

# NMR Study of Ligand Exchange and Electron Self-Exchange between Oxo-Centered Trinuclear Clusters $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CR})_6(4\text{-R}'\text{py})_3]^{+/0}$

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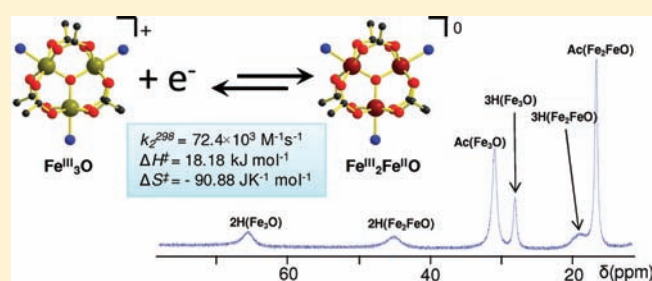
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**S** Supporting Information

**ABSTRACT:** The syntheses, single crystal X-ray structures, and magnetic properties of the homometallic  $\mu_3$ -oxo trinuclear clusters  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3](\text{ClO}_4)$  (**1**) and  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CAD})_6(4\text{-Mepy})_3](\text{NO}_3)$  (**2**) are reported (Ad = adamantane). The persistence of the trinuclear structure within **1** and **2** in  $\text{CD}_2\text{Cl}_2$  and  $\text{C}_2\text{D}_2\text{Cl}_4$  solutions in the temperature range 190–390 K is demonstrated by  $^1\text{H}$  NMR. An equilibrium between the mixed pyridine clusters  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CAD})_6(4\text{-Mepy})_{3-x}(4\text{-Phpy})_x](\text{NO}_3)$  ( $x = 0, 1, 2, 3$ ) with a close to statistical distribution of these species is observed in  $\text{CD}_2\text{Cl}_2$  solutions. Variable-temperature NMR line-broadening made it possible to quantify the coordinated/free 4-Rpy exchanges at the iron centers of **1** and **2**:  $k_{\text{ex}}^{298} = 6.5 \pm 1.3 \times 10^{-1} \text{ s}^{-1}$ ,  $\Delta H^\ddagger = 89.47 \pm 2 \text{ kJ mol}^{-1}$ , and  $\Delta S^\ddagger = +51.8 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$  for **1** and  $k_{\text{ex}}^{298} = 3.4 \pm 0.5 \times 10^{-1} \text{ s}^{-1}$ ,  $\Delta H^\ddagger = 91.13 \pm 2 \text{ kJ mol}^{-1}$ , and  $\Delta S^\ddagger = +51.9 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$  for **2**. A limiting D mechanism is assigned for these ligand exchange reactions on the basis of first-order rate laws and positive and large entropies of activation. The exchange rates are 4 orders of magnitude slower than those observed for the ligand exchange on the reduced heterovalent cluster  $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3]$  (**3**). In **3**, the intramolecular  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  electron exchange is too fast to be observed. At low temperatures, the 1/3 intermolecular second-order electron self-exchange reaction is faster than the 4-Phpy ligand exchange reactions on these two clusters, suggesting an outer-sphere mechanism:  $k_2^{298} = 72.4 \pm 1.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ,  $\Delta H^\ddagger = 18.18 \pm 0.3 \text{ kJ mol}^{-1}$ , and  $\Delta S^\ddagger = -90.88 \pm 1.0 \text{ J K}^{-1} \text{ mol}^{-1}$ . The  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3]^{+/0}$  electron self-exchange reaction is compared with the more than 3 orders of magnitude faster  $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(\text{py})_3]^{+/0}$  self-exchange reaction ( $\Delta\Delta G_{\text{exptl}}^{+298} = 18.2 \text{ kJ mol}^{-1}$ ). The theoretical estimated self-exchange rate constants for both processes compare reasonably well with the experimental values. The equilibrium constant for the formation of the precursor to the electron-transfer and the free energy of activation contribution for the solvent reorganization to reach the electron transfer step are taken to be the same for both redox couples. The larger  $\Delta G_{\text{exptl}}^{+298}$  for the 1/3 iron self-exchange is attributed to the larger ( $11.1 \text{ kJ mol}^{-1}$ ) inner-sphere reorganization energy of the **1** and **3** iron clusters in addition to a supplementary energy ( $6.1 \text{ kJ mol}^{-1}$ ) which arises as a result of the fact that each encounter is not electron-transfer spin-allowed for the iron redox couple.



## 1. INTRODUCTION

Ligand substitution and electron transfer reactions are two of the most widely investigated processes in coordination chemistry.<sup>1–5</sup> Most of these investigations are focused on mononuclear compounds, and comparatively little work is available for coordination clusters.<sup>6</sup> The behavior and properties of such coordination clusters is affected by the number and nature of constituent metal ions that can be regarded as their reaction centers. Due to multiple bridges holding coordination clusters together, modifications within the coordination polyhedra of the metal ions in the transition states are limited. This has consequences in terms of the reactivity of the metal centers and on the mechanism of ligand substitution reactions. For

paramagnetic clusters, the presence of magnetic interactions leads to the presence of different spin states which are populated as a function of the temperature and of the values of the spin–spin interactions.<sup>7</sup> This affects electron delocalization and electron/nuclear relaxation processes and can therefore influence the chemical reactivity at paramagnetic centers. The understanding of these phenomena is fundamental to developing new methods for coordination cluster synthesis which, in turn, is crucial to creating new magnetic materials, such as single molecule magnets (SMMs).<sup>8,9</sup>

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**Table 1.** Crystallographic Data for  $[\text{Fe}_3\text{O}(\mu\text{-O}_2\text{CCH}_3)_6\text{-}(4\text{-Phpy})_3](\text{ClO}_4) \cdot 2\text{MeOH} \cdot 2.5\text{H}_2\text{O}$  (**1**) and  $[\text{Fe}_3\text{O}(\mu\text{-O}_2\text{CAd})_6(4\text{-Mepy})_3](\text{NO}_3) \cdot 3.5\text{Stol}$  (**2**)

compound	1	2
chemical formula	$\text{C}_{47}\text{H}_{58}\text{ClFe}_3\text{N}_3\text{O}_{21.5}$	$\text{C}_{108.5}\text{H}_{139}\text{Fe}_3\text{N}_4\text{O}_{16}$
fw	1211.96	1922.79
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
<i>a</i>	7.6728(10)	12.8294(4)
<i>b</i> (Å)	13.847(2)	15.2913(4)
<i>c</i> (Å)	21.316(3)	27.2934(8)
$\alpha$ (deg)	90.535(12)	100.128(1)
$\beta$ (deg)	92.815(11)	92.063(1)
$\gamma$ (deg)	102.893(12)	109.350(1)
<i>V</i> (Å <sup>3</sup> )	2721.6(7)	4947.5(2)
<i>Z</i>	2	2
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.470	1.291
<i>F</i> (000)	1256	2048
$\mu$ (mm <sup>-1</sup> )	0.917	0.501
<i>T</i> (K)	150(2)	100(2)
$\lambda$ (Å)	0.71073	0.71073
measured reflns	16169	34427
unique reflns	10066	21413
unique reflns with [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	6641	16741
params	1245	675
<i>R</i> <sup>a</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0732	0.0671
<i>wR</i> <sup>a</sup> (all data)	0.2287	0.1386
<i>S</i> (all data) <sup>b</sup>	1.021	1.024
largest difference peak/hole (e/Å <sup>3</sup> )	+0.99/−0.39	+0.55/−1.49

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ .  
<sup>b</sup>  $\text{GoF} = \{ \sum [w(F_o^2 - F_c^2)^2] / 21 \}^{1/2}$ .

The reactivity of clusters is not limited to ligand exchange, formation and fragmentation reactions of coordination clusters, and intramolecular and intermolecular electron exchange processes are also of potential significance. In this regard, major progress has been made in the understanding of electron self-exchange reactions between oxo-centered ruthenium clusters of the type  $[\text{Ru}_3\text{O}(\text{O}_2\text{CCH}_3)_6\text{L}_3]$ .<sup>10–12</sup> This family of clusters is characterized by slow pyridine type L ligand exchange and extremely fast electron self-exchange reactions, as demonstrated by infrared spectroscopy.<sup>13,14</sup> The analogous family of iron clusters is characterized by faster ligand exchange and slower electron self-exchange reactions, which are both readily accessible for study using NMR spectroscopy.<sup>15–17</sup> In a recent study, the mechanisms of pyridine-type ligand exchange on mixed valence oxo-centered iron clusters  $[\text{Fe}^{\text{III}}_2\text{M}^{\text{II}}(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6\text{-}(4\text{-Rpy})_3]$  (*M* = Mn, Fe, Co, Ni) have been reported.<sup>17</sup> The goal of the present study is to extend the ligand exchange study to the oxidized iron complexes  $[\text{Fe}^{\text{III}}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CR}')_6\text{-}(4\text{-Phpy})_3]^+$  (*R'* = CH<sub>3</sub>, adamantane), followed by the study of the electron self-exchange reaction of the  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6\text{-}(4\text{-Phpy})_3]^{\pm/0}$  redox couple. In order to be able to give a detailed description of the self-exchange reaction, the X-ray data of the reactants as well as their magnetic susceptibility data were also investigated.

## 2. EXPERIMENTAL SECTION

**2.1. Syntheses.** All chemicals and solvents were purchased from Aldrich and used without further purification. The trinuclear complexes  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(\text{OH}_2)_3](\text{ClO}_4)$ ,  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CAd})_6\text{-}(\text{OH}_2)_3](\text{NO}_3)$ , and  $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3] \cdot 0.35$  4-Phpy  $\cdot$  3.3 MeCN (**3**) were prepared as previously reported (Ad = adamantane).<sup>17–19</sup> All manipulations of **3** were made in a glovebox under a N<sub>2</sub> atmosphere.

$[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3](\text{ClO}_4) \cdot 0.5\text{CH}_3\text{CN} \cdot 0.25(4\text{-Phpy})$  (**1**). A solution of 4-phenylpyridine (0.6 g, 4 mmol) in 20 mL of acetonitrile was added to a suspension of  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6\text{-}(\text{OH}_2)_3](\text{ClO}_4)$  (0.2 g, 0.29 mmol) in 5 mL of acetonitrile. The mixture was heated to 50 °C with stirring for 15–20 min; after cooling, compound **1** was obtained in 0.18 g (55%) yield. Calcd (Found; %) for  $\text{C}_{48.75}\text{H}_{48.3}\text{N}_{3.7}\text{O}_{17}\text{Fe}_3\text{Cl}$ : C, 50.38 (50.4); H, 4.23 (4.24); N, 4.52 (4.41).

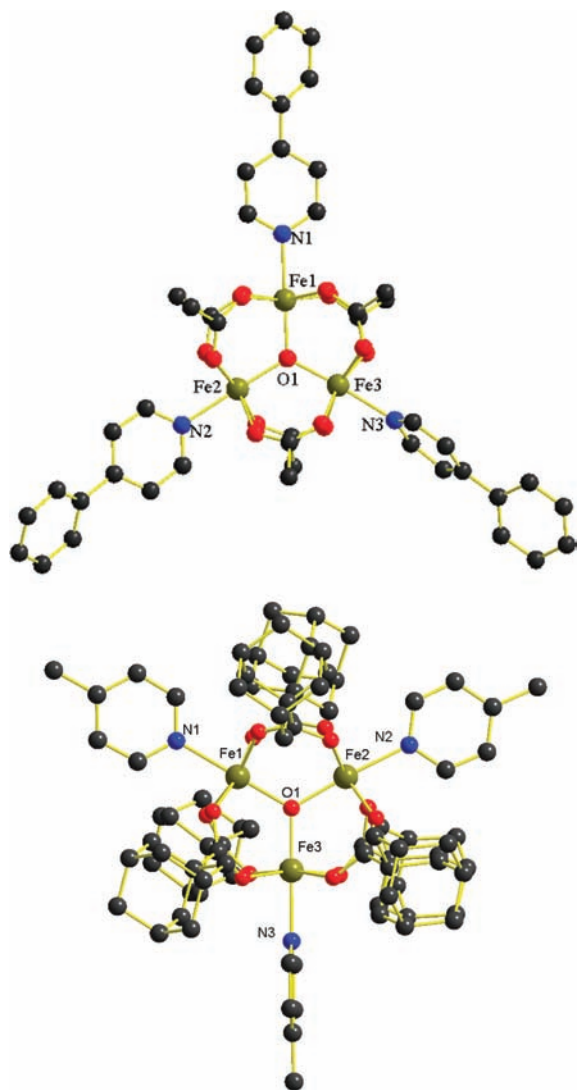
$[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CAd})_6(4\text{-Mepy})_3](\text{NO}_3) \cdot 0.5\text{MeCN} \cdot \text{H}_2\text{O}$  (**2**). A solution of 4-methylpyridine (0.3 g, 3.2 mmol) in 20 mL of acetonitrile was added to a suspension of  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CAd})_6(\text{OH}_2)_3](\text{NO}_3)$  (0.2 g, 0.15 mmol) in 5 mL of acetonitrile. The mixture was heated to 50 °C with stirring for 15–20 min; after cooling, compound **2** was obtained in 0.14 g (45%) yield. Calcd (Found; %) for  $\text{C}_{85}\text{H}_{114.5}\text{N}_{4.5}\text{O}_{17}\text{Fe}_3$  (**2**): C, 62.29 (62.2); H, 7.04 (6.91); N, 3.85 (3.83).

Compounds **1** and **2** are obtained analytically pure, but crystals suitable for X-ray measurements were obtained by recrystallization from MeOH and toluene, respectively. This explains the differences in the analytical compositions of the prepared (see above) and recrystallized compounds (Table 1).

**2.1. X-Ray Crystal Measurements.** Data were collected at 150 K on a Stoe IPDS II diffractometer for **1** at 100 K and on a Bruker SMART Apex CCD diffractometer for **2** using graphite-monochromated Mo *K* $\alpha$  radiation (Table 1). Structure solution by direct methods and full-matrix least-squares refinement against *F*<sup>2</sup> (all data) were carried out using the SHELXTL package.<sup>20</sup> All ordered non-H atoms were refined anisotropically; organic H atoms were placed in calculated positions. In the structure of **2**, the nitrate counterion was disordered over two sites; the two half-occupancy nitrates could be refined anisotropically with geometric similarity restraints and rigid-bond restraints on the temperature factors. The perchlorate ion in **1** was also disordered over two sites, with concomitant disorder of lattice water and methanol molecules; the half-occupancy chlorine atoms were refined anisotropically, with the half-occupancy oxygens and carbons isotropic. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 831029 and 831030. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK: <http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi>, e-mail: [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or fax: +44 1223 336033.

**2.3. Magnetic Measurements.** Magnetic susceptibility data (2–300 K) were collected on powdered polycrystalline samples on a Quantum Design MPMS-XL SQUID magnetometer under an applied magnetic field of 0.1 T. Magnetization isotherms were collected at 2 K between 0 and 5 T. All data were corrected for the contribution of the sample holder and the diamagnetism of the samples estimated from Pascal's constants.<sup>21,22</sup> The analysis of the magnetic data was carried out by the simultaneous fitting of the thermal dependences of  $\chi T$  and  $\chi$ , including impurity contribution and intermolecular interaction (*z*'<sup>2</sup>) according to eq 1.<sup>7</sup>

$$\chi(T) = \frac{\chi_t(T)}{\left[ 1 - \frac{2z'J\chi_t(T)}{Ng^2\beta^2} \right]} (1 - \rho) + \rho \frac{Ng^2\beta^2}{3kT} S(S + 1) \quad (1)$$



**Figure 1.** Molecular structures of the trinuclear cations in  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3](\text{ClO}_4)$  (**1**, above) and  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CAd})_6(4\text{-Mepy})_3](\text{NO}_3)$  (**2**, below). H atoms omitted for clarity.

The magnetic susceptibilities of the trinuclear clusters  $\chi(T)$  were calculated taking into account the energy levels associated with the spin Hamiltonians given in the Results section (Tables S2–S5, Supporting Information). The fitting procedure was carried out with an adapted version of *Visualizeur-Optimiseur* for Matlab<sup>23,24</sup> using a Levenberg–Marquardt nonlinear least-squares algorithm.

**2.4. NMR Measurements.** For <sup>1</sup>H NMR experiments, all samples were prepared under a N<sub>2</sub> atmosphere by weighing the clusters in 5 mm NMR tubes and adding 0.50 mL of solvent. The chemical shifts were referred to TMS using the residual signals from the solvent CD<sub>2</sub>Cl<sub>2</sub> (5.32 ppm) or C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> (5.98 ppm). The concentrations of the complexes were about 10 mM, and we used an excess of 4-Rpy to follow the ligand exchange process and to avoid a possible dissociation of the cluster coordinated ligand. The NMR spectra were recorded at 400 MHz on a Bruker DRX-400 spectrometer. Typical spectral conditions were 8000 data points for the time domain, the spectrum window typically set to 80 ppm, and the number of scans chosen between 32 and 512. The temperature was controlled within ±0.1 K using a Bruker BVT 3000 unit and was measured before or after spectral acquisition using a substitution method.<sup>25</sup>

**2.5. NMR Data Analyses.** Line widths and integrals of NMR signals were obtained by fitting Lorentzian functions to the experimental spectra using the “*NMRICMA 3.0*”<sup>26</sup> program for MATLAB. The adjustable parameters are the resonance frequency, intensity, line width, baseline, and phasing. Data analyses were carried out with the nonlinear least-squares fitting program *VISUALISEUR-OPTIMISEUR*<sup>24</sup> for MATLAB, using the Levenberg–Marquardt algorithm.

### 3. RESULTS

**3.1. Crystal Structures of 1 and 2.** The structures of the cationic trinuclear Fe<sup>III</sup><sub>3</sub>O complexes **1** and **2** are shown in Figure 1; both structures are of the familiar triangular oxo-centered “3d-basic carboxylate”-type characteristic of many trivalent 3d metal ions (Cr, V, Fe, Mn, Co).<sup>27</sup> Each of the crystallographically equivalent Fe<sup>III</sup> atoms has a distorted octahedral NO<sub>5</sub> coordination geometry. The bond distances and angles in the coordination sphere (Table 2) are typical for this class of compounds.<sup>27–33</sup> In both compounds, the μ<sub>3</sub>-oxo ligand lies in the center of the quasi-equilateral triangle of Fe<sup>III</sup> ions. In **1**, the Fe–Fe distances are 3.3114(12), 3.3095(13), and 3.3051(12) Å, while in **2** the corresponding distances are 3.2867(1), 3.3153(19), and 3.3019(1) Å. Similarly, in **1**, the three Fe–O(1) distances are 1.886(4), 1.922(5), and 1.923(4) Å, while in **2** they are 1.8962(15), 1.9105(15), and 1.9114(15) Å, and the Fe–O–Fe angles in both compounds are in the range 118.9(2)–120.7(2)°. The Fe–N distances in **1**, 2.177(5), 2.182(6), and 2.199(5) Å, are on average slightly shorter than those in **2**, 2.162(2), 2.159(2), and 2.170(2) Å, presumably reflecting the electronic differences in the *para* substituents of the pyridine ligands. The six carboxylates adopt *syn-syn* ( $\eta_1, \eta_1, \mu_2$ ) bridging modes. There is no significant difference between the Fe–O(carboxylate) distances in the two compounds: 1.999(4)–2.032(5) Å and 1.996(2)–2.043(2) Å in **1** and **2**, respectively. In both **1** and **2**, two pyridine rings are close to coplanar with the Fe<sub>3</sub> triangle, with the third approximately perpendicular to it. This orientation has been found to be not unusual for this type of cluster, with both pyridine orientations allowing overlap of the N p orbital with the Fe<sup>III</sup> 3d<sub>xy</sub> orbital.

The structure of the cationic “fully-oxidized” Fe<sup>III</sup><sub>3</sub>O cluster **1** can be compared with that of the corresponding mixed-valence Fe<sup>III</sup><sub>2</sub>Fe<sup>II</sup>O cluster **3**.<sup>17</sup> The differences are fairly typical for such pairs of complexes. In particular, in **1**, the three rather similar Fe–O(1) distances at *ca.* 1.97 Å are replaced in **3** by two shorter (both 1.844(1) Å) Fe<sup>III</sup>–O distances and one longer (2.021(2) Å) Fe<sup>II</sup>–O distance. However, in **3**, the Fe–N bond lengths show an opposite pattern: the two Fe<sup>III</sup>–N distances are both 2.228(3) Å, compared to the shorter Fe<sup>II</sup>–N distance of 2.212(2) Å, with the *trans* effect of the oxo-bridge dominating over the change in metal valence.

**3.2. NMR: Solution Structure and Mixed-Ligand Complexes.** The <sup>1</sup>H NMR signal assignments of  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3](\text{ClO}_4)$  (**1**) in the presence of an excess of 4-Phpy ligand in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 263 K are shown in Figure 2.

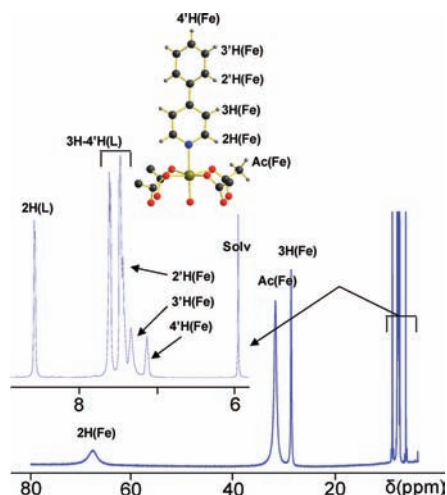
At this low temperature, the spectrum consists of six paramagnetically shifted signals for **1** and the signals for the free ligand. The assignments for **1** are based on the relative integrals (ratio of 6:2 for the acetate and the magnetically equivalent protons of coordinated 4-Phpy (2H or 3H)) and on the proximity to the paramagnetic center. The broad signal at 67.31 ppm was assigned to the two 2H(Fe) protons of the pyridine ring which are closest to the paramagnetic center.



**Table 2. Selected Structural Data: Bond Lengths [Å], Angles [°] and Plane Deviations [Å]**

compounds	T (K)	Fe <sup>III</sup> –N	Fe <sup>III</sup> –(μ <sub>3</sub> -O)	O–Fe <sup>III</sup> –O	Fe <sup>III</sup> –O <sub>4</sub> plane	(μ <sub>3</sub> O)–Fe <sub>3</sub> plane	ref
[Fe <sup>III</sup> <sub>2</sub> Fe <sup>II</sup> (μ <sub>3</sub> -O)(μ-O <sub>2</sub> CCH <sub>3</sub> ) <sub>6</sub> (4-Etpty) <sub>3</sub> ] <sup>a</sup>	163	2.230 (2.224)	1.856 (2.010)	166.5 (172.5)	0.23 (0.14)	0.000	34
[Fe <sup>III</sup> <sub>2</sub> Fe <sup>II</sup> (μ <sub>3</sub> -O)(μ-O <sub>2</sub> CCH <sub>3</sub> ) <sub>6</sub> (4-Phpy) <sub>3</sub> ] <sup>a</sup> (3)	140	2.228 (2.212)	1.844 (2.021)	164.3 (170.2)	0.26 (0.13)	0.02	17
[Fe <sup>III</sup> <sub>2</sub> Fe <sup>II</sup> (μ <sub>3</sub> -O)(μ-O <sub>2</sub> CC(CH <sub>3</sub> ) <sub>3</sub> ) <sub>6</sub> (py) <sub>3</sub> ] <sup>a</sup>	100	2.236 (2.199)	1.843 (2.040)	167.2 (175.0)	0.22 (0.09)	0.009	35
[Fe <sup>III</sup> <sub>3</sub> (μ <sub>3</sub> -O)(μ-O <sub>2</sub> CPh) <sub>6</sub> (py) <sub>3</sub> ] <sup>+</sup>	233	2.206	1.915	168.9	0.195	0.000	28
[Fe <sup>III</sup> <sub>3</sub> (μ <sub>3</sub> -O)(μ-O <sub>2</sub> CC(CH <sub>3</sub> ) <sub>3</sub> ) <sub>6</sub> (py) <sub>3</sub> ] <sup>+</sup>	295	2.186	1.905	169.3	0.171	0.009	33
[Fe <sup>III</sup> <sub>3</sub> (μ <sub>3</sub> -O)(μ-O <sub>2</sub> CCH <sub>3</sub> ) <sub>6</sub> (4-Phpy) <sub>3</sub> ] <sup>+</sup> (1)	150	2.186 <sup>b</sup>	1.910 <sup>b</sup>	168.9 <sup>b</sup>	0.193 <sup>b</sup>	0.001	<sup>c</sup>
[Fe <sup>III</sup> <sub>3</sub> (μ <sub>3</sub> -O)(μ-O <sub>2</sub> CAd) <sub>6</sub> (4-Mepy) <sub>3</sub> ] <sup>+</sup> (2)	100	2.164 <sup>b</sup>	1.906 <sup>b</sup>	170.4 <sup>b</sup>	0.166 <sup>b</sup>	0.008	<sup>c</sup>

<sup>a</sup> Values in parentheses are for Fe<sup>II</sup>. <sup>b</sup> Values correspond to average between crystallographic independent positions of atoms. <sup>c</sup> This work.

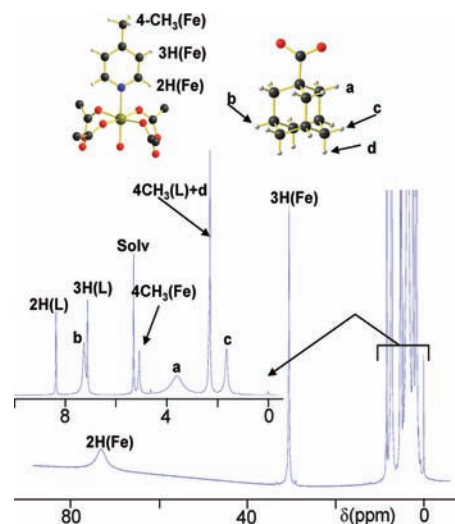


**Figure 2.** <sup>1</sup>H NMR spectrum of [Fe<sub>3</sub>(μ<sub>3</sub>-O)(μ-O<sub>2</sub>CCH<sub>3</sub>)<sub>6</sub>(4-Phpy)<sub>3</sub>·(ClO<sub>4</sub>) (1; 16 mM) with an excess of 4-Phpy (51.6 mM) at 263 K in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>.

The signals at 31.56 and 28.44 ppm, in a 6:2 ratio, were assigned to the acetate and 3H(Fe) of 4-Phpy protons, respectively. The signals at 7.17, 6.92, and 6.76 ppm correspond to the 2'H(Fe), 3'H(Fe), and 4'H(Fe) protons. The temperature dependence of the spectra is shown in Figure S1 (Supporting Information). The spectral behavior in CD<sub>2</sub>Cl<sub>2</sub> is similar to that observed in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>. The spectra confirm a solution structure of **1** with a C<sub>3</sub> axis of symmetry of the oxo-centered cluster, with six magnetically equivalent bridging acetates and three equivalent 4-Phpy coordinated ligands. The NMR spectra show also the signals of the free 4-Phpy ligand (2H(L), 3H-4'H(L))<sup>36</sup> and the residual <sup>1</sup>H signal of the deuterated solvent (5.91 ppm). The signal assignments are consistent with those of similar oxo-centered Fe<sup>III</sup> clusters.<sup>15,37</sup>

The spectrum of [Fe<sub>3</sub>(μ<sub>3</sub>-O)(μ-O<sub>2</sub>CAd)<sub>6</sub>(4-Mepy)<sub>3</sub>](NO<sub>3</sub>) (2) in CD<sub>2</sub>Cl<sub>2</sub> with an excess of 4-Mepy at 220 K is shown in Figure 3. The two equally populated signals at 73.11 and 30.52 ppm are assigned to the 2H and 3H protons of coordinated 4-Mepy.

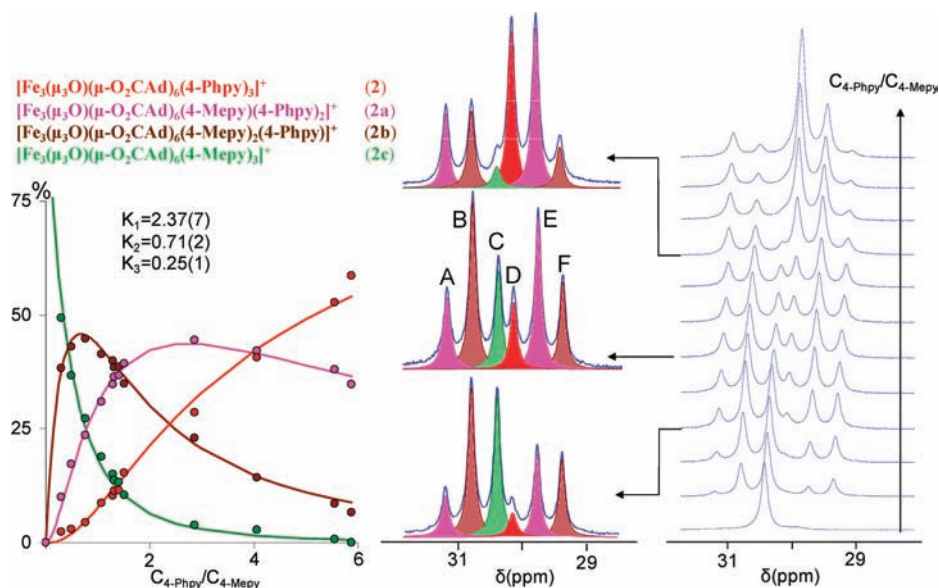
The signal at 5.09 ppm, with a population ratio of 3:2:2 with respect to the signals 2H(Fe) and 3H(Fe), has been assigned to the methyl group of coordinated 4-Mepy. The four signals a, b, c, and d (populations: 6:3:3:3) of the nonequivalent protons of the bridging adamantane-1-carboxylates are well separated due to favorable induced shifts and relaxation rates (see inset in Figure 3 and Figure S3, Supporting Information). The criteria for assignments of b, c, and d were the line widths which are dominated by



**Figure 3.** <sup>1</sup>H NMR spectrum of [Fe<sub>3</sub>(μ<sub>3</sub>-O)(μ-O<sub>2</sub>CAd)<sub>6</sub>(4-Mepy)<sub>3</sub>·(NO<sub>3</sub>) (2; 12.8 mM) with an excess of 4-Mepy (41.5 mM) at 220 K in CD<sub>2</sub>Cl<sub>2</sub>.

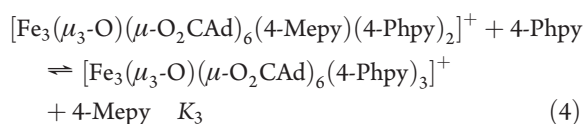
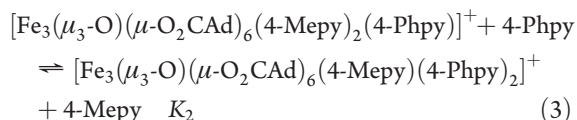
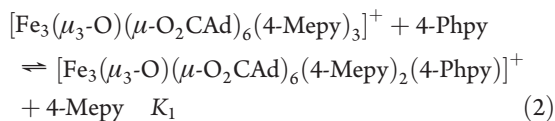
paramagnetic relaxation and are a function of the distance from the paramagnetic center. The signals of protons d and 4-CH<sub>3</sub>(L) of free 4-Mepy are superimposed (see Figure S3 for details). The spectra in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> are similar to those in CD<sub>2</sub>Cl<sub>2</sub> and correspond to six adamantane-1-carboxylates and three 4-Phpy's coordinated to the Fe<sub>3</sub>O central core (see also Figure S2, Supporting Information, for the temperature dependence). The NMR signal assignments for **1** and **2** are further confirmed by a similar evolution of relaxation times as a function of the temperature and the corresponding kinetic analyses (see kinetic section). The spectral assignments for [Fe<sup>III</sup><sub>2</sub>Fe<sup>II</sup>(μ<sub>3</sub>-O)(μ-O<sub>2</sub>CCH<sub>3</sub>)<sub>6</sub>(4-Phpy)<sub>3</sub>] (3) are reported in our previous work.<sup>17</sup>

In the temperature range of this study, the signals of the pyridine type ligands coordinated to the Fe<sup>III</sup><sub>3</sub> clusters **1** and **2** are well-separated from the signals of the free pyridine ligands. At low temperatures, the major contribution to the line-width is the paramagnetic relaxation due to the proximity of the Fe<sup>III</sup> ions, and at higher temperatures the ligand exchange contribution broadening dominates. At 293 K, the 3H pyridine signal line-width is narrow enough to probe, as an example, the stepwise substitution of 4-Mepy by 4-Phpy in **2**, to characterize the signals of the mixed clusters and to determine the equilibrium constants between the four clusters (Figure 4 and eqs 2–4). At 293 K, the ligand exchanges are slow on the NMR time scale, but the



**Figure 4.** Stepwise substitution of 4-Mepy by 4-Phpy in **2** (34.3 mM) followed by the successive addition of 4-Phpy (88.1 mM) in  $\text{CD}_2\text{Cl}_2$  at 293 K. Left: Percentage (%) of mixed ligand  $[\text{Fe}_3(\mu_3\text{O})(\mu\text{-O}_2\text{CAd})_6(4\text{-Mepy})_{3-x}(4\text{-Phpy})_x](\text{NO}_3)$  ( $x = 0, 1, 2, 3$ ) clusters versus the ratio  $C_{4\text{-Phpy}}/C_{4\text{-Mepy}}$  of free ligands; the solid lines are the best fit of the experimental data and  $K_i$  ( $i = 1, 2, 3$ ) represents the resulting equilibrium constants (see text). Middle: three selected deconvoluted  $^1\text{H}$  NMR spectra in the 3H py proton region of the coordinated 4-Mepy and 4-Phpy ligands. Right: experimental spectra (see Supporting Information for the integrals of the clusters signals: Table S1).

substitutions are fast compared to the mixing time of the cluster **2** solution and the stepwise addition of the 4-Phpy solution.



The homopyridine clusters **2** and **2c** show each a single 3H proton signal (C and D, respectively, in Figure 4) due to their  $C_3$  symmetry. The two mixed-pyridine clusters **2a** and **2b** show each two 3H proton signals with population ratios of 1:2 (A for 4-Phpy and E for 4-Mepy) and 2:1 (B for 4-Phpy and F for 4-Mepy), respectively. The assignments are based on the population ratios for **2a** and **2b**, and on the increase in the populations from **2** to **2c** with a stepwise increase of the  $C_{4\text{-Phpy}}/C_{4\text{-Mepy}}$  ratio of the concentrations of the free ligands.

The successive equilibrium constants  $K_1$ ,  $K_2$ , and  $K_3$  for the substitution reactions (eqs 2–4) were obtained from the integrals of the signals A–F (Table S1, Supporting Information) using eqs 5–8.

$$C_2 = 1/(1 + xK_1 + x^2K_1K_2 + x^3K_1K_2K_3) \quad (5)$$

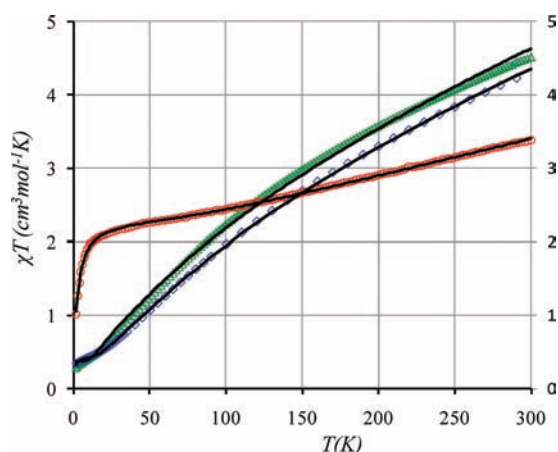
$$C_{2a} = xK_1/(1 + xK_1 + x^2K_1K_2 + x^3K_1K_2K_3) \quad (6)$$

$$C_{2b} = x^2K_1K_2/(1 + xK_1 + x^2K_1K_2 + x^3K_1K_2K_3) \quad (7)$$

$$C_{2c} = x^3K_1K_2K_3/(1 + xK_1 + x^2K_1K_2 + x^3K_1K_2K_3) \quad (8)$$

with  $x = C_{4\text{-Phpy}}/C_{4\text{-Mepy}}$  and  $C_2 + C_{2a} + C_{2b} + C_{2c} = 1$  were  $C_i$  is the mole fraction (in %) reported in Figure 4 as a function of  $C_{4\text{-Phpy}}/C_{4\text{-Mepy}}$ . The results of the simultaneous fitting of the four sets of mole fractions as a function of  $C_{4\text{-Phpy}}/C_{4\text{-Mepy}}$  with  $K_1$ ,  $K_2$ , and  $K_3$  as adjustable parameters are shown in Figure 4. The equilibrium constants decrease from  $K_1$  to  $K_3$  and the ratios  $K_2/K_1 = 0.30$  and  $K_3/K_2 = 0.35$  are close to 1/3, which indicates a statistical distribution of the two ligands between the mixed clusters in solution. Similar substitution reactions involving solvent molecules have been reported also on heterometallic ( $\text{Fe}_2\text{Co}$ ,<sup>17</sup>  $\text{Ru}_2\text{Zn}$ ,<sup>38</sup>  $\text{Ru}_2\text{Rh}$ ,<sup>39,41</sup>) and homometallic ( $\text{Ru}_3$ ,  $\text{Rh}_3$ <sup>39,42</sup>)  $\mu_3\text{-oxo}$  clusters.

**3.3. Solid State: Magnetic Susceptibility.** The results of magnetic susceptibility measurements on the polycrystalline clusters **1–3** are depicted in Figure 5. For  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3](\text{ClO}_4)$  (**1**), at room temperature, the  $\chi T$  product is  $4.51 \text{ cm}^3 \text{ K mol}^{-1}$ . This value is lower than the expected value ( $13.13 \text{ cm}^3 \text{ K mol}^{-1}$ ) for the presence of three  $\text{Fe}^{\text{III}}$  ions ( $^6\text{A}_{1g}$ ,  $S = 5/2$ ,  $g = 2$ ). Upon decreasing the temperature, the  $\chi T$  product at 0.1 T continuously decreases to reach  $0.29 \text{ cm}^3 \text{ K mol}^{-1}$  at 2 K, indicating antiferromagnetic interactions within the trinuclear complex. The evolution of the magnetic susceptibility of  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CAd})_6(4\text{-Mepy})_3](\text{NO}_3)$  (**2**) is similar to **1**. The value of  $\chi T$  for **2** (at 0.1 T) decreases with decreasing temperature from  $4.31 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at room temperature until  $0.34 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 2 K, which also suggests antiferromagnetic interactions. Due to the similarity in the molecular structures of **1** and **2** and identical  $\text{Fe}^{\text{III}}_3\text{O}$  paramagnetic centers, one expects similar magnetic exchange parameters and spectra of energy states distribution.



**Figure 5.** Magnetic susceptibility  $\chi T$  versus  $T$  plots data for compounds 1–3 (1,  $\Delta$ , green; 2,  $\diamond$ , blue; 3,  $\circ$ , red). The black solid lines correspond to the best fit according to the spin Hamiltonian (eq 10) with parameters indicated in Table S2 (Supporting Information).

For 3, at 300 K, the  $\chi T$  product is  $3.38 \text{ cm}^3 \text{ K mol}^{-1}$ , which is much lower than the expected value ( $11.75 \text{ cm}^3 \text{ K mol}^{-1}$ ) for the presence of two  $\text{Fe}^{\text{III}}$  ions ( $S = 5/2$ ) and one  $\text{Fe}^{\text{II}}$  ( $S = 2$ ) taking into account a  $g$  value of 2.0 (Figure 5). This indicates the presence of dominant antiferromagnetic interactions in this compound. The interpretation of the magnetic susceptibility data of the spin frustrated  $\text{Fe}^{\text{III}}_3\text{O}$  clusters 1 and 2 and of the mixed valence  $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}$  cluster 3 can be done using the general spin-Hamiltonian describing the isotropic exchange interactions in trinuclear clusters (eq 9).

$$H_t = -2J_a(S_1S_2 + S_2S_3) - 2J_bS_1S_3 \quad (9)$$

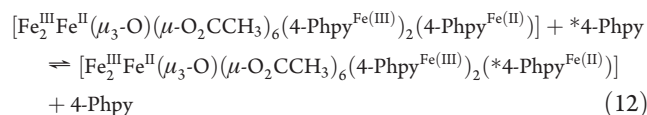
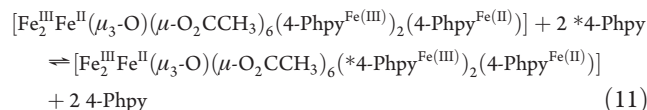
where  $J_a$  and  $J_b$  are exchange parameters (both  $\text{Fe}^{\text{III}}-\text{Fe}^{\text{III}}$  for 1 and 2 and  $\text{Fe}^{\text{II}}-\text{Fe}^{\text{III}}$  and  $\text{Fe}^{\text{III}}-\text{Fe}^{\text{III}}$  for 3) and  $S_i$  are the spin on the individual ions ( $S_1, S_2, \text{Fe}^{\text{III}}, S_3, \text{Fe}^{\text{III}}$  for 1 and 2 and  $\text{Fe}^{\text{II}}$  for 3). In the case of 1 and 2,  $S_1 = S_2 = S_3 = 5/2$ . And in the case of 3,  $S_1 = S_3 = 5/2$  and  $S_2 = 2$ . The eigenvalue of the spin-Hamiltonian (eq 10) was determined by using the Kambe vectors coupling method<sup>44</sup> with the following coupling schemes:  $S_{13} = S_1 + S_3$  and  $S_t = S_{13} + S_2$ .

$$E(S_t, S_{13}) = -J_a[S_t(S_t + 1) - S_{13}(S_{13} + 1)] - J_b[S_{13}(S_{13} + 1)] \quad (10)$$

Fits of the experimental data with the expression of the susceptibility based on the above spin Hamiltonian (for analytical equations, see ref 44 for 1 and 2 and ref 45 for 3) yielded one satisfactory set of parameters for compound 1 ( $J_a = -21.8(1) \text{ cm}^{-1}$ ,  $J_b = -31.9(4) \text{ cm}^{-1}$ ) and two sets of parameters for compound 2 ((a)  $J_a = -24.3(1) \text{ cm}^{-1}$ ,  $J_b = -30.6(2) \text{ cm}^{-1}$ ; (b)  $J_a = -28.6(7) \text{ cm}^{-1}$ ,  $J_b = -23.2(5) \text{ cm}^{-1}$ ) with  $g = 2$  (fix) (Supporting Information, Table S2). Obtaining two minima upon fitting of the magnetic susceptibility data of trinuclear clusters is not unusual.<sup>46–50</sup> The fit obtained with the set of parameters “a” is of superior quality and is shown in Figure 5. Energy level plots for fits of 1 and 2 reveal an  $S = 1/2$  ground state (Figures S4 and S5, Supporting Information). For the mixed valence cluster 3, a satisfactory fit was obtained for  $J_a = -22.2(2) \text{ cm}^{-1}$ ,  $J_b = -65.1(7) \text{ cm}^{-1}$ , and  $g = 2.014(7)$ . The ratio 3:1 of  $J_b/J_a$  for the mixed valence compound 3 is in good agreement with other reported ratios for the exchange coupling constants in

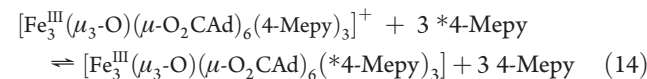
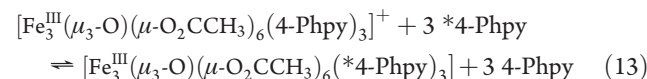
mixed-valent oxo-centered trinuclear iron complexes.<sup>51–53</sup> The energy diagrams indicate that two low-lying spin states  $S = 1$  and  $S = 2$ , with a gap of  $3 \text{ cm}^{-1}$ , are predominantly populated (Figure S6, Supporting Information).

**3.5. Ligand Exchange.** In a previous paper, the exchange reaction of the 4-Phpy ligand coordinated to the mixed-valence cluster  $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3]$  (3) and an excess of 4-Phpy could be followed in dichloromethane.<sup>17</sup> Because of the extremely fast intramolecular electron transfer on the NMR time scale, it was not possible to separate experimentally the intermolecular ligand exchange processes on the  $\text{Fe}^{\text{III}}$  (eq 11) and  $\text{Fe}^{\text{II}}$  (eq 12) centers from the fully coalesced 4-Phpy coordinated signal.



The observed intermolecular exchange process is slow on the NMR time scale with a line-broadening of the coordinated signal which is the sum of a paramagnetic broadening dominant at low temperatures and a kinetic broadening dominant at high temperatures. This exchange process was assigned to the 4-Phpy exchange on the two  $\text{Fe}^{\text{III}}$  centers (eq 11), with a slower exchange process at the single  $\text{Fe}^{\text{II}}$  center:  $k_{\text{ex}}^{\text{Fe}_2\text{Fe}^{\text{O}}} = 16.6 \pm 0.7 \times 10^3 \text{ s}^{-1}$ ,  $\Delta H^\ddagger = 60.32 \pm 1 \text{ kJ mol}^{-1}$ , and  $\Delta S^\ddagger = +34.8 \pm 4 \text{ J K}^{-1} \text{ mol}^{-1}$ .<sup>17</sup>

The intermolecular pyridine-type ligand exchanges on the fully oxidized  $\text{Fe}^{\text{III}}_3\text{O}$  clusters 1 (eq 13) and 2 (eq 14) are much slower than on the mixed-valence  $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}$  cluster.

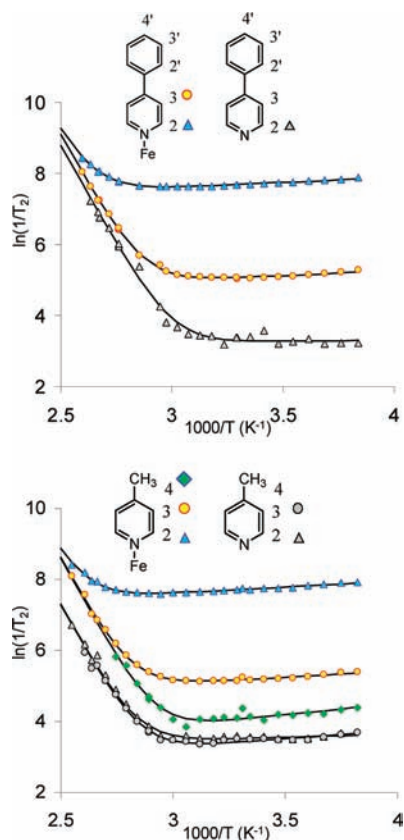


To have access to the kinetic exchange domain, the solvent  $\text{CD}_2\text{Cl}_2$  used for 3 was replaced by  $\text{C}_2\text{D}_2\text{Cl}_4$  (1,1,2,2-tetrachloroethane- $d_2$ ; MP =  $-43 \text{ }^\circ\text{C}$ ; BP =  $146 \text{ }^\circ\text{C}$ ) to study the 4-Phpy and 4-Mepy exchange on 1 and 2, respectively. The observed transverse relaxation rates of the coordinated protons  $1/T_2$  (2H, 3H, and  $\text{CH}_3$ , Figure 6) are the sum of the paramagnetic line-broadening  $1/T_{2m}$  and  $1/\tau_b$  (eq 15). The exchange rate constant  $k_{\text{ex}}$  of a particular ligand molecule is the inverse of the mean residence time  $\tau_b$  in the coordinated state. The transverse relaxation rates of the free ligand protons (2H and 3H, Figure 6) are given by eq 16, where  $P_b$  and  $P_f$  are the populations of the coordinated and free ligand, respectively. The temperature dependence of  $1/T_{2m}$ , which incorporates dipolar and contact contributions, is assumed to follow an Arrhenius behavior (eq 17). This term is much smaller for the free ligand. The temperature dependence of  $k_{\text{ex}}$  is described by the Eyring equation (eq 18).

$$1/T_{2b} = 1/T_{2m} + 1/\tau_b = 1/T_{2m} + k_{\text{ex}} \quad (15)$$

$$1/T_{2f} = 1/T_{2m} + 1/\tau_f = 1/T_{2m} + (P_b/P_f)k_{\text{ex}} \quad (16)$$



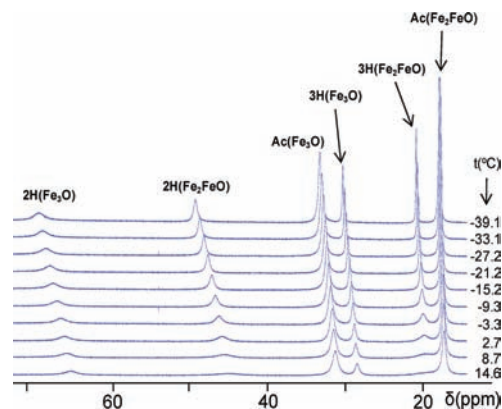


**Figure 6.**  $^1\text{H}$  transverse relaxation rates of the coordinated and free ligand in  $\text{C}_2\text{D}_2\text{Cl}_4$  solutions as a function of the temperature for  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3](\text{ClO}_4)$  (**1**; 16.0 mM and 51.6 mM excess ligand; top) and for  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CAD})_6(4\text{-Mepy})_3](\text{NO}_3)$  (**2**; 19.7 mM and 167.8 mM; bottom).

$$1/T_{2m} = 1/T_{2m}^{298} \exp[E_a/R(1/T - 1/298.15)] \quad (17)$$

$$\begin{aligned} k_{\text{ex}} &= k_B T/h \exp[\Delta S^\ddagger/R - \Delta H^\ddagger/RT] \\ &= k_{\text{ex}}^{298} T/298.15 \exp[-\Delta H^\ddagger/R(1/T - 1/298.15)] \end{aligned} \quad (18)$$

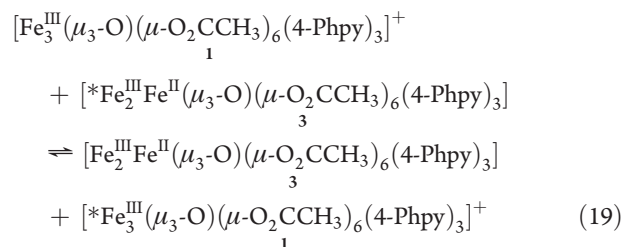
The results of the simultaneous fit of the transverse relaxation rates of each cluster are shown in Figure 6, and all experimental data (Table S6–S9) and fitted parameters (Table S10) are reported in the Supporting Information. The kinetic parameters are  $k_{\text{ex}}^{298} = 6.5 \pm 1.3 \times 10^{-1} \text{ s}^{-1}$ ,  $\Delta H^\ddagger = 89.47 \pm 2 \text{ kJ mol}^{-1}$ , and  $\Delta S^\ddagger = +51.8 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$  for **1** and  $k_{\text{ex}}^{298} = 3.4 \pm 0.5 \times 10^{-1} \text{ s}^{-1}$ ,  $\Delta H^\ddagger = 91.13 \pm 2 \text{ kJ mol}^{-1}$ , and  $\Delta S^\ddagger = +51.9 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$  for **2**. These ligand exchange rates for both  $\text{Fe}^{\text{III}}_3\text{O}$  clusters are more than 4 orders of magnitude slower than those observed for the ligand exchange on the  $\text{Fe}^{\text{III}}$  center of the  $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}$  cluster **3**. The rate law for the 4-Mepy exchange on cluster **2** was determined at 367 K (Figure S8 and Table S11 of the Supporting Information). At this high temperature, the kinetic contribution dominates the paramagnetic relaxation term, especially for the free ligand. The analysis of the transverse relaxation rates of the coordinated 2H( $\text{Fe}_3\text{O}$ ) and 3H( $\text{Fe}_3\text{O}$ ) and free 2H(L) ligand signals as a function of the increasing free ligand concentration shows, after subtraction of the paramagnetic relaxation term, a



**Figure 7.** Temperature dependence of  $^1\text{H}$  NMR spectra for  $[\text{Fe}^{\text{III}}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3](\text{ClO}_4)$  (0.0112 M),  $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3]$  (0.0118 M), and 4-Phpy (0.124 M) solution in  $\text{CD}_2\text{Cl}_2$ .

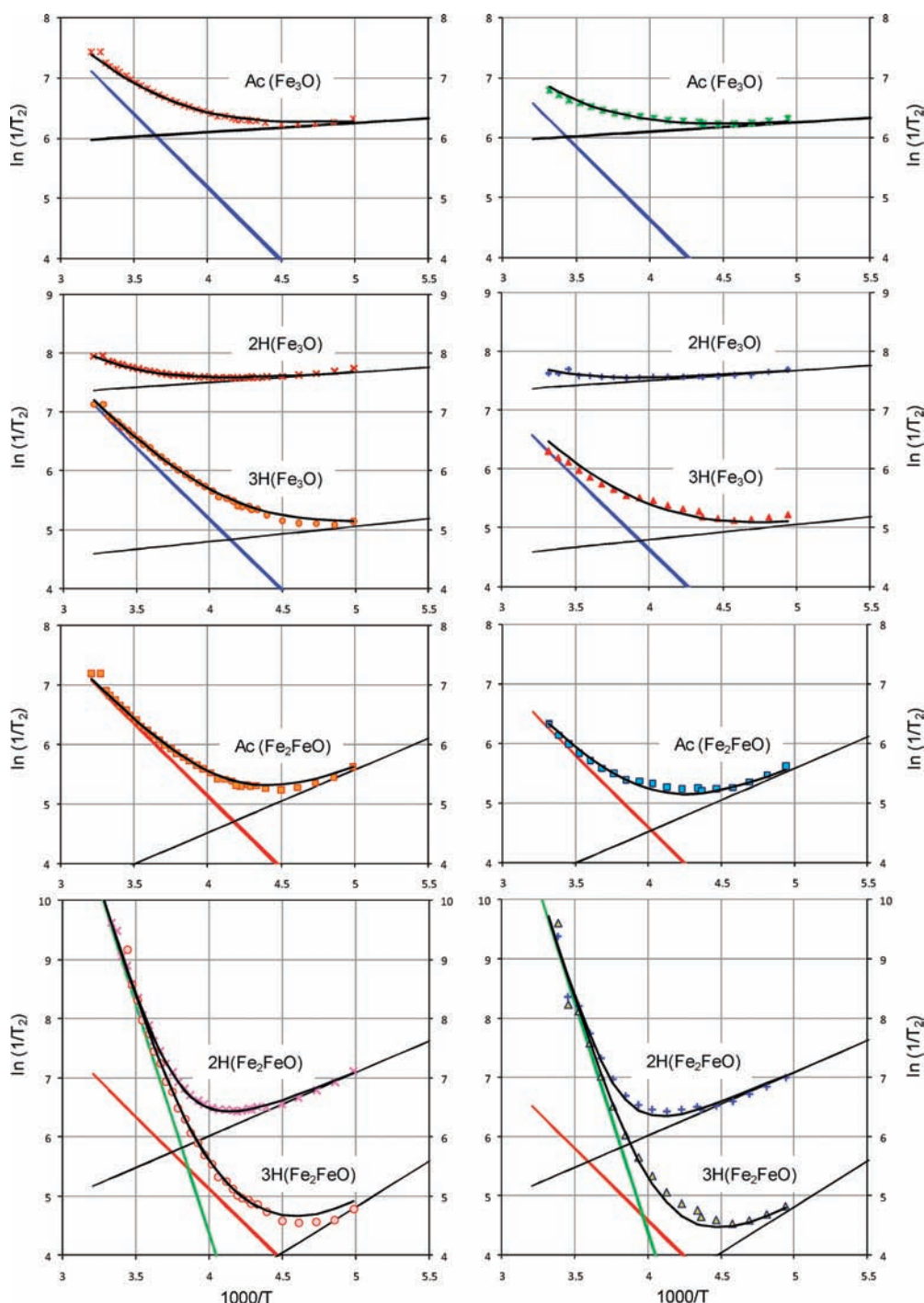
first-order rate law in cluster concentration for the exchange of the coordinated ligand:  $1/\tau_b = -[1]/([1]dt) = k_{\text{ex}}$  from the signals of the coordinated ligand signal (eq 15) and  $1/\tau_f = -[L]/([L]dt) = k_{\text{ex}}(P_b/P_f)$  from the signal of the free ligand (eq 16).

**3.6. Electron Self-Exchange.** NMR line-broadening has been used previously to study the electron transfer self-exchange reaction  $[\text{Fe}_3\text{O}(\mu\text{-O}_2\text{CCMe}_3)_6(\text{py})_3]^{+/0}$  at 296 K in dichloromethane.<sup>15</sup> Our variable-temperature studies of the ligand exchange on the  $\text{Fe}^{\text{III}}_3\text{O}$  cluster **1** and  $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}$  cluster **3** have been extended to the electron self-exchange reaction between these two species (eq 19). This is possible over a large temperature range, from 200 up to 312 K, thanks to the large chemical shifts and the nonoverlapping of the coordinated 2H and 3H signals of 4-Phpy and the  $\text{CH}_3$  acetate signals of both clusters (Figure 7).



Two variable-temperature experiments were performed, with different concentrations of **1** (0.0112 and 0.065 mM), **3** (0.0118 and 0.072 mM), and excess 4-Phpy (0.124 and 0.072 mM), in order to check the rate laws for the ligand exchange and the electron self-exchange reactions. The excess of free ligands also avoids a possible ligand dissociation at the highest temperatures.<sup>17</sup> At each temperature, the real and imaginary components of the  $^1\text{H}$  NMR spectra were simultaneously fitted with the chemical shifts, the transverse relaxation rates, the populations, the baseline, and the phase as adjustable parameters (Figures S9 and S10, Supporting Information). The transverse relaxation rates were corrected for the magnetic field inhomogeneity using the residual proton signal of the solvent  $\text{CD}_2\text{Cl}_2$ .

The transverse relaxation rates  $1/T_2^{\text{Fe}_3\text{O}}$  of the 2H and 3H( $\text{Fe}_3\text{O}$ ) (eq 20), and  $1/T_2^{\text{Fe}_2\text{FeO}}$  of the 2H and 3H( $\text{Fe}_2\text{FeO}$ ) protons (eq 21) are the sums of the ligand exchange, the electron self-exchange  $k_2$ , and the paramagnetic relaxation contributions.



**Figure 8.** Temperature dependence of the logarithm of the proton relaxation rates of the coordinated 4-Phpy ligand and of the acetate  $\text{CH}_3$  in a  $\text{CD}_2\text{Cl}_2$  solution of  $[\text{Fe}^{\text{III}}_3(\mu_3\text{-O})(\mu\text{-Ac})_6(4\text{-Phpy})_3](\text{ClO}_4)$  (left, 0.0112 M; right, 0.0065 M),  $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}(\mu_3\text{-O})(\mu\text{-Ac})_6(4\text{-Phpy})_3]$  (0.0118 M and 0.0068 M) with an excess of 4-Phpy (0.124 and 0.072 M). The bold curves (black) result from a simultaneous fit of all experimental data. The colored lines are the kinetic contributions to the relaxation rates: (blue)  $k_2[\text{Fe}_2\text{FeO}]$ , (red)  $k_2[\text{Fe}_3\text{O}]$ , (green)  $k_{\text{ex}}^{\text{Fe}_2\text{FeO}}$ . The thin black lines are the paramagnetic contributions.

The ligand exchange term is not relevant to describe the transverse relaxations rates of the  $\text{Ac}(\text{Fe}_3\text{O})$  and  $\text{Ac}(\text{Fe}_2\text{FeO})$  protons.

$$1/T_2^{\text{Fe}_3\text{O}} = k_{\text{ex}}^{\text{Fe}_3\text{O}} + k_2[\text{Fe}_2\text{FeO}] + 1/T_{2m} \quad (20)$$

$$1/T_2^{\text{Fe}_2\text{FeO}} = k_{\text{ex}}^{\text{Fe}_2\text{FeO}} + k_2[\text{Fe}_3\text{O}] + 1/T_{2m} \quad (21)$$

Furthermore, the  $k_{\text{ex}}^{\text{Fe}_3\text{O}}$  term can be neglected in the analysis of the 2H and 3H( $\text{Fe}_3\text{O}$ ) signals due to the slow ligand exchange

rate on **1** in the temperature range of this study. The temperature dependence of the contributions to  $1/T_2$  is given by eqs 17 and 18. All  $1/T_2$  experimental values (Table S13, S14, S16, and S17, Supporting Information), for the six protons of the dilute and concentrated solutions, over the whole temperature range, were fitted to eqs 21 and 22 (Figure 8). The detailed equations and the fixed and adjustable parameters are reported in Table S18 (Supporting Information). The resulting ligand exchange rate



**Table 3. Kinetic Parameters for Selected Ligand Exchange Reactions on Hexasolvates and on Trinuclear Oxo-Centered Metal Clusters of Di- and Trivalent Iron, Ruthenium, and Rhodium Cations**

compound	solv.	$k_{\text{ex}}^{298} \text{ s}^{-1}$	$\Delta H^\ddagger \text{ kJ mol}^{-1}$	$\Delta S^\ddagger \text{ J K}^{-1} \text{ mol}^{-1}$	$\Delta V^\ddagger \text{ cm}^3 \text{ mol}^{-1}$	mechanism	ref
$[\text{Ru}(\text{H}_2\text{O})_6]^{3+a}$	$\text{H}_2\text{O}$	$3.5 \times 10^{-6}$	89.8	-48.3	-8.3	$I_a$	56
$[\text{Ru}(\text{H}_2\text{O})_6]^{2+a}$	$\text{H}_2\text{O}$	$1.8 \times 10^{-2}$	87.8	+16.1	-0.4	$I_a$	56
$[\text{Ru}_3\text{O}(\mu\text{-O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^{+b}$	$\text{CD}_3\text{OD}$	$7.7 \times 10^{-4}$	103	+41		$D$	39
$[\text{Ru}_2\text{RhO}(\mu\text{-O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^{+b}$	$\text{CD}_3\text{OD}$	$9.9 \times 10^{-5}$	109	+44		$D$	39
$[\text{Ru}_3\text{O}(\mu\text{-O}_2\text{CCH}_3)_6(\text{py})_3]^{+d}$	$\text{CD}_3\text{CN}$	$2.4 \times 10^{-7}$	123	+41		$I_d/D$	42
$[\text{Ru}_2\text{ZnO}(\mu\text{-O}_2\text{CCH}_3)_6(\text{py})_3]^{+d}$	$\text{CD}_3\text{CN}$	$8.7 \times 10^{-5}$	112	+53		$D$	38
$[\text{Ru}_2\text{RuO}(\mu\text{-O}_2\text{CCH}_3)_6(\text{py})_3]^{+d}$	$\text{CD}_3\text{CN}$	$1.0 \times 10^{-5}$	122	+69		$I_d/D$	42
$[\text{Rh}(\text{H}_2\text{O})_6]^{3+a}$	$\text{H}_2\text{O}$	$2.2 \times 10^{-9}$	131	+29	-4.2	$I_a$	57
$[\text{Rh}_3\text{O}(\mu\text{-O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^{+}$	$\text{H}_2\text{O}$	$5 \times 10^{-3}$	99	+43	+5.3	$I_d$	40
$[\text{Ru}_2\text{RhO}(\mu\text{-O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^{+b}$	$\text{CD}_3\text{OD}$	$7.9 \times 10^{-5}$	103	+22		$D$	39
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	$\text{H}_2\text{O}$	2.4	108.6	+11.6	-9.6	$I_a$	58
$[\text{Cr}_3\text{O}(\mu\text{-O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^{+c}$	$\text{DMA}$	$5.2 \times 10^2$	107	+51	+9.6	$D$	59
$[\text{Cr}_3\text{O}(\mu\text{-O}_2\text{CCH}_3)_6(\text{py})_3]^{+d}$	$\text{CH}_3\text{NO}_2$	$1.4 \times 10^4$	127	+88	+10.2	$D$	60
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+a}$	$\text{H}_2\text{O}$	$1.6 \times 10^2$	64.0	+12.1	-5.4	$I_a$	61
$[\text{Fe}(\text{DMSO})_6]^{3+a}$	$\text{DMSO}$	$0.93 \times 10^4$	62.5	-16.7	-3.1	$I_a$	62
$[\text{Fe}(\text{DMF})_6]^{3+a}$	$\text{DMF}$	$6.3 \times 10^4$	42.3	-69.0	-0.9	$I$	62
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+a}$	$\text{H}_2\text{O}$	$4.2 \times 10^6$	41.4	+21.2	+3.8	$I_d$	63
$[\text{Fe}(\text{CH}_3\text{OH})_6]^{2+a}$	$\text{CH}_3\text{OH}$	$5.0 \times 10^4$	50.2	+12.6	+0.4	$I$	64
$[\text{Fe}(\text{CH}_3\text{CN})_6]^{2+a}$	$\text{CH}_3\text{CN}$	$6.6 \times 10^5$	41.4	+5.3	+3.0	$I_d$	65
$[\text{Fe}(\text{DMF})_6]^{2+a}$	$\text{DMF}$	$9.7 \times 10^5$	43.0	+13.8	+8.5	$I_d$	66
$[\text{Fe}_3\text{O}(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3]^{+} (1)^d$	$\text{C}_2\text{D}_2\text{Cl}_4$	$0.65 \pm 0.13$	$89.47 \pm 2$	$+51.8 \pm 6$		$D$	<i>e</i>
$[\text{Fe}_3\text{O}(\mu\text{-O}_2\text{CAd})_6(4\text{-Mepy})_3]^{+} (2)^d$	$\text{C}_2\text{D}_2\text{Cl}_4$	$0.34 \pm 0.05$	$91.13 \pm 2$	$+51.9 \pm 5$		$D$	<i>e</i>
$[\text{Fe}_2\text{NiO}(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3]^{+d}$	$\text{CD}_2\text{Cl}_2$	$1.2 \times 10^4$	67.9	+61.0		$D$	17
$[\text{Fe}_2\text{CoO}(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3]^{+d}$	$\text{CD}_2\text{Cl}_2$	$1.2 \times 10^4$	58.9	+30.7	+10.6	$D$	17
$[\text{Fe}_2\text{FeO}(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3]^{+} (3)^d$	$\text{CD}_2\text{Cl}_2$	$1.7 \times 10^4$	60.3	+38.2 <sup>f</sup>	+12.5	$D$	17

<sup>a</sup> Solvent exchange. <sup>b</sup>  $\text{H}_2\text{O} \rightarrow \text{py}$  substitution. <sup>c</sup>  $\text{H}_2\text{O} \rightarrow \text{DMA}$  substitution. <sup>d</sup> py or 4-Phpy exchange. <sup>e</sup> This work. <sup>f</sup> Corrected for the missing factor,  $R \ln(2/3)$ , in ref 17.

constant  $k_{\text{ex}}^{\text{Fe}_2\text{FeO}}$  and the corresponding activation parameters are the same, within experimental error, as those obtained in solutions containing only a single cluster. The simultaneous fit of the dilute and concentrated solutions confirms the expected rate laws: first order in 3 for the ligand exchange reaction and second order (first order in 1 and 3) for the electron self-exchange reaction. The kinetic parameters for the latter reaction are  $k_2^{298} = 72.4 \pm 1.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ,  $\Delta H_2^\ddagger = 18.18 \pm 0.3 \text{ kJ mol}^{-1}$ , and  $\Delta S_2^\ddagger = -90.88 \pm 1.0 \text{ J K}^{-1} \text{ mol}^{-1}$ .

## 4. DISCUSSION

**4.1. Ligand Exchange.** The understanding of the mechanism of the fast electron transfer reaction between the fully oxidized cluster  $[\text{Fe}^{\text{III}}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3]^{+}$  (1) and the mixed valence iron cluster  $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3]^{+}$  (3) (eq 20) requires as a prerequisite the knowledge of the rate and the mechanism of the coordinated/free pyridine ligand exchange reaction (eqs 12–14) on both species. Kinetic parameters for selected ligand exchange reactions on hexasolvates and on trinuclear oxo-centered clusters of di- and trivalent iron and, for comparison, ruthenium cations are reported in Table 3. The water exchange reaction on the high-spin  $\text{Fe}^{\text{III}}$  hexaqua ion ( $t_{2g}^3 e_g^2$ ) takes place through an associative interchange mechanism  $I_a$  according to the clearly negative activation volume  $\Delta V^\ddagger$  ( $-5.4 \text{ cm}^3 \text{ mol}^{-1}$ ), whereas the same reaction on the high-spin  $\text{Fe}^{\text{II}}$  hexaqua ion ( $t_{2g}^4 e_g^2$ ) occurs via a dissociative

interchange  $I_d$  mechanism with a corresponding positive activation volume  $\Delta V^\ddagger$  ( $+3.8 \text{ cm}^3 \text{ mol}^{-1}$ ). The more than 4 orders of magnitude faster water exchange rate of  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  and the change in mechanism can be attributed to the smaller charge, larger Fe–O distance (2.095 instead of 1.990 Å, according to solution-state EXAFS<sup>54</sup>), and larger occupancy of the  $t_{2g}$  orbitals, factors which overall favor a dissociative behavior for the  $\text{Fe}^{\text{II}}$  solvate. The same mechanistic behavior is observed for the non-aqueous solvent exchange reactions on these two ions, with a 1–2 orders of magnitude decrease in the exchange rates. The second row  $\text{Ru}^{\text{III}}$  and  $\text{Ru}^{\text{II}}$  hexa-aqua ions show similarities too, but also differences from the corresponding iron solvates. The ruthenium aqua ions are low-spin and not high-spin. One is also paramagnetic  $t_{2g}^5$ , and the other is diamagnetic  $t_{2g}^6$ . The water exchange mechanism is also clearly  $I_a$  for  $\text{Ru}^{\text{III}}$  with a  $\Delta V^\ddagger$  value of  $-8.3 \text{ cm}^3 \text{ mol}^{-1}$  and borderline  $I/I_d$  for  $\text{Ru}^{\text{II}}$  ( $\Delta V^\ddagger = -0.4 \text{ cm}^3 \text{ mol}^{-1}$  and  $\Delta S^\ddagger = +16.1 \text{ J K}^{-1} \text{ mol}^{-1}$ ). The water exchange rates are 8 orders of magnitude slower for the ruthenium than for the iron hexa-aqua ions but show, as in the case of iron, a 4 orders of magnitude faster exchange rate for the  $\text{Ru}(\text{H}_2\text{O})_6^{2+}$  than for  $\text{Ru}(\text{H}_2\text{O})_6^{3+}$ , with Ru–O distances of 2.122 and 2.029 Å.<sup>55</sup> The second row  $\text{Rh}^{\text{III}}$  hexa-aqua ion ( $t_{2g}^6$ ) reacts, as for the  $\text{Ru}^{\text{III}}$  congener, according to an  $I_a$  mechanism ( $\Delta V^\ddagger = -4.2 \text{ cm}^3 \text{ mol}^{-1}$ ), but with a more than 3 orders of magnitude smaller water exchange rate.

Oxo-centered carboxylate-bridged homotrimeric aqua complexes of the type  $[\text{M}_3\text{O}(\mu\text{-O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^{+}$  exchange water

Table 4. Kinetic Parameters for Selected Electron Self-Exchange Reactions of Mononuclear Complexes and Trinuclear Clusters

	solvent	$k_2^{298}$ ( $M^{-1}s^{-1}$ )	$\Delta d$ ( $\text{\AA}$ ) <sup>c</sup>	$\Delta H^\ddagger$ ( $\text{kJ mol}^{-1}$ )	$\Delta S^\ddagger$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )	ref
$[\text{Ru}(\text{H}_2\text{O})_6]^{3+/2+}$	$\text{H}_2\text{O}$ ( $\text{NaClO}_4$ )	$2.0 \times 10^1$	0.08	46.0	-65.7	71
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+/2+}$	$\text{H}_2\text{O}$ ( $\text{LiClO}_4$ )	1.1	0.13	46.4	-88	72
$[\text{Co}(\text{H}_2\text{O})_6]^{3+/2+}$	$\text{H}_2\text{O}$ ( $\text{NaClO}_4$ )	5	0.21	43.5	-92	7, 73
$[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$	$\text{D}_2\text{O}$ ( $\text{CF}_3\text{CO}_2^-$ )	$8.2 \times 10^2$	0.04	43.1	-46	75
$[\text{Co}(\text{NH}_3)_6]^{3+/2+}$	$\text{H}_2\text{O}$ ( $\text{CF}_3\text{SO}_3^-$ )	$2 \times 10^{-7}$	0.22			74, 76
$[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(\text{py})_3]^{+/0}$	$\text{CD}_2\text{Cl}_2$	$1.1 \times 10^8$	$0.01^d$	18.4	-29.3	10, 11
$[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(\text{py})_2(\text{CO})]^{0/-}$	$\text{CD}_2\text{Cl}_2$	$0.7 \times 10^{8a}$				12
$[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCMe}_3)_6(\text{py})_3]^{+/0}$	$\text{CD}_2\text{Cl}_2$	$3.7 \times 10^{4b}$				15
$[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3]^{+/0}$	$\text{CD}_2\text{Cl}_2$	$7.24 \pm 0.1 \times 10^4$	$0.09^c$	$18.18 \pm 0.3$	$-90.88 \pm 1.0$	this work

<sup>a</sup> 18–20 °C. <sup>b</sup> 23 °C. <sup>c</sup> Difference in the metal–ligand bond distances of the redox couples (solution EXAFS or solid state X-ray). <sup>d</sup> The R32 symmetry of the reductant cluster imposes equivalent  $\text{Ru}^{\text{II}}$  and  $\text{Ru}^{\text{III}}$  atoms. <sup>e</sup> Difference between the average iron–ligand bond distances of the single reductant  $\text{Fe}^{\text{II}}$  center and the average iron–ligand  $\text{Fe}^{\text{III}}$  bond distances of the three oxidant centers. The difference between the distant averages of the two reductant and the three oxidant  $\text{Fe}^{\text{III}}$  centers of the redox couple is only 0.03 Å (see Table S20, Supporting Information).

much faster than the corresponding mononuclear  $[\text{M}(\text{H}_2\text{O})_6]^{3+}$  ion:  $2.3 \times 10^2$  times faster for  $\text{Ru}^{\text{III}}$  and  $2.3 \times 10^6$  times faster for  $\text{Rh}^{\text{III}}$ . This strong acceleration of the water exchange is attributed to the *trans*-labilizing effect of the central oxo bridge. The X-ray-determined Rh–O bond lengths in  $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$  (2.016 Å)<sup>67</sup> and in  $[\text{Rh}_3\text{O}(\mu\text{-O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^{3+}$  (1.924 Å for Rh–( $\mu_3$ -O) and 2.116 Å for Rh–OH<sub>2</sub>)<sup>68</sup> explain this behavior: a 0.09 Å Rh bond shortening with the central oxygen and a 0.10 Å bond lengthening with the water oxygen compared to the Rh–OH<sub>2</sub> bond length in the hexa-aqua ion. The water exchange rate constants for the mixed-metal cluster  $[\text{Ru}_2\text{RhO}(\mu\text{-O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^{3+}$  are also dominated by the *trans* effect, however with values about 10 times smaller than those of the corresponding homonuclear clusters.<sup>39</sup>

The pyridine exchange rate on  $[\text{Ru}_3\text{O}(\mu\text{-O}_2\text{CCH}_3)_6(\text{py})_3]^{3+}$  is 3200 times slower than the water exchange on  $[\text{Ru}_3\text{O}(\mu\text{-O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^{3+}$ , indicating a strong leaving ligand dependence, as expected for a dissociative mechanism.<sup>42</sup> The exchange rate is even 15 times slower than the water exchange rate on  $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$ , indicating an overcompensation of the *trans*-labilizing effect by the retardation leaving-group effect of the pyridine ligand. This is also observed for the two iron clusters  $[\text{Fe}_3\text{O}(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3]^{3+}$  (1) and  $[\text{Fe}_3\text{O}(\mu\text{-O}_2\text{CAd})_6(4\text{-Mepy})_3]^{3+}$  (2) of this study: both exchange more than 2 orders of magnitude slower than water on  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ . The first order rate law and the large positive  $\Delta S^\ddagger$  values lead to the assignment of a limiting dissociative mechanism *D* for the coordinated/free pyridine type ligand exchange on both iron clusters.

The replacement of one trivalent ion in the homotrimeric clusters by a divalent ion produces an acceleration of the substitution process on the two remaining formerly trivalent ions. In  $[\text{Ru}_2\text{ZnO}(\mu\text{-O}_2\text{CCH}_3)_6(\text{py})_3]$  and  $[\text{Ru}_2^{\text{III}}\text{Ru}^{\text{II}}\text{O}(\mu\text{-O}_2\text{CCH}_3)_6(\text{py})_3]$ , the exchanges of the py ligand coordinated to the  $\text{Ru}^{\text{III}}$  are 360 and 42 times faster, respectively, than on  $[\text{Ru}_3\text{O}(\mu\text{-O}_2\text{CCH}_3)_6(\text{py})_3]^{3+}$ .<sup>38</sup> For the  $\text{Ru}_2^{\text{III}}\text{Ru}^{\text{II}}\text{O}$  cluster, it was concluded that the divalent state was delocalized over the three ruthenium ions on the basis of the ESCA and other spectroscopic measurements.<sup>69</sup> Therefore, the oxidation state of each ruthenium was described as +8/3. This acceleration of the 4-Phpy exchange process is even more important in the case of the replacement of an  $\text{Fe}^{\text{III}}$  by  $\text{Fe}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ , or  $\text{Ni}^{\text{II}}$  in the homotrimeric cluster 1: the increase of the rate constants for the exchange on the two remaining  $\text{Fe}^{\text{III}}$  is  $2 \times 10^4$ .<sup>17</sup> The solid state X-ray structures give insight into this behavior: the  $\text{Fe}^{\text{III}}-(\mu_3\text{O})$

distance decreases from 1.910 Å to 1.844 Å (–0.066) and the  $\text{Fe}^{\text{III}}-\text{N}$  distance increases from 2.187 Å to 2.228 Å (+0.041) on going from the  $\text{Fe}^{\text{III}}_3\text{O}$  cluster 1 to the  $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}$  cluster 3 (Table 2). On going from cluster 1 to the  $[\text{Fe}^{\text{III}}_2\text{M}^{\text{II}}\text{O}(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3]$  clusters, the changes of the  $\text{Fe}^{\text{III}}-(\mu_3\text{O})$  distances (+0.001 for Co and –0.028 Å for Ni) and of the  $\text{Fe}^{\text{III}}-\text{N}$  distances (+0.040 for Co and –0.003 Å for Ni) show the same trend, but to a lesser extent.<sup>17</sup> These observations indicate that the formally +3 oxidation state of iron in these mixed oxidation state (+3, +3, +2) clusters is better described by a value smaller than 3 due to the partial electronic delocalization over the three metal ion centers.

**4.2. Electron Self-Exchange.** In the temperature range of the NMR study, the py exchange on 1 ( $\text{Fe}_3\text{O}$ ) is orders of magnitude slower than the py exchange on 3 ( $\text{Fe}_2\text{FeO}$ ) and the 1/3 electron self-exchange (Table 4). The py exchange on 1 does therefore not contribute to the proton relaxation rates, as shown in Figure 8. At low temperatures, the 1/3 electron self-exchange has the largest contribution to the transverse relaxation rate; in other words, there is a larger occurrence of the redox process versus the py ligand exchange reaction on 3. This allows one to safely assign an *outer-sphere mechanism* to the electron self-exchange reaction.<sup>70</sup> At higher temperatures, the transverse relaxation rate of the first order py exchange reaction on 3 becomes larger than the second order redox process due the large difference in their  $\Delta H^\ddagger$  values: 60.3 and 18.18  $\text{kJ mol}^{-1}$ .

The outer-sphere mechanism consists of two steps: (a) a fast pre-equilibrium association of the reactants described by the pre-equilibrium constant  $K_{\text{os}}$ , (b) followed by the act of electron transfer with a rate constant  $k_{\text{et}}$ . The electron transfer within the outer-sphere precursor will only take place if the difference in the spin states of the oxidized and reduced form of the cluster corresponds to the transfer of a single electron. One has therefore to incorporate an “electronic spin probability factor”  $P_s$  in the analysis. In summary, the second order observed rate constant  $k_2$  for the self-exchange reaction between the two clusters can be written as in eq 22.

$$k_2 = K_{\text{os}}P_s k_{\text{et}} \quad (22)$$

In order to discuss semiquantitatively the constant  $k_2$  of the 3/1 redox couple, selected rate constants and activation parameters of mononuclear and cluster redox couples are reported in Table 4 for comparison. Some of the reported  $k_2$  values are very high, on the order of  $10^8 \text{ M}^{-1} \text{ s}^{-1}$  for the  $\text{Ru}_3\text{O}^{+/0}$  and  $\text{Ru}_3\text{O}^{0/-}$  couples,

but still below the diffusion-controlled limit of  $k_D = 1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .<sup>10</sup> Overall, they cover a range of 13 orders of magnitude.

The experimental determination of the formation constant  $K_{os}$  of the precursor is possible in suitable instances, typically when both reactants have opposite charges. In our case and in the examples of Table 4,  $K_{os}$  can be estimated from the electrostatic Eigen–Fuoss model (eqs 23 and 24), where  $d$  is the distance between both redox centers,  $\omega(d)$  is the work required to bring the reactants from infinity to the distance  $d$ , and  $\delta d$  is the spread of distances over which the reaction takes place.<sup>74</sup>

$$K_{os} = (4\pi N r^2 \delta d) \exp(-\omega(d)/RT) \quad (23)$$

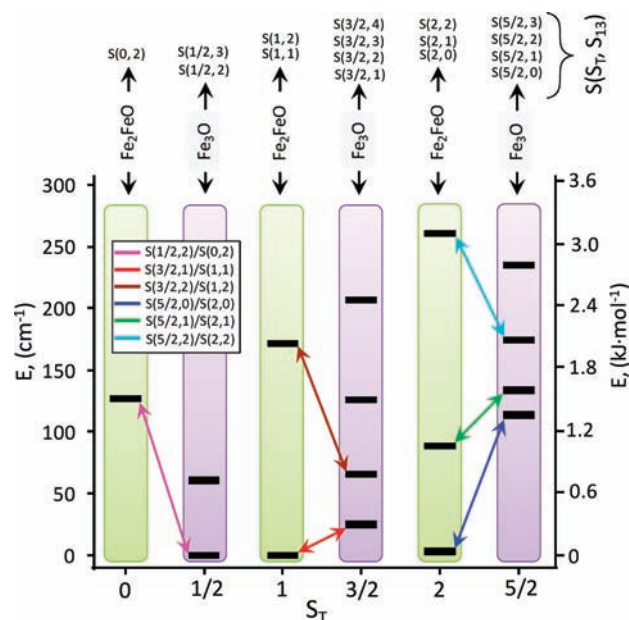
$$\omega(d) = z_A z_B e^2 / D_s r (1 + \beta d) \quad (24)$$

In the case of the  $+/0$  and  $0/-$  cluster redox couples the  $\omega(d)$  term is equal to unity, and eq 24, expressed in terms of  $\Delta G_{os}$ , reduces to eq 25.<sup>10</sup>

$$\Delta G_{os} = -RT \ln(4\pi N d^3 / 3000) \quad (25)$$

The trinuclear Ru and Fe clusters are nonspherical, with the shortest distance along the axis perpendicular to the  $M_3O$  plane (5.8 Å) and longer distances in all other directions. Meyer and co-workers have estimated  $K_{os}$  using a statistical model and the Eigen–Fuoss model (value in parentheses), assuming a close contact distance in the precursor complex  $d = 14$  Å:  $K_{os} = 0.14$  (6.9)  $\text{M}^{-1}$  and  $\Delta G_{os} = +5.0$  (−4.6)  $\text{kJ mol}^{-1}$ .<sup>10</sup> These two models produce  $K_{os}$  estimations for the preequilibrium step in dichloromethane differing by 1 order of magnitude. These authors conclude that the more reasonable agreement with experimental redox data for a  $\text{RuO}_3^{+/0}$  couple is obtained by the statistical approach. For the  $[\text{M}(\text{H}_2\text{O})_6]^{3+/2+}$  redox couples, the calculated  $K_{os}$  ( $\text{M}^{-1}$ ) values (eq 23) are smaller due to the repulsion effect of two positively charged aqua ions: 0.033  $\text{M}^{-1}$  for Ru, 0.005  $\text{M}^{-1}$  for Fe, and 0.017  $\text{M}^{-1}$  for Co in water.<sup>74</sup> For two opposite charged redox partners, the  $K_{os}$  values can be measured and are much larger; for example, a value of 1500  $\text{M}^{-1}$  has been obtained for the reaction of  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  with  $[\text{Fe}(\text{CN})_6]^{4-}$ .<sup>2</sup> The self-exchange rate for the  $[\text{Co}(\text{NH}_3)_6]^{3+/2+}$  redox couple ( $k_2 = 2 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C) is 10 orders of magnitude slower than that for  $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$ . This is a result of the fact that the electron transfer from the high-spin  $\text{Co}^{\text{II}} (t_{2g}^5 e_g^2)$  to low-spin  $\text{Co}^{\text{III}} (t_{2g}^6)$  is spin-forbidden. The interdiction derives from the fact that the electron transfer for the hexa-ammino and hexa-aqua Co complexes involves the simultaneous movement of three electrons, whereas for the other mono-nuclear complexes of Table 4, the redox processes involve the transfer of a single electron:  $\text{Fe}^{2+}(t_{2g}^4 e_g^2) \rightarrow \text{Fe}^{3+}(t_{2g}^3 e_g^2)$  and  $\text{Ru}^{2+}(t_{2g}^6) \rightarrow \text{Ru}^{3+}(t_{2g}^5)$ . The major processes by which the redox reaction for the two  $\text{Co}^{3+/2+}$  couples can occur is a preliminary thermal population of the excited states ( $\text{Co}^{3+}(t_{2g}^6 \rightarrow t_{2g}^5 e_g)$  or  $\text{Co}^{2+}(t_{2g}^5 e_g^2 \rightarrow t_{2g}^6 e_g)$ ) or spin orbit coupling with the excited state of cobalt(II). However, thermal excitation alone requires too much energy, and today it is believed that a quantum mechanical mixing of the  $\text{Co}^{\text{II}}$  excited state by spin orbit coupling provides a slightly lower energy pathway.<sup>74</sup>

The  $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(\text{py})_3]^{+/0}$  clusters have a spin state  $S = 1/2$  for the paramagnetic oxidized  $\text{Ru}^{\text{III}}_3$  form and a spin state  $S = 0$  for the reduced diamagnetic  $\text{Ru}^{\text{III}}_2\text{Ru}^{\text{II}}$  form. Due to strong magnetic interaction between the paramagnetic centers, these spin states are fully populated in the 200–300 K temperature range. The self-exchange redox reaction for this Ru couple



**Figure 9.** Low-energy spin states  $S(T, S_{13})$  of the clusters  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3]\text{ClO}_4$  (**1**) and  $[\text{Fe}_2\text{Fe}(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3]$  (**3**) versus spin  $S_T$  as determined from eq 10 with the exchange parameters ( $J_a$  and  $J_b$ ). The spin-allowed electron transfer processes depicted by arrows follow the selection rule  $S(S_T, S_{13}) \leftrightarrow S(S_T + 1/2, S_{13})$ .

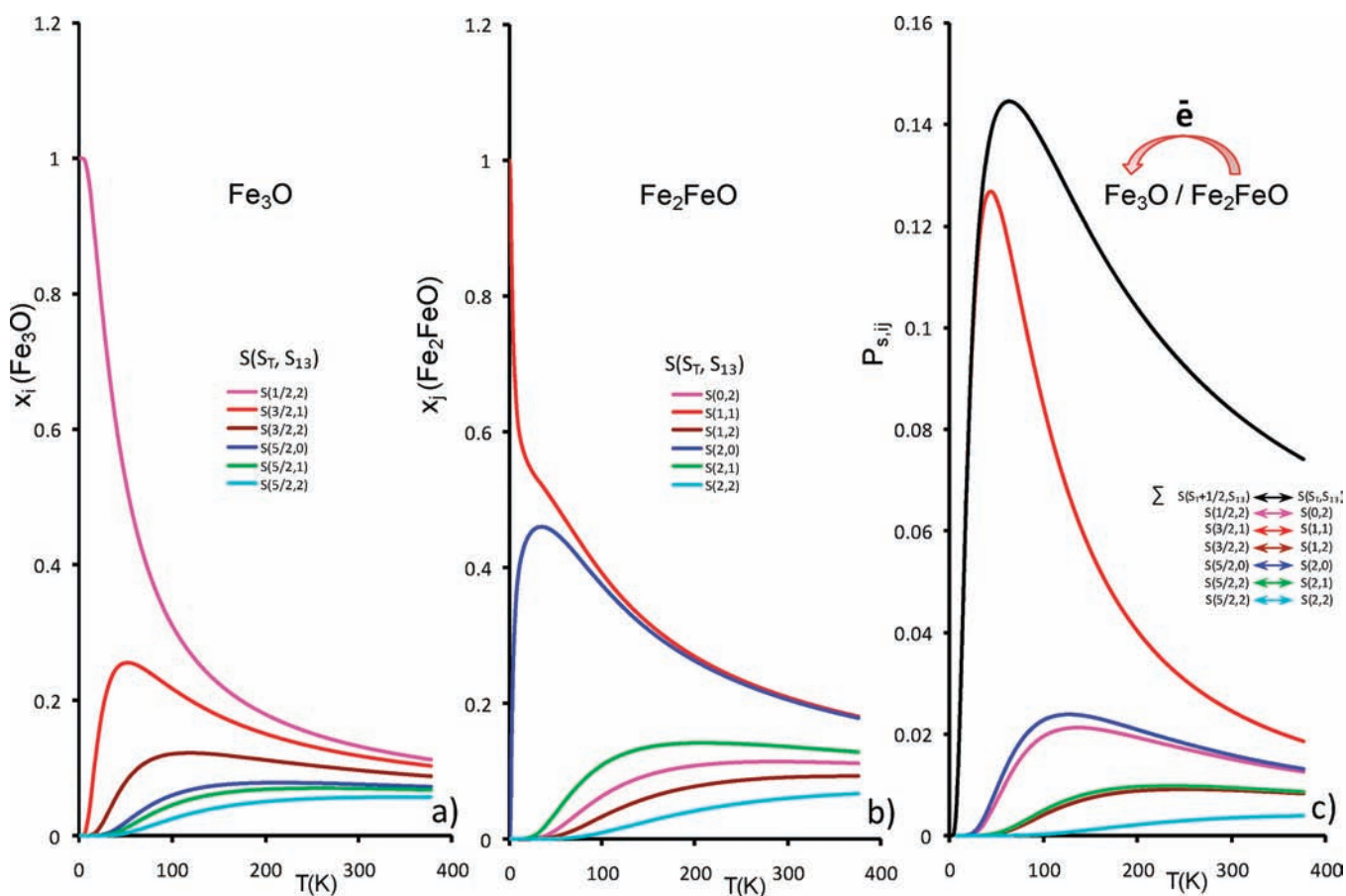
involves the exchange of a single electron, without other electron reorganization, and is therefore spin-allowed.

The situation for the three Fe clusters **1**, **2**, and **3** is totally different with large numbers of thermal populated spin states in the temperature range of the NMR kinetic study (190–300 K). The variable temperature magnetic susceptibility measurements on these polycrystalline clusters have made it possible to calculate the Boltzmann energy distribution of the different spin states of these clusters in the solid state using eq 10 with the exchange parameters  $J_a$  and  $J_b$  (section 3.3; Figures S4–S6 and Tables S2–S5, Supporting Information). For the oxidized forms  $[\text{Fe}^{\text{III}}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3]^+$  and  $[\text{Fe}^{\text{III}}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CAd})_6(4\text{-Mepy})_3]^+$ , the total spin  $S_T$  has half-integer values from 1/2 to 15/2, with a 20  $\text{kJ mol}^{-1}$  energy range. For the reduced form  $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3]^0$ , the  $S_T$  values are integers from 0 to 7, with a 29  $\text{kJ mol}^{-1}$  energy range. Low-energy spin state  $S(T, S_{13})$  levels as a function of  $S_T$  are represented in Figure 9 for both clusters of the couple  $[\text{Fe}^{\text{III}}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(4\text{-Phpy})_3]^{+/0}$ .

Assuming similar molecular structures and magnetic interactions in the solid state and in dichloromethane solution, the spin states energy distribution diagram can be used to determine the electronic spin probability factor  $P_s$  for the self-exchange reaction **1/3**. The total number of spin states amounts to 27 for the oxidized form and to 24 for the reduced form. The temperature dependence of the normalized ( $\sum x_i = 1$ ) mole fractions of the spin states  $x_i(\text{Fe}^{\text{III}}_3\text{O})$  and  $x_j(\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O})$  of clusters **1** and **3** were calculated (Figure 10; Table S19 and Figure S11, Supporting Information).

The probability of an encounter event of the oxidized **1** and reduced **3** clusters of given spin states  $i$  and  $j$  is equal to the product  $P_{s,ij} = \{x_i(\text{Fe}^{\text{III}}_3\text{O})\} \times \{x_j(\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O})\}$  of the mole fractions of the reactants in those spin states. Among the 648 ( $24 \times 27$ ) possible couple of spin states, only those encounters





**Figure 10.** Temperature dependence the mole fractions of selected spin state  $S(S_T, S_{13})$  of  $\text{Fe}_3\text{O}$  (a) and  $\text{Fe}_2\text{FeO}$  (b) with the probabilities  $P_{s,ij}$  of the corresponding spin-allowed electron transfer self-exchange processes defined as the products of the mole fractions  $x_i(\text{Fe}_3\text{O})$  and  $x_j(\text{Fe}_2\text{FeO})$  (c). The black curve is the sum  $P_s$  of the 24 probabilities  $P_{s,ij}$  of spin-allowed self-exchanges.

involving the transfer of a single electron  $S(S_T, S_{13}) \leftrightarrow S(S_T + 1/2, S_{13})$  are spin-allowed. Some of them are depicted by arrows in Figure 9. The “electronic spin probability factor”  $P_s$  represents the overall probability of an electron transfer to occur during an encounter. It is the sum  $P_s = \sum P_{s,ij}$  of the 24 probabilities of spin-allowed self-exchanges. As shown in Figure 10, the most probable transition in terms of spin probability is  $\text{Fe}^{\text{III}}_3\text{O}(3/2,1) \leftrightarrow \text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}(1,1)$ . The sum of the 24 probabilities of spin-allowed self-exchanges gives the electronic spin probability factor  $P_s = \sum P_{s,ij}$  which decreases from 0.104 to 0.084 with increasing temperature between 200 to 300 K. In this temperature range,  $P_s$  has a typical entropy-driven behavior with  $\Delta G_p^{298} = +6.1 \text{ kJ mol}^{-1}$ ,  $\Delta H_p = -1.1 \text{ kJ mol}^{-1}$ , and  $\Delta S_p = -24 \text{ J mol}^{-1} \text{ K}^{-1}$ .

For the outer-sphere self-exchange electron-transfer step within the encounter complex, a vibrational energy trapping barrier  $\Delta G_{\text{et}}^*$  exists to the transfer step of the excess electron (eq 26).

$$\Delta G_{\text{et}}^* = \Delta G_{\text{in}}^* + \Delta G_{\text{out}}^* \quad (26)$$

$\Delta G_{\text{in}}^*$  is related to the inner-sphere (vibrational) and  $\Delta G_{\text{out}}^*$  to the outer-sphere (solvent) reorganization energies. Both energies can be estimated from theory or experiments as shown by Kubiak and co-workers for  $\text{Ru}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{py})_3^{+0,11}$

The inner-sphere reorganization barrier is given by eq 27, where the summation is on the number of bonds undergoing vibration (including both molecules for each bond),  $\Delta d$  is the

change in bond distance between the oxidized and reduced forms, and  $f_{\text{in}}^r$  is the reduced force constant for each bond (eq 28) obtained from the individual force constants for the reduced and oxidized species using  $f_{\text{in}}$  (eq 29), where  $\nu_{\text{in}}$  is the frequency of vibration and  $\mu$  is the reduced mass.

$$\Delta G_{\text{in}}^* = 0.5 \sum f_{\text{in}}^r (\Delta d/2)^2 \quad (27)$$

$$f_{\text{in}}^r = 2f_{\text{in}}^{\text{ox}} f_{\text{in}}^{\text{red}} / (f_{\text{in}}^{\text{ox}} + f_{\text{in}}^{\text{red}}) \quad (28)$$

$$f_{\text{in}} = 4\pi^2 \nu_{\text{in}} \mu \quad (29)$$

The calculations (details in the Supporting Information) were performed for the three iron centers of the redox couple **1/3**, using vibrational data from Cannon and co-workers<sup>19</sup> and the X-ray data of Table 2, leading to  $\Delta G_{\text{in}}^* = \Delta G_{\text{in}}^*(\text{Fe}-\text{N}) + \Delta G_{\text{in}}^*(\text{Fe}-\mu_3-\text{O}) + \Delta G_{\text{in}}^*(4 \times \text{Fe}-\text{Ac}) + \Delta G_{\text{in}}^*(4-\text{Phpy}) = 0.2 \text{ kJ mol}^{-1} + 7.9 \text{ kJ mol}^{-1} + 5.2 \text{ kJ mol}^{-1} + 2.3 \text{ kJ mol}^{-1} = 15.6 \text{ kJ mol}^{-1}$ .

Meyer and co-workers<sup>10</sup> have calculated  $\Delta G_{\text{out}}^*$  using a dielectric continuum treatment (eq 30) in the solvent dichloromethane for the  $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(\text{py})_3]^{+0}$  couple.

$$\Delta G_{\text{out}}^* = e^2/8a(1/D_{\text{op}} - 1/D_s) \quad (30)$$

The van der Waals radii,  $a$ , of the nonspherical reactants has been chosen as  $7 \text{ \AA}$ .<sup>11</sup>  $D_{\text{op}}$  and  $D_s$  are the solvent optical dielectric constant and the static dielectric constant, respectively.  $D_{\text{op}}$  is

**Table 5. Calculated and Experimental Kinetic Parameters for the Self-Exchange Reactions  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6\text{-}(4\text{-Phpy})_3]^{+/0}$  and  $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(\text{py})_3]^{+/0}$  in Dichloromethane**

	$\text{Fe}_3\text{O}^{+/0}$	$\text{Ru}_3\text{O}^{+/0}$
$K_{\text{os}}^{298}, \text{M}^{-1}$	0.14 <sup>a</sup>	0.14 <sup>a</sup>
$\Delta G_{\text{os}}^{298}, \text{kJ mol}^{-1}$	+ 5.0 <sup>a</sup>	+ 5.0 <sup>a</sup>
$P_s^{298}$	$8.4 \times 10^{-2}$	
$\Delta G_{P_s}^{298}, \text{kJ mol}^{-1}$	+6.1	
$\Delta G_{\text{in}}^{298}, \text{kJ mol}^{-1}$	+15.6	+4.5 <sup>b</sup>
$\Delta G_{\text{out}}^{298}, \text{kJ mol}^{-1}$	+11.3 <sup>a</sup>	+11.3 <sup>a</sup>
$k_{2,\text{calcd}}^{298}, \text{s}^{-1}$	$1.37 \times 10^{6c}$	$1.41 \times 10^{9c}$
$\Delta G_{\text{calcd}}^{298}, \text{kJ mol}^{-1}$	+38.0 <sup>d</sup>	+20.8 <sup>d</sup>
$k_{2,\text{exp}}^{298}, \text{s}^{-1}$	$7.24 \times 10^4$	$1.1 \times 10^{8a}$
$\Delta G_{\text{exptl}}^{298}, \text{kJ mol}^{-1}$	+45.27	+27.1 <sup>a</sup>
$\Delta G_{\text{exptl}}^{298} - \Delta G_{\text{calcd}}^{298}, \text{kJ mol}^{-1}$	+7.3	+6.3

<sup>a</sup> Ref 10. <sup>b</sup> Ref 11. <sup>c</sup>  $\nu_{\text{et}} = 6.21 \times 10^{12} \text{ s}^{-1}$ . <sup>d</sup>  $\Delta G_{\text{calcd}}^{298} = \Delta G_{\text{os}}^{298} + \Delta G_{P_s}^{298} + \Delta G_{\text{in}}^{298} + \Delta G_{\text{out}}^{298}$ .

relatively independent of temperature, while  $D_s$  is temperature-dependent ( $\theta = -\partial \ln D_s / \partial \ln T$ ). The only parameter specific to the  $\text{Ru}_3\text{O}^{+/0}$  couple in the calculation is the van der Waals radii. Considering the similarity in geometry and in the size of the  $\text{Fe}_3\text{O}^{+/0}$  couple, the same value can be used, leading to  $\Delta G_{\text{out}}^{298} = 11.3 \text{ kJ mol}^{-1}$ ,  $\Delta H_{\text{out}}^* = 14.6 \text{ kJ mol}^{-1}$ , and  $\Delta S_{\text{out}}^* = +10.9 \text{ J mol}^{-1} \text{ K}^{-1}$ .

At this point, a comparison of the theoretically estimated and the experimental values of the kinetic parameters for the electron self-exchange reactions can be performed (Table 5). The experimental rate constant  $k_{2,\text{exptl}}$  is given by eq 31 (Eyring transition state model), and the calculated rate constant  $k_{2,\text{calcd}}$  is given by eq 32 (classical Marcus model).

$$k_{2,\text{exptl}} = (k_B T/h) \exp(-\Delta G_{\text{exp}}^{\ddagger}/RT) \\ = (k_B T/h) \exp(-\Delta H_{\text{exp}}^{\ddagger}/RT) \exp(-\Delta S_{\text{exp}}^{\ddagger}/R) \quad (31)$$

$$k_{2,\text{calcd}} = \nu_{\text{et}} \exp(-(\Delta G_{\text{os}} + \Delta G_{P_s} + \Delta G_{\text{in}}^* + \Delta G_{\text{out}}^*)/RT) \\ = \nu_{\text{et}} \exp(-\Delta G_{\text{calcd}}^*/RT) \quad (32)$$

In the latter equation, the transition state factor ( $k_B T/h = 6.21 \times 10^{12} \text{ s}^{-1}$  at 298.15 K) is not appropriate and is replaced by an effective frequency  $\nu_{\text{et}}$  representing the reciprocal average time required to pass the transition state point at the apex of the free energy barrier ( $10^{12}$  to  $10^{14} \text{ s}^{-1}$ ).<sup>77</sup> The difference of  $\sim 7 \text{ kJ mol}^{-1}$  between the calculated  $\Delta G_{\text{calcd}}^{298}$  and experimental  $\Delta G_{\text{exptl}}^{298}$  values for both redox couples, which corresponds to an overestimation by a factor  $\sim 15$  in the self-exchange rate constants  $k_2^{298}$ , is reasonably small considering the uncertainty in some parameters used to estimate the different components of the free energies of activations. These small differences may be due to the arbitrary choice of the  $\nu_{\text{et}}$  value of  $6.21 \times 10^{12} \text{ s}^{-1}$ , which may well be on the order of  $10^{11} \text{ s}^{-1}$ , and/or due to too small values of  $\Delta G_{\text{in}}^{298}$  due, for example, to the difficulty in taking rigorously into account the vibrational-mode mixing. The calculated  $\Delta \Delta G_{\text{calcd}}^{298} = 17.2 \text{ kJ mol}^{-1}$  and experimental  $\Delta \Delta G_{\text{exptl}}^{298} = 18.2 \text{ kJ mol}^{-1}$  differences between the values for the iron and the ruthenium clusters are practically the same. In

the calculations, the formation constants  $K_{\text{os}}^{298}$  of the precursors and the free energies of activation  $\Delta G_{\text{out}}^{298}$  for the solvent reorganization were assumed to be identical. The difference lies in the difference  $\Delta \Delta G_{\text{in}}^{298} \approx 11 \text{ kJ mol}^{-1}$  of the inner-sphere reorganization (vibrational) energies and in the electronic spin probability factor  $P_s^{298} = 0.084$  ( $\Delta G_{P_s}^{298} = 6.1 \text{ kJ mol}^{-1}$ ), which is not relevant for the  $\text{Ru}_3\text{O}^{+/0}$  redox couple.

## 5. CONCLUSION

In the solid state, the two fully oxidized  $[\text{Fe}_3\text{O}(\mu\text{-O}_2\text{CCH}_3)_6\text{-}(4\text{-Phpy})_3](\text{ClO}_4)$  (**1**) and  $[\text{Fe}_3\text{O}(\mu\text{-O}_2\text{CAd})_6(4\text{-Mepy})_3](\text{NO}_3)$  (**2**) clusters show three quasi-equivalent  $\text{Fe}^{\text{III}}$  atoms, while the neutral mixed valence  $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}(\mu\text{-O}_2\text{CCH}_3)_6\text{-}(4\text{-Phpy})_3](\text{ClO}_4)$  (**1**) cluster is characterized by shorter  $\text{Fe}^{\text{III}}\text{-O}$  and much longer  $\text{Fe}^{\text{II}}\text{-O}$  distances. The NMR spectra in dichloromethane solution correspond to structures of **1** and **2** with a  $C_3$  axis of symmetry of the oxo-centered clusters. In the solution of **3**, one would expect a splitting of the six signals of **1** in a 2:1 ratio corresponding to the  $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}$  core of cluster **3**. This is not the case due to the very fast intramolecular electron exchange even at a low temperature (200 K). The analysis of magnetic susceptibility data of the solid compounds was performed with the Kambe vectors coupling method using 27 possible spin states for the oxidized forms **1** and **2** and 24 for the reduced form **3**. Typical antiferromagnetic interactions between the paramagnetic centers were found for the homovalent  $\text{Fe}^{\text{III}}_3\text{O}$  (**1**,  $J_a = -21.8(1) \text{ cm}^{-1}$ ,  $J_b = -31.9(4) \text{ cm}^{-1}$ ; **2**,  $J_a = -24.3(1) \text{ cm}^{-1}$ ,  $J_b = -30.6(2) \text{ cm}^{-1}$ ) and the mixed valence  $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}$  (**3**,  $J_a = -22.2(2) \text{ cm}^{-1}$ ,  $J_b = -65.1(7) \text{ cm}^{-1}$ ) clusters.

The variable temperature line-shape NMR analysis of solutions of each cluster in the presence of an excess of the pyridine base showed that these exchange reactions occur with  $D$  limiting dissociative mechanisms. The first order exchange rates at 298.15 K are  $0.65 \text{ s}^{-1}$  for **1** and  $0.34 \text{ s}^{-1}$  for **2** ( $\text{Fe}^{\text{III}}_3\text{O}$ ) but are much larger with a value of  $1.7 \times 10^4 \text{ s}^{-1}$  for the reduced form **3** ( $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}$ ). Due to the slow ligand exchanges on the NMR time scale on the homovalent  $\text{Fe}^{\text{III}}_3\text{O}$  clusters, individual signals for the mixed ligand cluster  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CAd})_6(4\text{-Mepy})_{3-x}\text{-}(4\text{-Phpy})_x](\text{NO}_3)$  ( $x = 0, 1, 2, 3$ ) could be observed. A quantitative analysis of the populations of the mixed ligands clusters shows a statistical distribution of these species as a function of the ratio of the concentrations 4-Mepy/4-Phpy of the excess of noncoordinated pyridine-type ligands.

The electron self-exchange rate between **1** and **3** has been followed simultaneously with the ligand exchange on **3**. At low temperatures, the self-exchange reaction is faster than both 4-Phpy ligand exchange reactions on these two clusters, allowing the assignment of an outer-sphere redox process. The 1/3 iron cluster electron self-exchange is more than 3 orders of magnitude faster than the  $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(\text{py})_3]^{+/0}$  self-exchange. The calculated self-exchange rates for both processes compare reasonably well with the experimental data. The equilibrium constant for the formation of the precursor to the electron-transfer and the free energy of activation contribution for the solvent reorganization to reach the electron transfer step have been considered the same for both compounds. The difference of the rates is explained by the larger ( $11.1 \text{ kJ mol}^{-1}$ ) inner-sphere reorganization energy for the 1/3 iron clusters, which could be calculated thanks to the availability of crystal structures and infrared spectra for both forms of the redox couple. The

second reason is a supplementary energy ( $6.1 \text{ kJ mol}^{-1}$ ), called the electronic spin probability factor, which arises from the fact that each encounter is not spin-allowed, due to the high spin multiplicity of both iron clusters. This is not the case for the ruthenium redox couple, where both forms are in a low spin ground state.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Temperature dependence of  $^1\text{H}$  NMR spectra, transverse relaxation rates, and chemical shifts for compounds 1–2. Relative energy of the spin states ( $S(S_T, S_{13})$ ) for clusters 1–3. Summary of the results of the fitting of the proton relaxation rates for 1 and 2 and a mixture of 1 and 3. Fitting of proton relaxation rates of the coordinated 4-Phpy and 4-Mepy ligands. Fitting of the real and imaginary parts of NMR spectra of mixtures of 1 and 3 in  $\text{CD}_2\text{Cl}_2$ . Comparison between the bond lengths of the oxidized and reduced forms and estimation of  $\Delta G_{\text{in}}^*$  for the  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CCH}_3)_6(\text{Rpy})_3]^{+/0}$  redox couples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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