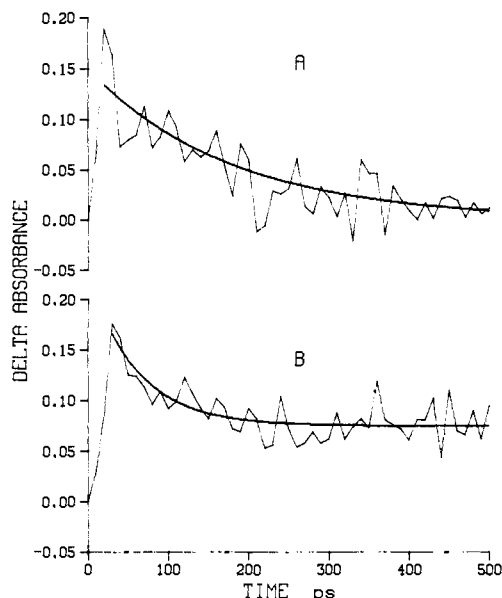


**Figure 1.** Changes in absorbance of a  $2 \times 10^{-4}$  M solution of **1** in butyronitrile at 20 ps following a 0.5-mJ, 1-ps, 600-nm laser flash. Cell path length, 2 mm. Filters that reject stray light cut out the 490–620-nm wavelength region, while the sharp cutoff at 440 nm is due to the intense absorption of the porphyrin Soret band at 421 nm.

a 1-ps laser flash at 600 nm.<sup>12</sup> The formation and decay of the porphyrin cation were monitored at 460 and 650 nm,<sup>13</sup> while the formation of the naphthoquinone anion and the *N,N*-dimethylanilinium cation were monitored at 480<sup>14</sup> and 470 nm,<sup>15</sup> respectively. All measurements were performed in butyronitrile at 21 °C. Each transient could be described by a single exponential rise or decay.<sup>16</sup> Quantum yields of charge separation were determined as described previously.<sup>5</sup>

Excitation of either **1** or **2** results in formation of a transient spectrum due to  $P^+Q^-$  with a rate constant of  $1.1 \times 10^{11} \text{ s}^{-1}$  (Figure 1). In compound **2** the  $P^+Q^-$  state decays cleanly back to the ground state with a rate constant of  $5.6 \times 10^9 \text{ s}^{-1}$  (Figure 2A). For compound **1** the transient due to  $P^+Q^-$  decays more rapidly with a rate constant of  $1.4 \times 10^{10} \text{ s}^{-1}$  to a state that possesses absorbance in the blue region of the spectrum characteristic of  $D^+$  and  $Q^-$  with no persistent changes in the red which would indicate the presence of the porphyrin cation (Figure 2B). The resultant  $D^+PQ^-$  state decays to the ground state of **1** with a lifetime of 2.45  $\mu\text{s}$ . A comparison between the rate constants for the competitive reactions  $DP^+Q^- \rightarrow DPQ$  and  $DP^+Q^- \rightarrow D^+PQ^-$  indicates that  $D^+PQ^-$  is formed from  $DP^+Q^-$  in about 71% yield. This yield is consistent with the measured transient absorbance spectra using the known extinction coefficients for  $D^+$ ,  $P^+$ , and  $Q^-$ .<sup>5,13-15</sup>

The measured electron-transfer rate constants for **1** and **2** all agree within a factor of 2 with the values predicted by our rate vs. free energy of reaction data. Thus, our results show that it is possible to design molecules that produce high-quantum-yield long-lived charge separation provided that three requirements are met. First, the distances between the various donors and acceptors must be highly restricted. Second, for a given donor-acceptor distance the dependence of the electron transfer rates on the free energy of reaction must be known. Third, more than a single optimized electron-transfer step is necessary to achieve long-lived



**Figure 2.** Transient absorbance decays measured at 460 nm of  $2 \times 10^{-4}$  M solutions of (A) **2** and (B) **1** in butyronitrile following a 0.5-mJ, 1-ps, 600-nm laser pulse. The superimposed smooth curves are the exponential fits to the data.

radical ion pair states in a manner analogous to photosynthesis.<sup>17</sup>

**Acknowledgment.** This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Department of Energy, under Contract W-31-109-Eng-38.

**Supplementary Material Available:** NMR and visible spectral data for **1**–**3** and numbering scheme for compounds (3 pages). Ordering information is given on any current masthead page.

(17) Moore, T. A.; Gust, D.; Mathis, P.; Mialocq, J.-C.; Chachaty, C.; Bensasson, R. V.; Land, E. J.; Doizi, D.; Liddell, P. A.; Lehman, W. R.; Nemeth, G. A.; Moore, A. L. *Nature (London)* **1984**, *307*, 630.

### Protons on a Cluster Surface. Reversible Generation of Agostic (C–H–M) Hydrogens from Iron Hydrides (Fe–H–Fe) on a Saturated Triiron Cluster

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Bridging hydrogens are familiar structural features in borane, metallaborane, and metal cluster chemistry.<sup>1</sup> Although not as familiar, metal carbon bridging hydrogens, agostic hydrogens, have been identified in a significant number of hydrocarbyl-metal complexes.<sup>2</sup> We have recently reported the ferraboranes  $H-Fe_3(CO)_9BH_4$  (I)<sup>3</sup> and  $HFe_3(CO)_{10}BH_2$  (II) as well as the anions formed by respective cluster deprotonation.<sup>4</sup> The structures of I and II can be contrasted with those of the isoelectronic hydrocarbyl complexes IIIa and IVa.<sup>5</sup> The mobility of the hydrogens

(12) The 600-nm, 1-ps, 0.5-nJ output of a mode-locked  $Ar^+$  synchronously pumped dye laser was amplified to 2.5 mJ by using a four-stage dye amplifier pumped by a frequency-doubled Nd-YAG laser operating at 10 Hz. A 2.0-mJ pulse was used to generate a picosecond continuum probe pulse, while a 0.5-mJ pulse was used for sample excitation. Absorbance measurements were made with a double-beam spectrometer which employed optical multichannel detection. Time delays between pump and probe pulses were accomplished with an optical delay line.

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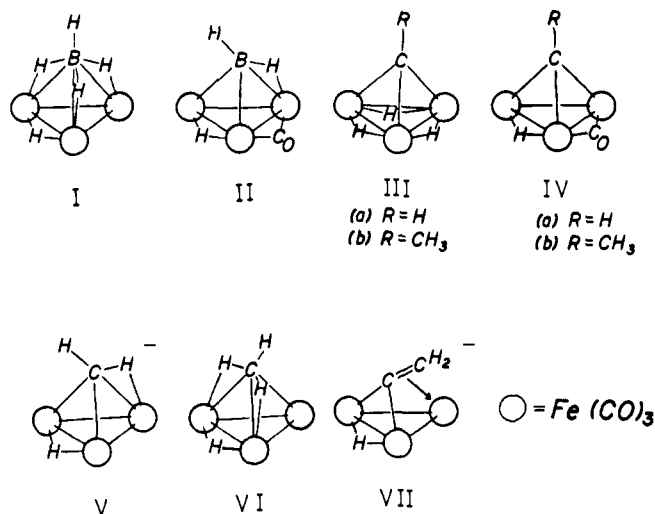
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on I and II and the increase in this mobility on deprotonation has led us to examine the behavior of IIIa and IIIb on deprotonation. The results demonstrate the net conversion of an Fe–H–Fe interaction to a C–H–Fe interaction on deprotonation of IIIa and the reverse on reprotonation. In contrast, deprotonation of IIIb results in H<sub>2</sub> elimination and the formation of a vinylidene cluster anion. These being saturated systems, we suggest relative charge effects are important in controlling the formation and destruction of C–H–M interactions in metal clusters.

Deprotonation of IIIa to form the PPN (bistriphenylphosphineiminium) salt was carried out<sup>6</sup> and, as expected, the infrared spectrum indicates molecular symmetry lower than C<sub>3v</sub>. Unexpectedly, however, the <sup>1</sup>H NMR at low temperature (Figure 1) exhibits three types of protons, one of which cannot result from a structure derived by simple proton removal from IIIa unless the hydrogens are rearranged. That is, the resonances at δ 6.6 and –20.3 can be attributed to CH and FeHFe protons on a structure like IIIa but that at δ –10.1 cannot. This chemical shift permits either a terminal FeH or an agostic<sup>2</sup> hydrogen. However, the <sup>13</sup>CH coupling constant strongly favors the latter. In addition, the δ 6.6 and –10.1 resonances exhibit an 18-Hz splitting, which was demonstrated by selective decoupling to be due to geminal HH coupling. This is strong evidence for a CH<sub>2</sub> unit in this anion. Thus, we suggest structure V as the structure of the anion,<sup>7</sup> i.e., an asymmetrically bound CH<sub>2</sub> fragment capping the metal triangle. On deprotonation, then, an Fe–H–Fe interaction has been converted into a C–H–Fe interaction.

Cluster rearrangements in trimetal systems that require an intermediate or transition state similar to structure V have been

(5) The ethylidene derivative IIIb has been fully described. Wong, K. S.; Fehlner, T. P. *J. Am. Chem. Soc.* **1981**, *103*, 966. Wong, K. S.; Haller, K. J.; Dutta, T. K.; Chipman, D. M.; Fehlner, T. P. *Inorg. Chem.* **1982**, *21*, 3197. DeKock, R. L.; Wong, K. S.; Fehlner, T. P. *Ibid.* **1982**, *21*, 3203.

(6) Treatment of 2 mmol of [(CO)<sub>4</sub>FeC(O)H] Na in THF (formed in situ by the reaction of NaHB(OCH<sub>3</sub>)<sub>3</sub> with Fe(CO)<sub>5</sub>) with 4 mmol of Fe(CO)<sub>5</sub> and 4 mmol of commercial BH<sub>3</sub>·THF at 25 °C for 1 h yielded a mixture of hydrocarbyl anions. Removal of the solvent followed by acidification with phosphoric acid and extraction with hexane yielded a mixture of neutral hydrocarbyl clusters. As IIIa and IVa,b deprotonate on silica gel, column chromatography followed by elution with CH<sub>3</sub>OH and centrifugal thin-layer chromatography on the acidified eluate under acidic conditions yielded 0.2 mmol of IIIa. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>, 20 °C) δ 11.5 (s, 1 H, J<sub>CH</sub> = 166 Hz), –24.3 (s, 3 H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>, 20 °C) {<sup>1</sup>H} 232.0 (s, 1 C), [coupled, d, J<sub>CH</sub> = 166 Hz], 205.4 (s, 9 C); mass spectrum, p<sup>+</sup> 436 (9 CO), Fe<sub>3</sub>C<sub>10</sub>H<sub>4</sub>O<sub>9</sub> (435.784 measured 435.790 calcd). Treatment of a hexane solution of IIIa with a methanol solution of PPNCl results in quantitative deprotonation. Extraction of the salt recovered from the methanol layer with (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O yields V. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>, –60 °C) δ 7.7–7.5 (m, 30 H), 6.6 (d, 1 H, J<sub>HH</sub> = 18, J<sub>CH</sub> = 150 Hz), –10.1 (d, 1 H, J<sub>HH</sub> = 18, J<sub>CH</sub> = 65 Hz), –20.3 (s, 1 H); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, –80 °C) {<sup>1</sup>H} δ 216.5 (2 CO), 215.4 (4 CO), 215.2 (1 CO), 214.4 (2 CO); δ 133.0, 131.3, 128.8, 26.2 (PPN<sup>+</sup>); δ 118.5 (μ-C) [selective {<sup>1</sup>H}]: δ <sup>1</sup>H –10.1, d, J<sub>CH</sub> = 155 Hz; δ <sup>1</sup>H 6.8, d, J<sub>CH</sub> = 67 Hz; IR (CH<sub>2</sub>C(O)CH<sub>3</sub>) 2045 w, 1997 s, 1975 s, 1951 s, 1930 sh, cm<sup>–1</sup>.

(7) Note that the <sup>1</sup>H chemical shifts of the analogous ferraborane II are strikingly similar to those of V<sup>4</sup> and the HH coupling constant is similar to that observed for the anion of I.

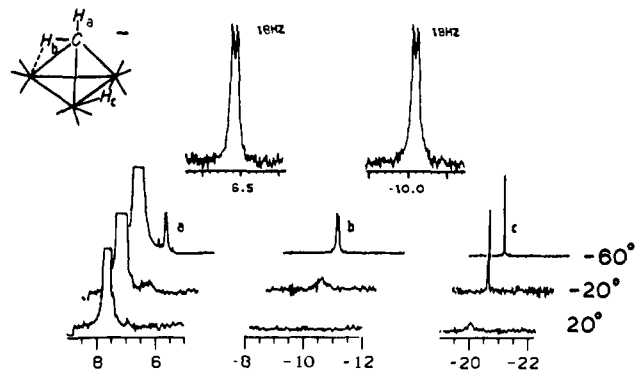


Figure 1. Proton NMR spectra 300 MHz, of [HFe<sub>3</sub>(CO)<sub>9</sub>CH<sub>2</sub>] PPN (V). The complex resonance at δ 7.6 is due to the PPN cation. The inset of the expanded δ 6.6 and –10.1 signals is taken from the spectrum of the N(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub><sup>+</sup> salt.

well documented.<sup>8–11</sup> However, V, constitutes the first example of the direct detection of such a species. On warming (Figure 1) the δ 6.6 and –10.1 signals broaden and collapse and then, at higher temperatures, the δ –20.3 signal also broadens and collapses. Coalescence was not observed below the decomposition temperature. Thus, although the low-energy structure of the anion possesses a C–H–Fe interaction, at higher temperatures the hydrogens appear to move freely over the available cluster sites. Indeed, spin saturation transfer experiments demonstrate exchange of the two CH protons even at –60 °C.

Protonation of V at low temperature results in the formation of an intermediate that, on the basis of the <sup>1</sup>H NMR, has more than one C–H–Fe interaction.<sup>12</sup> On warming, this intermediate decays into a second intermediate and finally into IIIa.<sup>13</sup> Hence we postulate kinetically controlled protonation on a C–Fe edge forming VI<sup>14</sup> which then ultimately rearranges to IIIa.<sup>15</sup> Clearly, the various isomers formed by hydrogen rearrangement do not differ by large energies.<sup>16</sup>

For contrast, as well as to investigate the role of a substituent on C–H–Fe formation, the deprotonation of IIIb<sup>5</sup> has been examined. A stronger base is required, e.g., N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, and deprotonation is accompanied by quantitative elimination of H<sub>2</sub> to form the known vinylidene cluster anion VII.<sup>17</sup> Protonation of VII in the presence of H<sub>2</sub> at 1 atm pressure and 25 °C regenerates IIIb in 70% yield. The mechanism of this interconversion is under investigation.

(8) For the triosmium analogue of IIIa exchange of the μ-H and CH protons has been demonstrated in an NMR study. VanderVelde, D. G.; Shapley, J. R. *Abstr. Pap.—Am. Chem. Soc.* **1984**, *187th*, INORG 128. See also: Shapley, J. R.; Strickland, D. S.; St. George, G. M.; Churchill, M. R.; Bueno, C. *Organometallics* **1983**, *2*, 185 and references therein.

(9) For the triruthenium analogue of IIIb with substituents X other than CH<sub>3</sub>, reductive elimination of CH<sub>3</sub>X in the presence of certain donor ligands suggests the intermediacy of C–H–Ru interactions. Duggan, T. P.; Barnett, D. J.; Muscatella, M. J.; Keister, J. B. *Abstr. Pap.—Am. Chem. Soc.* **1984**, *188th*, INORG. 251. See also: Bavaro, L. M.; Montangero, P.; Keister, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 4977 and references therein.

(10) In the triiron ketylidene system [Fe<sub>3</sub>(CO)<sub>9</sub>(CCO)]<sup>2–</sup> diprotonation leads to IVa. Kolis, J. W.; Holt, E. M.; Shriver, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 7307.

(11) Other related systems are reviewed in: Deeming, A. J. "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley: New York, 1980. Bradley, J. S. *Adv. Organomet. Chem.* **1983**, *22*, 1.

(12) An excess of CF<sub>3</sub>COOH was mixed with a solution of V in CD<sub>2</sub>Cl<sub>2</sub> at –80 °C. Resonances at δ –7.1 (3 H) and –20.8 (1 H) are attributed to VI.

(13) We have spectroscopic evidence for the existence of an isomer of IIIa existing in equilibrium with the characterized isomer in solution at 25 °C. This isomer has the same spectroscopic signature as the second intermediate. Isomerization in another iron cluster has been recently reported. Horwitz, C. P.; Shriver, D. F. *Organometallics* **1984**, *3*, 756.

(14) A static structure of VI with 3 CHFe and 1 FeHFe interactions is also possible. Despite uncertainty in the structure, it is clear that the initial site of protonation is on a FeC edge and is not the most stable one.

(15) Kinetic control of cluster protonation has been reported previously: Stevens, R. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1982**, *104*, 6454.

(16) We have pointed out that the differences between the η<sup>2</sup> and η<sup>1</sup> geometries for CH<sup>–</sup> in HFe<sub>4</sub>(CO)<sub>12</sub>CH are subtle ones. Fehlner, T. P.; Housecroft, C. E. *Organometallics* **1984**, *3*, 764.

(17) Lourdichi, M.; Mathieu, R. *Nouv. J. Chim.* **1982**, *6*, 231.

As compounds containing C-H-M interactions constitute attractive models for the activation of CH bonds,<sup>18</sup> the factors promoting the formation of agostic hydrogens have been extensively discussed.<sup>2</sup> In mononuclear systems, a minimal requirement appears to be an unsaturated metal site.<sup>2</sup> Even at the phenomenological level, these new results show that for metal clusters a model focusing on protons on a main group-metal cluster surface chasing available charge is more appropriate than CH bonds satisfying unsaturated metal centers. Although the full implications of these observations will only be revealed by appropriate theoretical treatments presently in progress, the formation of V clearly shows that multinuclear coordination of carbon induces significantly different behavior than mononuclear coordination.

**Acknowledgment.** The support of the National Science Foundation (CHE 8408251) and the aid of Dr. C. E. Housecroft with the <sup>13</sup>C NMR are gratefully acknowledged.

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## Tungsten(IV) Aqua Ion

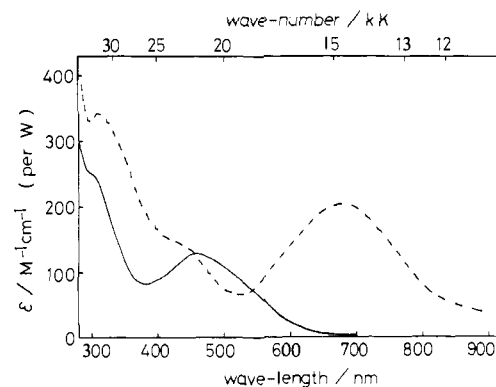
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Aqueous chemistry of molybdenum in oxidation states II-V is now well understood.<sup>1</sup> Aqua ions of molybdenum in these oxidation states show characteristic dimeric or trimeric structures containing metal-to-metal bonds,<sup>1</sup> and studies on their interconversion,<sup>2</sup> ligand substitution,<sup>3,4</sup> and redox properties<sup>1,4,5</sup> have provided basically important information on the reactivities of the metal-to-metal bonded cluster compounds. Other early transition metals in the second and the third transition series are also known to have extensive chemistry of metal-to-metal bond,<sup>6</sup> but their aqueous chemistry has been virtually unchallenged.<sup>7</sup> In this paper, we focus on tungsten(IV) as a comparison with the characteristic trimeric molybdenum(IV) ion  $[\text{Mo}_3(\mu_3\text{-O})(\mu\text{-O})_3(\text{H}_2\text{O})_9]^{4+}$ .<sup>8,9</sup> A number of tungsten(IV) trimers with different ligands are known.<sup>10</sup> Only one complex containing the  $\text{W}_3(\mu_3\text{-O})(\mu\text{-O})_3$  unit ( $[\text{W}_3\text{O}_4\text{F}_9]^{5-}$ ) has been reported,<sup>11</sup> however, and it was not known if a stable aqua ion of tungsten(IV) exists and is trimeric. We wish to report here the preparation and properties of the new orange tungsten(IV) aqua ion  $[\text{W}_3(\mu_3\text{-O})(\mu\text{-O})_3(\text{H}_2\text{O})_9]^{4+}$ .

Reaction of trivalent metal compounds with stoichiometric amounts of quinque- (or sexi-) valent ones, which is a standard



**Figure 1.** Absorption spectra of  $[\text{W}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$  (—) and its reduced form,  $\text{W}^{\text{III,III,IV}}(\text{aq})$ , (---) in 2 M *p*-toluenesulfonic acid.

method to prepare  $[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$ ,<sup>12</sup> did not give satisfactory results in the case of tungsten. Instead, following procedures that were carried out under a nitrogen atmosphere gave the desired tungsten(IV) aqua ion. Potassium hexachlorotungstate(IV),  $\text{K}_2[\text{WCl}_6]$  (8.5 g, 0.017 mmol),<sup>13</sup> in 100 cm<sup>3</sup> of 2 M HCl, was kept at 95 °C for 2.5 h and then treated with a cation exchange column (Dowex 50W-X8 in H<sup>+</sup> form) at room temperature. The orange aqua ion was eluted with 2 M *p*-toluenesulfonic acid (HPTS), indicating that the aqua ion carries similar charge (4+) to the molybdenum(IV) trimeric aqua ion.<sup>14,15</sup> The yield was ca. 25% based on tungsten. The orange ion was prepared also from  $(\text{NH}_4)_2[\text{W}^{\text{V}}\text{OCl}_5]$ .<sup>16</sup> A solution of the tungsten(V) complex in 2 M HCl was filtered to remove blue precipitate after heating at 95 °C for 2.5 h and the filtrate submitted to chromatography. The yield of the orange ion was ca. 13% based on tungsten. The ion was less stable than the molybdenum(IV) aqua ion and slowly oxidized within several hours under a nitrogen atmosphere at room temperature.

Tungsten content of the orange ion was determined by the atomic absorption analysis.<sup>17</sup> The oxidation state was determined by titration with cerium(IV). Results were consistent with the quadrivalent state of tungsten in the aqua ion (the oxidation equivalent is 1.9–2.0 times of the tungsten content).

The reaction of the tungsten(IV) aqua ion with thiocyanate, oxalate, and nitritotriacetate gave tungsten(IV) complexes of these ligands. The X-ray crystal analysis of the purple thiocyanate complex revealed the trinuclear structure,  $[\text{W}_3(\mu_3\text{-O})(\mu\text{-O})_3(\text{NCS})_9]^{5-}$ .<sup>18</sup> Reduction of the orange aqua ion in 2 M HPTS by zinc amalgam gave a green species, of which the oxidation state of tungsten was 3.3–3.4 as determined by the cerium(IV) titration. From these various observations, we conclude that the orange aqua ion is the trinuclear tungsten(IV) ion  $[\text{W}_3(\mu_3\text{-O})(\mu\text{-O})_3(\text{H}_2\text{O})_9]^{4+}$ .

The tungsten(IV) aqua ion shows an absorption peak at 455 nm ( $\epsilon$  125 M<sup>-1</sup> cm<sup>-1</sup> per W) in 2 M HPTS and in 2 M HClO<sub>4</sub> (Figure 1).<sup>19</sup> The green aqua ion,  $\text{W}_3^{\text{III,III,IV}}(\text{aq})$ , shows two peaks

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(3) For recent example: Finholt, J. E.; Leupin, P.; Sykes, A. G. *Inorg. Chem.* 1983, 22, 3315–3318 and references cited therein.

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(6) See, for example: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; pp 822–901.

(7) The dimeric tungsten(V) aqua ion is obtained as a reaction product on reacting  $[\text{W}^{\text{V}}_2\text{O}_4(\text{edta})]^{2-}$  ( $\text{edta}^{4-}$  = ethylenediaminetetraacetate(4-) ion) with 2 or 3 M HCl (Soares, A. B.; Taylor, R. C.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* 1980, 1101–1104).

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(9) (a) Murmann, R. K.; Shelton, M. E. *J. Am. Chem. Soc.* 1980, 102, 3984–3985. (b) Rogers, K. R.; Murmann, R. K.; Schlemper, E. O.; Shelton, M. E. *Inorg. Chem.* 1985, 24, 1313–1322.

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(13) Kennedy, D.; Peacock, R. D. *J. Chem. Soc.* 1963, 3392–3397.

(14) Another orange species, eluted with 1 M HPTS, degraded quickly after the elution. This species appears to contain coordinated chloride ion(s) as observed for the corresponding molybdenum(IV) species (Ojo, J. F.; Sasaki, Y.; Taylor, R. S.; Sykes, A. G. *Inorg. Chem.* 1976, 15, 1006–1009).

(15) We found that  $[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$  can be prepared from  $\text{K}_2\text{MoCl}_6$  similarly as the preparation of the tungsten(IV) aqua ion.

(16) Collenberg, O. *Z. Anorg. Allg. Chem.* 1918, 102, 247–276.

(17) Atomic absorption analysis of tungsten was seriously disturbed by various foreign ions involved in the solution. Thus the calibration curve was carefully determined in the presence of the same amount of foreign ions as the sample solution.

(18) Segawa, M.; Kabuto, C.; Sasaki, Y., unpublished results. The anion crystallizes as  $(\text{NH}_4)_2[(\text{C}_2\text{H}_5)_4\text{N}]_3[\text{W}_3\text{O}_4(\text{NCS})_9] \cdot n\text{H}_2\text{O}$ . Crystals belong to the monoclinic space group  $P2_1/C$  with 4 formula units in a cell with dimensions  $a = 22.065$  (3) Å,  $b = 14.819$  (2) Å,  $c = 19.896$  (2) Å,  $\beta = 96.73$  (3)°, and  $V = 6460.6$  (3) Å<sup>3</sup>. Refinement of the structure using 4331 reflections gave  $R = 0.084$ . Average bond distances and angles: W–W, 2.534; W–O(cap), 2.039; W–O(bridge), 1.911; W–N, 2.110 Å; W–O(cap)–W, 76.91°; W–O(bridge)–W, 83.10°.