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Polyoxometalates

Multiple Reversible Protonation of Polyoxoanion Surfaces: Direct Observation of Dynamic Structural Effects from Proton Transfer**

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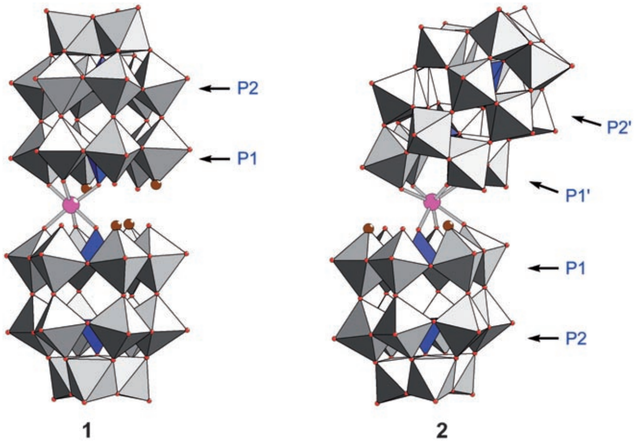
Proton transfer is one of the most fundamental reactions impacting myriad chemical, biological, and geological processes. As a consequence, single- and multiple-proton transfer events have been the subject of many books and reviews for decades.[1] For instance, protonation can profoundly influence the geometric and electronic structures as well as reactivities of metal oxides.[2] These properties, in turn, directly impact metal-oxide applications in catalysis, sensor technology, electrochemistry, and other areas.[3] Transition-metal oxygen anion clusters (polyoxometalates or "POMs")[4] have long been proposed as soluble models of metal-oxide-supported heterogeneous catalysts in proton transfer and electron transfer reactions where the solid phase is usually ill-defined from the molecular point of view. Recent interest in the structure of protonated POMs in the context of fuel cell electrolytes[5] derives, in part, from the high thermal stability and proton mobility in these systems. However, a detailed knowledge of some aspects of protonated POM systems still remains rather elusive despite years of investigation.[6] Unless both the structural consequences of protonation/deprotonation (static effects) and the nature of proton transfer processes (dynamic effects) are thoroughly characterized, the task of extracting unequivocal mechanistic information at the molecular level is highly problematic. On the basis of both experimental and theoretical evidence, the bridging oxygen atoms in POMs generally have a higher electron density and basicity than terminal oxygen atoms and are thus the predominant protonation sites, forming monoprotonated μ-OH group(s).[4b,6]

In contrast to previous work, we present the structural and spectroscopic studies of two related polyoxoanions, establishing that multiple diprotonated terminal oxygen ligands in polyoxoanions can be completely deprotonated and reprotonated. The unique situation of intramolecular hydrogen bonding in these systems is believed to play an important role in stabilizing the diprotonated configuration. Their distinct protonation behavior also suggests that the proton chemistry of lacunary species can be quite different from that of plenary POMs, on which most prior research is based. The studies herein provide additional insights into the chemistry of protons on polyoxoanion surfaces.

The complexes $[\{P_2W_{15}O_{54}(H_2O)_2\}_2Zr]^{12-}$ (**1**) and $[\{P_2W_{15}O_{54}(H_2O)_2\}Zr\{P_2W_{17}O_{61}\}]^{14-}$ (**2**) are prepared as dimethylammonium salts from the tri(tungsten)-vacant polyanion precursor α-$[P_2W_{15}O_{56}]^{12-}$, a ligand for which a high propensity and versatility in coordinating metal ions is well-documented. The solid-state structures of **1** and **2** (Figure 1) have been established by single-crystal X-ray diffraction,[7] and both complexes have been characterized by elemental analysis, thermogravimetry, potentiometric titration, and spectroscopic methods.



1 **2**

Figure 1. Solid-state structures of polyanions **1** and **2**. Terminal and bridging oxo groups on $\{WO_6\}$ octahedra (gray) and $\{PO_4\}$ tetrahedra (blue) are shown as small red spheres, while the terminal aqua ligands on W are highlighted as larger brown balls. Zr atoms are depicted as magenta spheres. Complex **1** (C_2 symmetry) has two unique phosphorus atoms: P1 and P2; **2** (C_1 symmetry) has four different phosphorus atoms: P1, P2, P1′, and P2′.

Polyanion **1** is composed of two $\{P_2W_{15}\}$ subunits on either side of a single six-coordinate Zr^{IV} center. Compound **1** possesses approximate C_2 symmetry with the twofold axis running through the Zr atom in the lacunary "pocket" that relates the two $\{P_2W_{15}\}$ units, which are slightly offset from each other. Close inspection of the lacunary pocket of **1** reveals that, among the four noncoordinating terminal oxo groups in each $\{P_2W_{15}\}$ unit, every second position is diprotonated. The W−OH$_2$ bond lengths (e.g. W12−O53, see Figure 2), averaging 2.20(2) Å, are significantly longer than those of their unprotonated counterparts (e.g. W11−O52), averaging 1.72(2) Å. Although a similar diprotonation pat-

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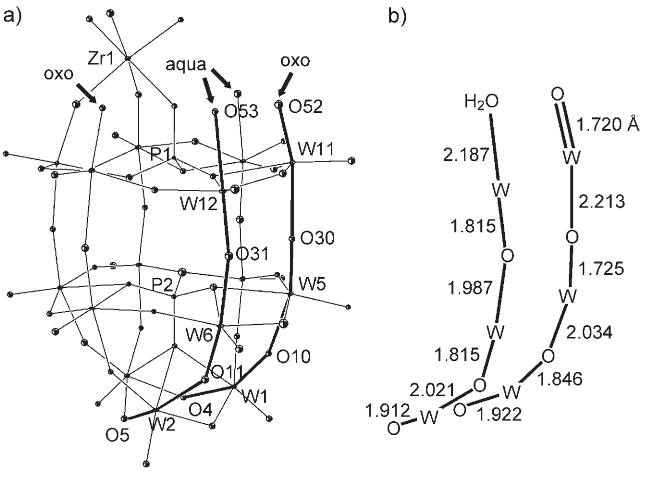

Figure 2. *Trans* bond alternation pattern in **1**. a) Only a half unit of **1** is shown for clarity. The two selected neighboring longitudinal chains are highlighted with darker bonds; b) the selected chains with W–O bond lengths (in Å).

tern on every second W=O terminal oxo group was observed in a few Keggin derivatives,[8] there has been no report of the reversible dynamic behavior that we discuss below. There is not yet an adequate explanation why some terminal oxygen atoms are diprotonated instead of all terminal oxygen atom being monoprotonated (delocalization of protonation). It would seem reasonable that the all-monoprotonated configuration would be at lower energy than the adopted alternating unprotonated–diprotonated configuration. A seemingly defensible rationale for the alternating protonation pattern is that it facilitates the formation of hydrogen-bonding donor–acceptor pairs by increasing the polarity of the $O^{\delta-}$–$H^{\delta+}\cdots O^{\delta-}$ units involving two adjacent oxygen atoms.[9] In fact, within the lacunary pocket of **1**, distances between the aqua oxygen atoms and their neighboring oxo groups (from the same and adjacent $\{P_2W_{15}\}$ units) range from 2.61(3) to 3.20(3) Å, indicating the formation of a complex network of intra-POM hydrogen bonds. A similar unprotonated–diprotonated hydrogen-bonding configuration is also found in anion **2**, where a seven-coordinate Zr^{IV} atom joins two different polyanion ligands: a protonated α-$[P_2W_{15}O_{54}(H_2O)_2]^{8-}$ ion and a monovacant, nonprotonated α_2-$[P_2W_{17}O_{61}]^{10-}$ ion.

Figure 2 also clearly documents the long-range pattern of *trans* bond length alternation,[10] a cooperative result of the *trans* effect as protonation withdraws electron density from all oxygen atoms throughout the $\{P_2W_{15}\}$ unit, not just from the protonated ones. On the basis of this static model, one can reasonably expect that proton transfer to or from terminal oxygen positions in the $\{P_2W_{15}\}$ moiety, if applicable, will create a "muscle-flexing"-like motion involving essentially all atoms, which should be reflected in turn by NMR chemical shift changes. Thus, with the sites of protonation pinpointed by crystallography and the long-range multibond static structural perturbation of diprotonation clear, we turned to NMR spectroscopy to assess possible dynamic effects of proton transfer. Attempts to directly observe these protons using ^{1}H NMR spectroscopy were hampered by the fast exchange of aqua ligand protons with the solvent, D_2O; additional difficulty stems from very large water and counterion peaks, as expected. However, solution ^{31}P NMR spectroscopy provides insightful information as it is very sensitive to nuclear motions within the POM framework.

Indeed, ^{31}P NMR experiments show that the chemical shifts are very sensitive to pH value.[11] The ^{31}P NMR spectrum of **1** (6 mM) in D_2O displays two peaks at $\delta = -7.09$ (P1) and −12.36 ppm (P2), consistent with the C_2 symmetry of the polyanion in the solid state. Despite its lacunary pocket, **1** is completely stable in aqueous solution over a wide pH range (3–9) at room temperature. This stability allows proton transfer reactions to proceed smoothly without inducing decomposition of the polyanion. Addition of base to this solution causes significant chemical shift movements (Figure 3 a), indicative of structural transformation associated with removing some of the aqua protons. Specifically, after the addition of one equivalent of NaOD (0.05 M), the P1 resonance moves downfield to $\delta = -6.87$ ppm, whereas the P2 resonance moves upfield to $\delta = -12.58$ ppm. The narrow peak widths in the NMR spectra indicate that the aqua, hydroxo, and/or oxo forms of **1** are all in the fast exchange limit on the NMR time scale. Further addition of OD^- is accompanied by continuous chemical shift movements until eight equivalents of base are added, consistent with deprotonation of all aqua sites to oxo groups. Significantly, we also find that these processes, monitored by ^{31}P NMR spectroscopy, are quantitatively reversed by successive addition of the same amount of acid (DCl, 0.05 M). Thus, the alternating diprotonation pattern is restored on the polyanion surface. Unfortunately, our efforts to crystallize deprotonated forms of **1** did not yield X-ray quality crystals, where the direct comparison of different forms could potentially afford additional insight.

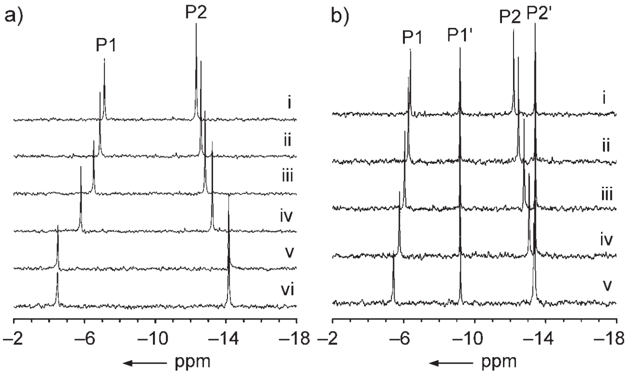

Figure 3. Effect of successively adding 0.05 M NaOH/D_2O solution to samples of a) **1** and b) **2** (both 6 mM in D_2O). ^{31}P NMR measured at 161.9 MHz relative to H_3PO_4 (85 %). Titration of **1**: a) i) No NaOD added; ii) 1; iii) 2; iv) 4; v) 8; and vi) 10 equiv of NaOD added. Titration of **2**: b) i) No NaOD added; ii) 0.25; iii) 0.50; iv) 1; and v) 2 equiv of NaOD added.

The titration of a solution of **2**, nevertheless, provides complementary evidence that fully supports the above arguments. Complex **2** (6 mM) in D_2O exhibits a four-line spectrum corresponding to the four unique phosphorus atoms in this C_1-symmetric anion. Upon addition of OD^-, the response of the four resonances is distinctly different (Figure 3b). One set of peaks ($\delta = -6.38$ and -12.21 ppm) shift downfield and upfield, respectively, analogous to the signals observed for **1**. Therefore, these two peaks in the spectrum of **2** are assigned to the protonated α-$[P_2W_{15}O_{54}(H_2O)_2]^{8-}$ unit (P1 and P2), which is effectively identical to the corresponding unit in **1**. The other two peaks ($\delta = -9.19$ and -13.41 ppm), in marked contrast, show no sign of movement; they are clearly attributed to the two phosphorus atoms (P1′ and P2′) on the α_2-$[P_2W_{17}O_{61}]^{10-}$ moiety, which is known to be stable towards protonation in the pH range of titration shown in Figure 3b (pH < 6). This result is in complete agreement with the solid-state structure and unambiguously demonstrates that proton transfer indeed takes place on the aqua oxygen positions. Unlike **1**, polyanion **2** starts to irreversibly decompose to unidentified species upon addition of more than 2.5 equivalents of NaOD (pD > 6), presumably owing to the instability of the $[P_2W_{17}O_{61}]^{10-}$ ligand at this high pH. However, for up to two equivalents of base, the chemical shift changes are also continuous and completely reversible.

Potentiometric titration experiments provide the final evidence in this study. They afford the stoichiometry of the multiple protonation events while confirming the implications of the X-ray crystallography and ^{31}P NMR spectroscopy experiments. Specifically, titration of **1** (Figure 4) establishes that it has eight titratable protons that are removed in two clear steps ($pK_{a1} \approx 4.5$ and $pK_{a2} \approx 5.8$).[12] These reproducible results indicate that the tetraaqua complex **1** behaves as a multisite "diprotic" Brønsted acid, with the removal of one proton from each of the four aqua groups in the primary stage (forming the all-hydroxy form of **1**, $[\{P_2W_{15}O_{54}(OH)_2\}_2Zr]^{16-}$) and further removal of the remaining four protons in the secondary stage (forming the unprotonated anion $[(P_2W_{15}O_{56})_2Zr]^{20-}$).

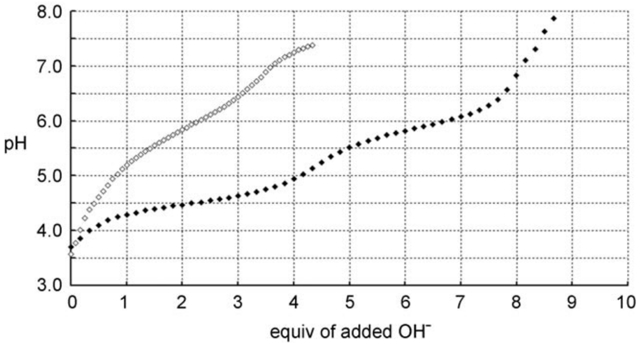

Figure 4. pH titration curves of **1** (◆) and **2** (◇).

$$[\{P_2W_{15}O_{54}(OH_2)_2\}_2Zr]^{12-} \xrightleftharpoons{-4\,H^+} [\{P_2W_{15}O_{54}(OH)_2\}_2Zr]^{16-} \xrightleftharpoons{-4\,H^+} [\{P_2W_{15}O_{56}\}_2Zr]^{20-} \quad (1)$$

However, the pH titration of **2** (Figure 4) is complicated by the competing decomposition reactions when more than two equivalents of base are added, and is thus not as informative as that of **1** in this more basic region. Consistent with the NMR experiments, the titration of **2** is completely reversible for up to two equivalents of base.

Herein, we have demonstrated the critical role of diprotonated aqua ligands in the dynamic proton chemistry of POMs. The complementary structural and spectroscopic evidence from examination of the two related complexes indicates that the protons of multiple terminal aqua ligands on the surfaces of polyoxotungstates can be removed in a stepwise and reversible fashion within the stability limit of the polyanions. The dynamic structural changes within the cluster framework of the polyoxoanions, induced by unusual quantitatively reversible multiple protonation behavior have been documented by solution ^{31}P NMR spectroscopy. Analogous long-range but readily reversed structural changes induced by multiple diprotonation of terminal oxygen sites may be operable in the surface layers of the metal oxides used as acid catalysts, proton conductors, and membrane-based sensors.

Experimental Section

The lacunary ligand $Na_{12}[P_2W_{15}O_{56}]\cdot 18\,H_2O$ was prepared according to the literature method.[13] The syntheses of complexes of **1** and **2** were discovered serendipitously during the course of our work on asymmetric (enantiopure) polyoxoanions.[14] The detailed synthetic procedures are as follows.

$[(CH_3)_2NH_2]_{12}\mathbf{1}\cdot 21\,H_2O$: A sample of D-saccharic acid (monopotassium salt; 0.17 g, 0.69 mmol) was dissolved in HCl solution (20 ml, 0.075 M), and $ZrOCl_2\cdot 8\,H_2O$ (0.18 g, 0.56 mmol) was added. Solid $Na_{12}[P_2W_{15}O_{56}]\cdot 18\,H_2O$ (1.0 g, 0.23 mmol) was quickly added in one portion with vigorous stirring. After stirring for 30 min at room temperature, $(CH_3)_2NH_2Cl$ (0.45 g, 5.5 mmol) was added to the clear solution, which was then cooled at 5 °C for 24 h, producing prismatic crystals (0.15 g, 15.3 % based on W).

$[(CH_3)_2NH_2]_{14}\mathbf{2}\cdot 27\,H_2O$: A sample of $ZrO(NO_3)_2\cdot 6\,H_2O$ (0.16 g, 0.47 mmol) was dissolved in H_2O (15 ml), and (+)-dimethyl L-tartrate (0.25 g, 1.4 mmol) was added. The mixture was then heated at reflux for 2 h before cooling to room temperature. $(CH_3)_2NH_2Cl$ (0.4 g, 4.9 mmol) was then added to this solution. Subsequently, solid $Na_{12}[P_2W_{15}O_{56}]\cdot 18\,H_2O$ (1.0 g, 0.23 mmol) was quickly added in one portion with vigorous stirring. After stirring for 5 min at room temperature, the solution was heated to 70 °C for 20 min. Slow evaporation of the solution at room temperature produced a needle-like crystalline solid, which was subsequently washed with ethyl alcohol (5 ml) and diethyl ether (5 ml). The crude product (0.25 g) was purified by recrystallization from HCl solution (14 ml, 0.05 M) saturated with $(CH_3)_2NH_2Cl$ (0.1 g) to yield a crystalline solid (0.22 g, 22.2 % based on W).

The pH titrations of **1** and **2** in aqueous solutions (0.5 mM) with 0.05 M NaOH or HCl to assess the protonation states were performed using a Corning 240 pH meter equipped with an Orion micro-pH combination electrode at room temperature. Acid/base titration experiments monitored by ^{31}P NMR spectroscopy were carried out in NMR tubes, in which the solutions were well-shaken upon the addition of deuterated acid or base.

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[1] a) R. P. Bell, *The Proton in Chemistry*, Cornell University Press, Ithaca, **1973**; b) *Proton Transfer in Hydrogen-Bonded Systems*, NATO ASI Series 291 (Ed.: T. Bountis), Plenum, New York, **1992**; c) G. A. Jeffrey, W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer, Berlin, **1991**; d) R. A. Copeland, S. I. Chan, *Annu. Rev. Phys. Chem.* **1989**, *40*, 671.

[2] Y. Izumi, K. Urabe, A. Onaka, *Zeolite, Clay, and Heteropoly Acid in Organic Reactions*, Kodansha, Tokyo, VCH, Weinheim, **1992**.

[3] G. E. Brown, Jr., *Science* **2001**, *294*, 67.

[4] a) M. T. Pope in *Comprehensive Coordination Chemistry II*, *Vol. 4* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier Science, New York, **2004**, chap. 4.10, pp. 635–678; b) C. L. Hill in *Comprehensive Coordination Chemistry II*, *Vol. 4* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier Science, New York, **2004**, chap. 4.10, pp. 679–759; c) L. Cronin in *Comprehensive Coordination Chemistry II*, *Vol. 7* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier Science, New York, **2004**, chap. 7.1, pp. 1–56; d) *Polyoxometalate Chemistry for Nano-Composite Design* (Eds.: T. Yamase, M. T. Pope), Kluwer, Dordrecht, **2002**; e) *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications* (Eds.: M. T. Pope, A. Müller), Kluwer, Dordrecht, **2001**; f) M. Misono, *Chem. Commun.* **2001**, 1141.

[5] a) D. E. Katsoulis, *Chem. Rev.* **1998**, *98*, 359; b) A. B. Bourlinos, K. Raman, R. Herrera, Q. Zhang, L. A. Archer, E. P. Giannelis, *J. Am. Chem. Soc.* **2004**, *126*, 15358; c) B. Smarsly, H. Kaper, *Angew. Chem.* **2005**, *117*, 3876; *Angew. Chem. Int. Ed.* **2005**, *44*, 3809.

[6] For representative experimental and theoretical work in this area, see: a) A. Dolbecq, A. Guirauden, M. Fourmigué, K. Boubekeur, P. Batail, M.-M. Rohmer, M. Bénard, C. Coulon, M. Sallé, P. Blanchard, *J. Chem. Soc. Dalton Trans.* **1999**, 1241; b) V. W. Day, W. G. Klemperer, D. J. Maltbie, *J. Am. Chem. Soc.* **1987**, *109*, 2991; c) T. M. Che, V. W. Day, L. C. Francesconi, W. G. Klemperer, D. J. Main, A. Yagasaki, O. M. Yaghi, *Inorg. Chem.* **1992**, *31*, 2920; d) R. G. Finke, B. Rapko, R. J. Saxton, P. J. Domaille, *J. Am. Chem. Soc.* **1986**, *108*, 2947; e) X. López, C. Bo, J. M. Poblet, *J. Am. Chem. Soc.* **2002**, *124*, 12574, and references therein.

[7] X-ray crystallography: Crystal data for **1** at 173 K: triclinic, space group $P1$, $a=15.325(2)$, $b=21.014(3)$, $c=22.173(3)$ Å, $\alpha=83.639(3)$, $\beta=89.636(3)$, $\gamma=84.175(3)°$, $V=7059.8(18)$ Å^3, $Z=2$. The refinement converged to $R(F_o)=0.0715$, $wR(F_o^2)=0.1948$, and GOF = 1.012 for 67054 reflections with $I>2\sigma(I)$. Crystal data for **2** at 173 K: triclinic, space group $P\bar{1}$, $a=13.370(2)$, $b=13.400(2)$, $c=45.498(8)$ Å, $\alpha=88.422(4)$, $\beta=82.290(4)$, $\gamma=61.940(4)°$, $V=7122(2)$ Å^3, $Z=2$. The refinement converged to $R(F_o)=0.0526$, $wR(F_o^2)=0.1027$, and GOF = 1.027 for 25554 reflections with $I>2\sigma(I)$. Details of structural solution and refinement can be found in the Supporting Information. CCDC-631877 and 631878 (**1** and **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[8] a) N. Leclerc-Laronze, M. Haouas, J. Marrot, F. Taulelle, G. Hervé, *Angew. Chem.* **2006**, *118*, 145; *Angew. Chem. Int. Ed.* **2006**, *45*, 139; b) K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Kikichi, N. Mizuno, *Science* **2003**, *300*, 964; c) D. G. Musaev, K Morokuma, Y. V. Geletii, C. L. Hill, *Inorg. Chem.* **2004**, *43*, 7702; d) B. Hedman, *Acta Chem. Scand. Ser. A* **1978**, *32*, 439.

[9] T. Steiner, *Angew. Chem.* **2002**, *114*, 50; *Angew. Chem. Int. Ed.* **2002**, *41*, 48.

[10] Despite the fact the long/short bond length phenomenon has been observed in structural coordination chemistry dating back to Pauling and that analogous alternation of *trans* bond lengths was noted in a tetrameric Keggin complex by Hervé and coworkers[8a] and in a few isopolyvanadates by Klemperer and coworkers,[6b] the associated proton transfer processes themselves have barely been studied; see: L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Drystals; An Introduction to Modern Structural Chemistry*, 3rd ed., Cornell University Press, Ithaca, **1960**.

[11] pH dependence of ^{31}P NMR chemical shifts has been noticed in a wide range of the phosphorus-containing POMs. For examples, see reference [6d] and: a) C. Rong, M. T. Pope, *J. Am. Chem. Soc.* **1992**, *114*, 2932; b) F. Taube, I. Andersson, S. Angus-Dunne, A. Bodor, I. Tóth, L. Pettersson, *Dalton Trans.* **2003**, 2512.

[12] The observed pK_a values might be slightly different from their true values since the dissociation constants are too close to each other (i.e. $\Delta pK_i<4$) for the two stages to be distinguished quantitatively.

[13] R. Contant, *Inorg. Synth.* **1990**, *27*, 106.

[14] a) X. Fang, T. M. Anderson, C. L. Hill, *Angew. Chem.* **2005**, *117*, 3606; *Angew. Chem. Int. Ed.* **2005**, *44*, 3540; b) X. Fang, T. M. Anderson, Y. Hou, C. L. Hill, *Chem. Commun.* **2005**, 5044.

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