an order of magnitude of these enthalpies. Empirical evaluations of ionic hydration enthalpies for M^{z+} cations show that they should scale as z^2/r, where r is the crystal radius.[31] Table 7 gives the mean values that we will use in this work. They have been obtained for each values of the global ionic charge z by averaging available experimental data.[31]

Let us consider then the first step, i.e., the substitution of chloro ligands by hydroxo ones within the coordination sphere of a bipyridyl Mn^{III} cation:

$$Mn^{III}(bpy)Cl_3(H_2O) + 3H_2O \rightarrow Mn^{III}(bpy)(OH)_3(H_2O) + 3HCl$$

Using the molecular structure determined in this work and Table 8, we are able to make an energetic balance $\Delta H = 1124 + (3 \times 182) - 1587 - (3 \times 16) = +35$ kJ mol^{-1} for the substitution of chloro by hydroxo ligands. This positive value means that the driving force for the reaction cannot be attributed to a better charge distribution in the products than in the reactants. The driving force should then come from the hydration of H^+ ($\Delta H_{hydr} = -1091$ kJ mol^{-1}) and Cl^- ions ($\Delta H_{hydr} = -381$ kJ mol^{-1})[31] obtained by breaking the H−Cl bond. Let us now look at the possible protonation of this hydroxo-aquo complex. Table 8 shows that the $z = +1$ dihydroxo-diaquo species is the most stable complex from an electrostatic point of view. The complexes with $z = +2$ and $z = +3$ are less stable, because of the increased repulsion between H atoms. However, owing to a better solvation than the monocharged complexes, their occurrence cannot be ruled out.

Having checked the stability of hydroxoaquobipyridyl-Mn^{III} cations, it is now time to have a look at the disproportionation reaction. As shown above, two possibilities have to be considered:

$$2[(bpy)Mn^{III}(H_2O)_4]^{3+} \rightarrow [(bpy)Mn^{II}(H_2O)_4]^{2+} + [(bpy)Mn^{IV}(H_2O)_4]^{4+}$$

$$2[(bpy)Mn^{III}(H_2O)_4]^{3+} \rightarrow [Mn^{II}(H_2O)_6]^{2+} + [(bpy)_2Mn^{IV}(H_2O)_2]^{4+}$$

For the first reaction we estimate from the data given in Table 8: $\Delta H = +319$ kJ mol^{-1}. This disproportionation appears then to be intrinsically unfavorable. However, with a change in ionic hydration enthalpies of about −800 kJ mol^{-1}, this disproportionation pathway is not unlikely. The second reaction is much more favorable than the first as from Table 8 we compute $\Delta H = -515$ kJ mol^{-1}. The occurrence of dibipyridyl-Mn^{IV} cations in crystalline structures is then easily explained. However, as the first disproportionation pathway cannot be excluded, the formation of dibipyridyl-Mn^{III} cations could also occur according to

$$[(bpy)Mn^{III}(H_2O)_4]^{3+} + [(bpy)Mn^{II}(H_2O)_4]^{2+} \rightarrow [(bpy)_2Mn^{III}(H_2O)_2]^{3+} + [Mn^{II}(H_2O)_6]^{2+}$$

as from Table 8, we obtain $\Delta H = -531$ kJ mol^{-1}.

Our M values show also that fully aquo species are not particularly stable from an electrostatic point of view. Removing protons from the aquo ligands should reduce the repulsive interactions. Table 8 gives the M values obtained after successive removal of protons from the complexes $[(bpy)Mn^{IV}(H_2O)_4]^{4+}$, $[(bpy)_2Mn^{IV}(H_2O)_2]^{4+}$, and $[(bpy)_2Mn^{III}(H_2O)_2]^{3+}$. All the hydrolyzed species appears to be intrinsically stables, the most stables being $(bpy)Mn^{IV}(OH)_4$, $[(bpy)_2Mn^{IV}O(OH)]^+$, and $[(bpy)_2Mn^{III}(OH)_2]^+$. With these data it becomes possible to analyze the polycondensation reactions. Three kind of oligomers have been crystallized from aqueous solutions: dimers, trimers and tetramers. Looking at the crystal structures, we see that in all cases condensation has proceeded through oxolation. With

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(30) Komorowski, L. *Chem. Phys. Lett.* **1987**, *134*, 536.
(31) Smith, D. W. *J. Chem. Educ.* **1977**, *54*, 540.

Table 8. Electrostatic Balance Energy (*M*) of Molecular or Ionic Species Considered in This Work

Mn oxidation state	molecule or complex	*M* value (kJ mol^{-1})
−	H_2O	−182
−	HCl	−16
−	bpy	−26
−	CH_3COOH	−179
II	$[Mn(H_2O)_6]^{2+}$	−2190
II	$[(bpy)Mn(H_2O)_4]^{2+}$	−1463
III	$[(bpy)Mn(H_2O)_4]^{3+}$	−594
III	$[(bpy)Mn(OH)(H_2O)_3]^{2+}$	−1276
III	$[(bpy)Mn(OH)_2(H_2O)_2]^{+}$	−1599
III	$(bpy)Mn(OH)_3(H_2O)$	−1587
III	$(bpy)MnCl_3(H_2O)$	−1124
IV	$[(bpy)Mn(H_2O)_4]^{4+}$	+594
IV	$[(bpy)Mn(OH)(H_2O)_3]^{3+}$	−394
IV	$[(bpy)Mn(OH)_2(H_2O)_2]^{2+}$	−1053
IV	$[(bpy)Mn(OH)_3(H_2O)]^{+}$	−1974
IV	$(bpy)Mn(OH)_4$	−2397
IV	$[(bpy)MnO(OH)_3]^{-}$	−2054
IV	$[(bpy)_2Mn(H_2O)_2]^{4+}$	+487
IV	$[(bpy)_2Mn(OH)(H_2O)]^{3+}$	−334
IV	$[(bpy)_2Mn(OH)_2]^{2+}$	−866
IV	$[(bpy)_2MnO(OH)]^{+}$	−1111
IV	$(bpy)_2MnO_2$	−1106
III	$[(bpy)_2Mn(H_2O)_2]^{3+}$	−388
III	$[(bpy)_2Mn(OH)(H_2O)]^{2+}$	−917
III	$[(bpy)_2Mn(OH)_2]^{+}$	−1297
III	$(bpy)_2MnO(OH)$	−1262
III−III	$[(bpy)(H_2O)_3Mn(OH)Mn(H_2O)_3(bpy)]^{5+}$	−1476
III−III	$[(bpy)(H_2O)_3MnOMn(H_2O)_3(bpy)]^{4+}$	−2335
III−III	$[(bpy)(H_2O)MnO(AcO)_2Mn(H_2O)(bpy)]^{2+}$	−4350
III−III	$[(bpy)(H_2O)_2MnO_2Mn(bpy)(H_2O)_2]^{2+}$	−1957
III−IV	$[(bpy)(H_2O)_2MnO_2Mn(bpy)(H_2O)_2]^{3+}$	−1737
III−IV	$[(bpy)_2MnO_2Mn(bpy)_2]^{3+}$	−1182
IV−IV	$[(bpy)(H_2O)_2MnO_2Mn(H_2O)_2(bpy)]^{4+}$	−1416
IV−IV−IV	$[Mn_3O_4(bpy)_4(H_2O)_2]^{4+}$	−5037
IV−IV−IV−IV	$[Mn_4O_6(bpy)_6]^{4+}$	−2746

the aid of Table 8, it is easy to check out the monomers which are probably involved in such reactions.

The most simple condensation reaction involves the formation of a μ_2-hydroxo (olation) or a μ_2-oxo bridge (oxolation) between two Mn^{III} species obtained from hydrolysis of $Mn^{III}(bpy)Cl_3(H_2O)$. For the olation reaction, a possible scheme is:

$$[(bpy)Mn^{III}(OH)(H_2O)_3]^{2+} + [(bpy)Mn^{III}(H_2O)_4]^{3+} \rightarrow [(bpy)(H_2O)_3Mn^{III}OHMn^{III}(H_2O)_3(bpy)]^{5+} + H_2O$$

with $\Delta H = +212$ kJ mol^{-1}. For oxolation we should have

$$[(bpy)Mn^{III}(OH)(H_2O)_3]^{2+} + [(bpy)Mn^{III}(OH)(H_2O)_3]^{2+} \rightarrow [(bpy)(H_2O)_3Mn^{III}OMn^{III}(H_2O)_3(bpy)]^{4+} + H_2O$$

with $\Delta H = +35$ kJ mol^{-1}. Oxolation is then clearly the favored pathway for condensation, in agreement with experiments. In fact this μ-oxo dimer can be isolated only in the presence of acetic acid. Single-crystal X-ray diffraction has demonstrated[32] the occurrence of two μ-acetato ligands in the structure, leading to the following composition $[(bpy)(H_2O)Mn^{III}O(AcO)_2Mn^{III}(H_2O)(bpy)]Cl_2$ (Figure 2a). Formation of such a species from solute precursors may be written as

$$2[(bpy)Mn^{III}(OH)_2(H_2O)_2]^{+} + 2AcOH \rightarrow [(bpy)(H_2O)Mn^{III}O(AcO)_2Mn^{III}(H_2O)(bpy)]^{2+} + 5H_2O$$

According to Table 8, $\Delta H = -1704$ kJ mol^{-1}, putting into evidence the strong stabilization brought to the structure by the acetate bridges.

One may wonder if a di-μ-oxo bridge would also stabilize the dimer. Let us first consider the formation of di-μ-oxo Mn^{III}dimer according to

$$2[(bpy)Mn^{III}(OH)_2(H_2O)_2]^{+} \rightarrow [(H_2O)_2(bpy)Mn^{III}O_2Mn^{III}(bpy)(H_2O)_2]^{2+} + 2H_2O$$

According to Table 8, $\Delta H = +877$ kJ mol^{-1}, a rather unfavorable value. Taking into account ionic hydration energies is here of no help as $\Delta(\Delta H_{hydr})$ is estimated at -880 kJ mol^{-1}, just enough to compensate for the Mn−Mn and O−O ionic repulsions within the dimer. Another driving force such as disproportionation should then be invoked:

$$2[(bpy)Mn^{III}(OH)_2(H_2O)_2]^{+} + [(bpy)Mn^{III}(H_2O)_4]^{3+} \rightarrow [(H_2O)_2(bpy)Mn^{III}O_2Mn^{IV}(bpy)(H_2O)_2]^{3+} + [Mn^{II}(H_2O)_6]^{2+} + bpy$$

Now we have $\Delta H = -161$ kJ mol^{-1}, showing clearly the importance of the disproportionation process to get di-μ-oxo dimers in solution. In fact, a tripositive mixed-valence Mn^{III}−Mn^{IV} dimer has been isolated in the solid-state, but with each manganese atom coordinated to two bipyridyl ligands. Looking at the previous reaction this means that the free bpy molecule should react with the freshly formed dimer according to:

$$[(H_2O)_2(bpy)Mn^{III}O_2Mn^{IV}(bpy)(H_2O)_2]^{3+} + 2bpy \rightarrow [(bpy)_2Mn^{III}O_2Mn^{IV}(bpy)_2]^{3+} + 4H_2O$$

Table 8 leads for such a substitution $\Delta H = -121$ kJ mol^{-1}, a rather favorable value. Finally, we have to check the stability of this dimer against dissociation:

$$[(bpy)_2Mn^{III}O_2Mn^{IV}(bpy)_2]^{3+} + 2H_2O \rightarrow [(bpy)_2Mn^{III}(OH)_2]^{+} + [(bpy)_2Mn^{IV}(OH)_2]^{2+}$$

With $\Delta H = -617$ kJ mol^{-1}, the dimer should dissociate. However, owing to the ionic hydration energies of the reactants and the products about +1600 kJ mol^{-1} are lost in this dissociation, rendering it thermodynamically unfavorable.

Under acidic conditions the disproportionation of Mn^{III} into Mn^{IV} species should be complete, and one may wonder about the formation of Mn^{IV} dimers according to

$$2[(bpy)Mn^{IV}(OH)_2(H_2O)_2]^{2+} \rightarrow [(bpy)(H_2O)_2Mn^{IV}O_2Mn^{IV}(bpy)(H_2O)_2]^{4+} + 2H_2O$$

Again with $\Delta H = +326$ kJ mol^{-1}, formation of a di-μ-oxo dimer is not intrinsically favorable and must be assisted by hydration $\Delta(\Delta H_{hydr}) \sim -3200$ kJ mol^{-1}. However, no di-μ-oxo Mn^{IV} dimers have been isolated in this work. Instead tetrapositive tricyclic Mn^{IV} trimers have been characterized. These trimers could be obtained through condensation of two trihydroxo-monobipyridyl cations with one dihydroxo-dibipyridyl cation:

$$2[(bpy)Mn^{IV}(OH)_3(H_2O)]^{+} + [(bpy)_2Mn^{IV}(OH)_2]^{2+} \rightarrow [Mn^{IV}{}_3O_4(bpy)_4(H_2O)_2]^{4+} + 4H_2O$$

The energy change for this reaction is evaluated as $\Delta H = -951$

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[32] Frapart, Y. Ph.D. Thesis, Université de Paris−Sud, 1996.

kJ mol^{-1}, rendering the trimer intrinsically much more stable than a mixture of the monomers. As hydration energies contribute to about −2300 kJ mol^{-1} to this reaction, formation of this trimer is energetically very favorable and could explain why a more unstable di-μ-oxo dimer has never been observed.

A tetrapositive Mn^{IV} chainlike tetramer has also been characterized in the solid-state. It could be formed from two tetra-hydroxo-mono-bipyridyl cations and two dihydroxo-dibipyridyl cations:

$$2(bpy)Mn^{IV}(OH)_4 + 2[(bpy)_2Mn^{IV}(OH)_2]^{2+} \rightarrow [Mn^{IV}{}_4O_6(bpy)_6]^{4+} + 6H_2O$$

With an energy change evaluated as $\Delta H = +2688$ kJ mol^{-1}, the formation of this chainlike tetramer from a mixture of monomers appears to be very unlikely. The driving force should then lie in the difference in hydration between a tetrapositive and two dipositive complexes estimated as −3200 kJ mol^{-1}. This intrinsic instability of a chainlike tetramer could explain the difference in behavior experimentally observed with two closely related molecules such as bipyridine (bpy) and phenanthroline (phen). With bipyridine, both tricyclic and chainlike structures are observed, whereas with phenanthroline, only the tri-cyclic trimer has been characterized. As shown above, formation of the chainlike tetramer has been attributed to a better hydration of the product relative to the reactants. Phenanthroline having two more carbon atoms than bipyridine should be the most hydrophobic ligand. Hydration energies of bipyridine complexes should then be more negative than those of phenanthroline. It is thus not surprising that the chainlike tetramer is not formed with phenanthroline ligands owing its lower hydration energy.

Conclusion

The main feature which has motivated this study was the rather surprising difference in reactivity between the mononuclear complexes $Mn^{III}(bpy)Cl_3(H_2O)$ and $Mn^{III}(phen)Cl_3(H_2O)$ in aqueous solutions. With bipyridine, three kind of Mn−oxo complexes have been isolated as single-crystals: a cyclic mixed valence dimer $[(bpy)_2Mn^{III}O_2Mn^{IV}(bpy)_2]^{3+}$, a tricyclic Mn^{IV} trimer $[Mn^{IV}{}_3O_4(bpy)_4(H_2O)_2]^{4+}$ and a chainlike Mn^{IV} tetramer $[Mn^{IV}{}_4O_6(bpy)_6]^{4+}$ whereas with phenanthroline only the cyclic dimer and the tri-cyclic trimer are observed. Single-crystals of $Mn^{III}(bpy)Cl_3(H_2O)$ have been grown which allowed us to get the structure of this mononuclear starting unit. We used then partial charge models to explain our experimental observations. Without taking explicitly into account the molecular potential (SIPCM approach), the following conclusions have been reached:

(i) The $Mn^{III}(bpy)Cl_3(H_2O)$ complex hydrolyses in water leading to $Mn^{III}(bpy)(OH)_3(H_2O)$ and HCl species. After ionic dissociation of HCl molecules and protonation of the hydroxo Mn^{III} complex, the stable form at pH ∼ 1.4 is the tetraaquo complex $[Mn^{III}(bpy)(H_2O)_4]^{3+}$.

(ii) Disproportionation of the aquo complex leads to the following species $[(bpy)Mn^{IV}(H_2O)_2(OH)_2]^{2+}$, $[(bpy)Mn^{IV}(H_2O)_3(OH)]^{3+}$, $[Mn^{II}(H_2O)_6]^{2+}$, and $[(bpy)_2Mn^{IV}(H_2O)_2]^{4+}$.

(iii) The dihydroxo and the monohydroxo complexes are able to condense through oxolation and olation, respectively. The best match in mean electronegativity with the solvent is obtained for the di-μ-oxo cyclic dimer $[(bpy)(H_2O)_2Mn^{IV}O_2Mn^{IV}(H_2O)_2(bpy)]^{4+}$. Further hydrolysis and condensation with monomeric $[(bpy)_2Mn^{IV}(H_2O)_2]^{4+}$, lead to the tricyclic trimer and chainlike tetramer.

(iv) Raising the pH allows the free bpy molecules formed after disproportionation to bind the Mn^{III} species rather than to Mn^{IV} species which are more inert toward substitution reactions. Further hydrolysis and condensation between $[(bpy)_2Mn^{III}(H_2O)_2]^{3+}$ and $[(bpy)_2Mn^{IV}(H_2O)_2]^{4+}$ complexes then lead to the cyclic mixed-valence dimer.

The broad features of this system can thus be explained by the SIPCM approach. However, this model tells us nothing about possible disproportionation pathways under acidic conditions, neither why the chainlike tetramer is not observed with phenanthroline. Taking explicitly into account the molecular potential (SDPCM approach) has allowed us to compare the various complexes on an energetic basis and discriminate between intrinsically stables structures and structures stabilization brought through hydration of the charged complexes. A deeper insight in our system is then reached:

(i) Substitution of chloro by hydroxo ligands is not thermodynamically favorable. It however occurs owing to the strong ionic hydration energies of H^+ and Cl^- species which provide the necessary driving force. The most stable hydroxo complex appears to be $[(bpy)Mn^{III}(OH)_2(H_2O)_2]^+$.

(ii) Direct electron transfer between two $[(bpy)Mn^{III}(H_2O)_4]^{3+}$ cations is either assisted by the solvent, or associated with the transfer of a bpy ligand from Mn^{II} toward Mn^{IV}. Additional Mn^{IV} and Mn^{III} species are thus obtained, the most stables being $(bpy)Mn^{IV}(OH)_4$, $[(bpy)_2Mn^{IV}O(OH)]^+$, and $[(bpy)_2Mn^{III}(OH)_2]^+$.

(iii) Oxolation is thermodynamically more favorable than olation. Among the Mn oxo-complexes observed in the solid-state, only $[(bpy)(H_2O)Mn^{III}O(AcO)_2Mn^{III}(H_2O)(bpy)]^{2+}$ and $[Mn^{IV}{}_3O_4(bpy)_4(H_2O)_2]^{4+}$ are intrinsically stables relative to a mixture of monomers. Formation of $Mn^{III}-Mn^{III}$ di-μ-oxo dimers is not thermodynamically favorable versus to that of $Mn^{III}-Mn^{IV}$ di-μ-oxo dimers whose stability is ruled by interaction with the solvent.

(iv) Finally chainlike tetramers are highly unstable structures. Their formation should then be assisted by the solvent. With bipyridine, the balance between hydration and internal forces is in favor of hydration and the tetramer is observed. This is probably not the case with the more hydrophobic ligand phenanthroline and just the cyclic dimer and tricyclic trimer are observed.

Our calculations also clearly show that substitution of an oxo bridge by two carboxylato bridges is a strongly stabilizing factor (∼ −2600 kJ mol^{-1}). It is thus not surprising to find that such a μ-oxo-di-μ-carboxylato bridge has been invoked in the OEC to explain EXAFS data.[33] Formation in aqueous solution of a chainlike $[MnO_2MnO(RCO_2)_2MnO_2Mn]$ core then remains the challenge for the quest of Mn-oxo tetramers which would mimic the OEC.

Supporting Information Available: Listings of complete atomic coordinates and anisotropic displacement parameters, bond distances, and angles for $Mn(bpy)Cl_3(H_2O)$ (3 pages). Ordering information is given on any current masthead page.

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