Heteropolyniobates

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Soluble Heteropolyniobates from the Bottom of Group IA**

Yu Hou, May Nyman, and Mark A. Rodriguez*

The Group V polyoxometalates (POMs) of Nb and Ta are considerably different from the well-known V, Mo, and W POMs. The latter self-assemble via acidification of aqueous monomeric oxoanions:[1] many cluster geometries and dimensions[2] are accessible with addenda metals from across the transition-metal,[3] rare-earth,[4] and even actinide series,[5] and they have rich, accessible redox chemistry. Nb and Ta POMs assemble and are stable only in highly alkaline solutions, limiting chemistry with most addenda metals, and are devoid of aqueous redox chemistry.[6] The most enigmatic characteristic of polyoxoniobates (PONb) is illustrated in the hexametalate series $[Nb_6O_{19}]^{8-}$. This is the only PONb cluster thus far that crystallizes as salts with all alkali-metal counterions,[7] and the solubility trend (Cs salt most soluble, Li salt least soluble) is opposite what is expected from classical aqueous behavior—this trend is rarely observed for water-soluble salts. We have exploited this unexpected solubility phenomenon to probe ion association in solution and found that $Cs_8[Nb_6O_{19}]$ and $Rb_8[Nb_6O_{19}]$ are dissolved as essentially neutral species with Cs/Rb directly bonded to the eight faces of the octavalent cluster,[8] further mystifying the profound solubility trend of $[Nb_6O_{19}]^{8-}$. The interrelated phenomena of solubility and ion pairing in aqueous media are ubiquitous, affecting many synthetic and natural processes (i.e. contaminant transport, crystallization and dissolution, self-assembly, electron transfer),[9] and their importance in POM chemistry has also been recognized.[10] PONbs provide a rare model system for investigating these universal aqueous processes. Herein we present a simple addendum to the general synthesis of heteropolyniobates,[11] which provides highly-soluble K^+, Rb^+, and Cs^+ heteropolyniobate salts, opening up new possibilities for this emergent branch of POM chemistry. Furthermore, a new POM geometry is reported that is a "hybrid" between the most common POM geometries, the Lindqvist ion and the Keggin ion.

Heteropolyniobates such as the Keggin derivatives were only first reported in 2002,[11] with the use of relatively brief hydrothermal processing and a narrow pH range (10.5–12.5). This general procedure afforded $K_{12}[Ti_2O_2][SiNb_{12}O_{40}]\cdot 16H_2O$ (**A**),[11] $Na_{14}[H_2Si_4Nb_{16}O_{56}]\cdot 45.5H_2O$ (**B**),[11] $Na_{16}[TNb_{12}O_{40}]\cdot 4H_2O$ (T = Si,Ge) (**C**),[12] $Na_{12}[Ti_2O_2][TNb_{12}O_{40}]\cdot xH_2O$ and $Na_{10}[Nb_2O_2][TNb_{12}O_{40}]\cdot xH_2O$ (T = Si or Ge) (**D**),[13] $Na_{15}[(PO_2)_3PNb_9O_{34}]\cdot 22H_2O$ (**E**),[14] $K_{10}[Nb_2O_2][GeNb_{12}O_{40}]\cdot 11H_2O$ (**F**),[15] $Li_{13}K[SiNb_{12}(OH)_2O_{38}]\cdot 17H_2O$ (**G**),[7b] and most recently $K_{10}[Nb_2O_2(H_2O)_2][SiNb_{12}O_{40}]\cdot 12H_2O$ (**H**).[16] Many of these are composed of polyanions linked into framework-like layers or chains through corner- (**H**) or edge-sharing of Ti=O and Nb=O caps (**A**, **D**, and **F**). Even those clusters that are considered to be isolated in the crystalline lattice, separated only by water molecules and alkali-metal counterions (**C**, **E**, and **G**), are insoluble, and thus neither solution characterizations nor solution stabilities were documented. The one exception is **B**, yet its solubility is also limited. We presume **B** is more soluble because its charge density (defined as charge/number cluster atoms) is lower, more comparable to that of the Group VI polyoxometalates.[6]

Thus far, no heteropolyniobates (i.e. Keggin derivatives) of Cs or Rb have been produced to determine if the inverse solubility trend is universal for PONb. Yet the Li, Na, and K PONb salts listed above are sparingly soluble, suggesting this reverse solubility trend is not limited to the hexametalate. Herein we report a general procedure that provides pure Rb and Cs heteropolyniobates, illustrated by two examples, the α-Keggin ion and an unprecedented cluster geometry that is a fusion of two Lindqvist ions and a Keggin-ion fragment, $[SiNb_{18}O_{54}]^{14-}$ (**1**). All are extremely soluble and therefore characterizable by solution techniques such as NMR spectroscopy and ESI-MS. With this discovery, we show that the unprecedented solubility trend of alkali-metal POM salts is indeed universal for PONb chemistry. This opens up new possibilities for exploring solution-phase applications and behavior, especially for those applications considered promising for PONbs, including homogeneous catalysis and microbiological applications.

Compounds $Cs_{13}Na[SiNb_{18}O_{54}]\cdot 22H_2O$ (**Cs1**), $Rb_{12}Na_2[SiNb_{18}O_{54}]\cdot 25H_2O$ (**Rb1**), and $K_{10}Na_2[H_2SiNb_{18}O_{54}]\cdot 33H_2O$ (**K1**), were prepared hydrothermally using alkali-metal salts (Cs, Rb, and K) of $[Nb_6O_{19}]^{8-}$ as the Nb and counterion source along with sodium silicate as Si heteroatom precursor. Hydrothermal processing produced clear solutions, and slow vapor diffusion of methanol into the aqueous reaction solution gave single crystals of **Cs1**, **Rb1**, and **K1**. Employing this diffusion method is imperative to obtain these three compounds. For instance, if the mother liquor is instead evaporated after hydrothermal processing, a gel-like phase precipitates. The mother liquor from which polyanion **1** will crystallize requires a Si/Nb ratio of 1:18–1:24 and a pH value of 12.5–13.0. The analogous reaction with $Na_7[HNb_6O_{19}]\cdot 14H_2O$[7c] only gave the starting material. The synthesis of the α-Keggin compound $Rb_{13}[H_3SiNb_{12}O_{40}]\cdot 30H_2O$ (**Rb2**) is similar to that reported previously for $Na_{16}[SiNb_{12}O_{40}]\cdot 4H_2O$.[12] However, while the sodium salt of

[*] Dr. Y. Hou, Dr. M. Nyman, Dr. M. A. Rodriguez
Sandia National Laboratories
Albuquerque, NM, 87185 (USA)
E-mail: mdnyman@sandia.gov

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the dodecaniobate Keggin structure was obtained immediately upon cooling the reaction solution to room temperature, the Rb salt is again crystallized by diffusion of methanol into the reaction solution.

Compounds **Cs1**, **Rb1**, and **K1** contain the isostructural $[SiNb_{18}O_{54}]^{14-}$ polyanion which is shown in Figure 1. It consists of two complete $[Nb_6O_{19}]^{8-}$ Lindqvist units which are linked by a $[SiNb_6O_{26}]$ Keggin fragment through eight Nb-O-Nb bonds and two Si-O-Nb bonds through corner-sharing to form a C-shaped structure. The geometry of this polyanion has not been recognized previously in any POM systems. The $[SiNb_6O_{26}]$ unit is a B-type hexavacant Keggin fragment which is formed by removing two triads of corner-sharing NbO_6 octahedra from the plenary α-Keggin cluster. In comparison, A-type hexavacant can be described as a half unit of the hexavacant Wells-Dawson structure presented by $[X_2W_{12}O_{40}]^{14-}$, in which three WO_6 octahedra have been removed from three different W_3O_{13} triads in each half of the $[X_2W_{12}O_{48}]^{14-}$ polyanions. This is the first observation of the hexavacant Keggin structural unit in polyoxoniobate chemistry, although there are examples in polyoxotungstate chemistry.[17] The two Si–O bonds connected to the Lindqvist units are slightly longer than those that are linked to the triad in the half Keggin units (see Table S2 in the Supporting Information (SI)). Nb–O_t (t = terminal) bonds range from 1.72 to 1.81 Å, Nb–O_b (b = bridging) bonds range from 1.80 to 2.21 Å, and Nb–O_c (c = central) bonds range from 2.14 to 2.57 Å (see Table S2 in the SI).

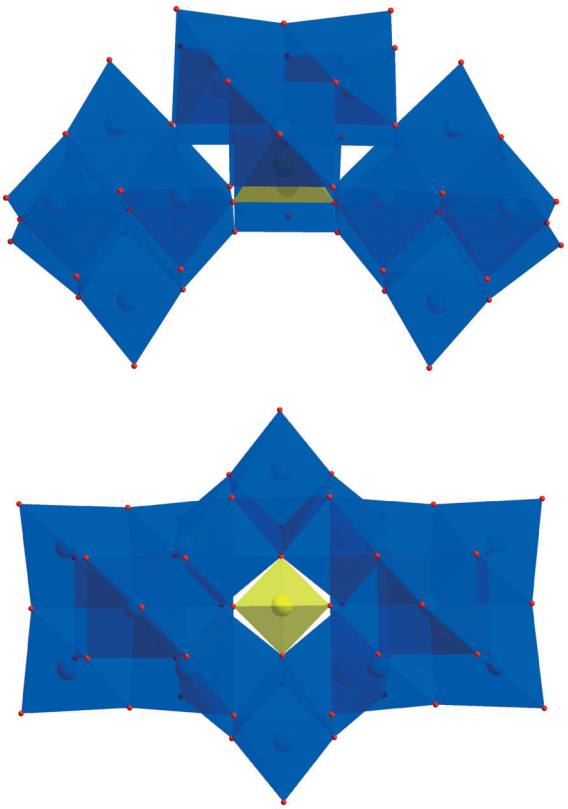

Figure 1. The structure of polyanion **1** in polyhedral representation; blue Nb, yellow Si, red oxygen.

Bond valence sum (BVS) calculations and charge balance requirements for **Cs1** and **Rb1** all support chemical and structural models without protons associated with the cluster. The 14 charge-balancing cations per cluster (thirteen Cs^+ ions and one Na^+ ion in **Cs1**; 12 Rb^+ ions and 2 Na^+ ions in **Rb1**) are found in 14 fully occupied crystallographic sites. It is worth to mention that in both compounds **Cs1** and **Rb1**, Cs^+ and Rb^+ ions, but not Na^+ ions, are associated with the $[SiNb_{18}O_{54}]^{14-}$ cluster through 1–5 bonds. This phenomenon has also been found in the compound $Cs_6Na_2[Nb_6O_{19}]\cdot 18H_2O$[7a] with six Cs^+ ions associated with the Lindqvist cluster, and two Na^+ ions hydrated and not directly bonded to the cluster. In the structures of **Cs1** and **Rb1**, two Cs^+ or Rb^+ ions, respectively, bond inside the cavity of the Keggin fragment, which likely help stabilize the C-shaped structure. These alkali-metal ions form four bonds each with Nb–O–Nb bridging oxygen atoms of polyanion **1**, and each bridges to a second polyanion cluster. This is typical of Cs or Rb in POM lattices and is usually indicative of poor solubility, yet all salts of **1** are highly soluble, even hygroscopic. The **K1** lattice contains $10\,K^+$ and $2\,Na^+$ ions, which suggests the polyanion in **K1** should be diprotonated. We could not locate the two proton positions by BVS calculations; therefore, they are likely disordered in the structure. One K^+ ion is located in the cavity, deeper than the Rb or Cs centers in their respective structures, and forms two bonds to the Si–O–Nb bridging oxygen atoms and four additional bonds to Nb–O–Nb bridging oxygen atoms. The K^+ ion does not bridge to additional polyanions. It is therefore self-evident that K^+ has the ideal size to fit inside the cavity.

The sodium ions in all three structures of **1** obviously are from the sodium silicate precursor. However, if the synthesis is done without intentionally added Na^+ (i.e. tetraethylorthosilicate as Si precursor) small amounts of crystalline **1** still form, the Na^+ obviously scavenged from impurities such as in the niobium oxide which is the precursor for the synthesis of alkali-metal salts of $[Nb_6O_{19}]^{8-}$.[7a] Qualitatively, we observe that the rate (Cs < Rb < K) of crystallization correlates with the alkali metal, suggesting the Cs salt is indeed the most soluble, the K salt is the least soluble and the Rb salt is intermediate. Furthermore, the yields are relatively low and follow this same solubility trend, indicating the high solubility is the limit in obtaining higher yields in reasonable time.

Polyanion **2** presents the well-known Keggin structure with Rb^+ as counterion. Its synthesis differs from that of **1** in two ways: 1) the Nb/Si ratio is much lower (ca. 3:1), and 2) Nb_2O_5 is utilized as a precursor instead of the Lindqvist ion. One could argue that both parameters may play a role in the final product. An interesting feature of this polyanion is that the central SiO_4 exhibits pseudo-tetrahedral geometry with one Si–O bond (1.671 Å) longer than the other three Si–O bonds (1.634 Å). There are thirteen charge-balancing Rb^+ counterions per cluster found in the lattice, indicating the cluster is triply protonated. Again, BVS calculations on the $[SiNb_{12}O_{40}]^{16-}$ Keggin unit did not locate the positions of these protons, which means they are disordered, most likely on bridging O_b oxygen atoms. This is certainly not unprecedented and was observed previously in PONb clusters.[7a,b,18] Furthermore, alcohol diffusion as a method of crystallization

induces ion pairing, even H^+–polyanion association, whereas crystallization directly from water more often produces unprotonated PONb clusters. This crystallization trend has been demonstrated in the series of hexaniobate Lindqvist salts.[7a] Like the $[SiNb_{18}O_{54}]^{14-}$ polyanion, Rb^+ cations are directly bonded to each $[H_3SiNb_{12}O_{40}]^{13-}$ Keggin ion in the lattice, with 2–6 Rb–O_b or Rb–O_t bonds per Rb^+ ion. The Rb salt of α-$[SiNb_{12}O_{40}]^{16-}$ is considerably more soluble than the previously reported Na, K, and Li salts in that 1) it could only be crystallized from the mother liquor by methanol diffusion, and 2) it is readily redissolved and shown to be stable by ^{29}Si NMR spectroscopy (see below). This is consistent with the reverse solubility trend observed previously for $[Nb_6O_{19}]^{8-}$, increased solubility with larger alkali-metal radius, and increased direct cation–anion association.

The high solubility of Cs, Rb, and K salts of **1** and **Rb2** provided an unprecedented opportunity for the characterization of heteropolyniobate Keggin derivatives in aqueous solution. The ^{29}Si NMR spectra of **Cs1**, **Rb1**, and **K1** recorded in D_2O solution agree with the structures determined by single-crystal X-ray diffraction. Each spectrum features a single peak at $\delta = -77.7$ (**Cs1**), −77.5 (**Rb1**), and −77.2 ppm (**K1**), which indicates that there are no impurities or any minor phases containing Si (Figure 2 and SI). We have also determined by ^{29}Si NMR spectroscopy that polyanion **1** is stable in aqueous solution, without any added base or electrolytes. Furthermore, powder diffraction of the crystalline salts revealed that the single-crystal structures obtained are representative of the bulk material (see Figure S1 in the SI). The solution ^{29}Si NMR spectrum of **Rb2** also shows one single peak at $\delta = -72.6$ ppm (Figure 2), and the solution is also stable over time. The peak position matches that observed by solid-state NMR spectroscopy of the Na salt of the siliconiobate Keggin ion.[12]

Since the salts of **1** and **Rb2** could be crystallized from the mother liquor only by alcohol diffusion, we wanted to investigate the effect of hydrothermal processing versus the effect of alcohol diffusion on the self-assembly of the Nb_{12} and Nb_{18} polyanions. Furthermore, we were interested in determining if the low yields were a result of mixed species in the reaction solution or of high solubility and thus low crystallization rate. We utilized ESI-MS (electrospray-ionization mass spectrometry) to determine what species are present in the mother liquor in comparison to a solution in which the pure, crystalline polyanion salt is redissolved. For **Cs1**, we found that the Nb_{18} cluster (and fragments thereof) with associated Cs^+, Na^+, and H^+ ions dominated both the hydrothermal reaction solution as well as the solution of pure, redissolved **Cs1**. (Figure 3; see also Table S3 and Figure S8 in the SI). Thus the function of the hydrothermal processing is to provide the energy (likely aided by protonation[19]) to fragment the Lindqvist ions so they may react with SiO_4, the end result being self-assembly of heteropolyanions. The methanol is merely the non-solvent to provide solution conditions conducive to crystallization of the very soluble Rb, Cs, and sometimes K salts of heteropolyniobates.

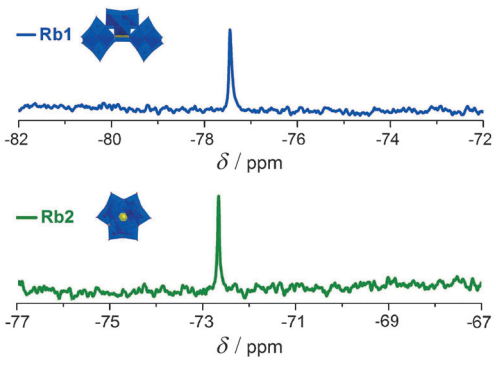

Figure 2. ^{29}Si NMR spectra of **Rb1** and **Rb2** in D_2O. See SI for spectra of **K1** and **Cs1**.

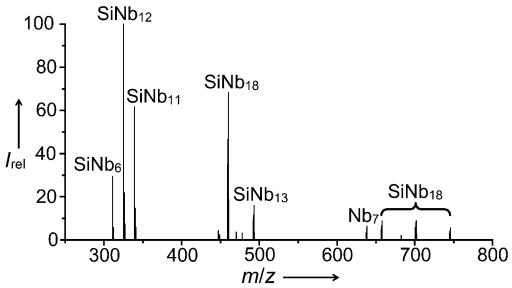

Figure 3. ESI-MS of **Cs1**, fragmentation voltage 50 V.

The studies reported here have revealed the universality of the rare solubility trend of polyoxoniobates, first observed for the $[Nb_6O_{19}]^{8-}$ Lindqvist ion. That is, PONb salts of Rb^+ and Cs^+ have excellent water solubility while Li^+ and Na^+ provide poor solubility, even linked frameworks, and K^+ has provided examples of both linked frameworks[15] and soluble clusters.[7a] Furthermore, for the first time, we are able to characterize the dodecaniobate Keggin ion in solution and have confirmed that it is indeed stable. This opens the possibility to investigate further chemistry and applications of heteropolyniobates, including ion association in solution, incorporation into functional surfaces and materials, homogeneous catalysis, and microbiological applications. In addition to **1**, we have identified other unprecedented polyniobate geometries and compositions (in both solid state and solution) utilizing the simple synthetic strategy introduced here, and these will be reported in due time.

Experimental Section

General methods and instrumentation are summarized in the SI.

Synthesis of **Cs1**: $Cs_8[Nb_6O_{19}]\cdot 14H_2O$ (0.958 g, 0.44 mmol) and $Na_2SiO_3\cdot 9H_2O$ (0.041 g, 0.146 mmol) were combined in 8 mL of deionized water in a 23 mL Teflon liner for a Parr reactor. The mixture was stirred for 10 min and placed in an oven at 190 °C for 19 h, resulting in a clear solution after cooling to room temperature. Colorless crystals were obtained by diffusion of methanol into the reaction solution after 8 days with 15 % yield based on Si.

Synthesis of **Rb1**: The synthetic procedure was similar to that for **Cs1**, but using $Rb_8[Nb_6O_{19}]\cdot 14H_2O$ (0.389 g, 0.22 mmol) and $Na_2SiO_3\cdot 9H_2O$ (0.021 g, 0.073 mmol). Colorless crystals suitable for

X-ray diffraction were formed by diffusion of methanol into the reaction solution after 5 days with 21% yield based on Si.

Synthesis of **K1**: The synthetic procedure was similar to that for **Cs1**, but using $K_8[Nb_6O_{19}]\cdot 16H_2O$ (0.321 g, 0.22 mmol) and $Na_2SiO_3\cdot 9H_2O$ (0.021 g, 0.073 mmol). Single crystals for X-ray diffraction were obtained by diffusion of methanol into the reaction solution after 4 days with 28% yield based on Si.

Synthesis of **Rb2**: RbOH (0.364 g, 6.5 mmol) was dissolved in H_2O (8 mL). Amorphous Nb_2O_5 (0.35 g, 1.3 mmol) and tetraethylorthosilicate (TEOS; 0.18 g, 0.9 mmol) were added and stirred at room temperature for 30 min. The mixture was transferred into a 23 mL autoclave and placed in an oven at 190 °C for 20 h, forming a clear solution. Diffusion of methanol into the reaction solution yielded a white solid. Redissolving of this white solid in a minimum amount of water and repeated diffusion of methanol into this solution yielded the single-crystal-quality product **Rb2** (yield 26% based on Nb).

Single-crystal X-ray diffraction of **Cs1**, **Rb1**, **K1**, and **Rb2** was performed at 100 K on a Bruker AXS SMART-CCD diffractometer with graphite monochromated $Mo_{K\alpha}$ (0.71073 Å) radiation. Data collection and reduction were carried out with SMART 5.054 (Bruker, 1998) and SAINT 6.02 (Bruker, 2001) software, respectively. Numerical absorption correction from face indexing was applied. The structures were solved by Direct Methods (program SIR97) and refined by full-matrix least-squares on F^2 (SHELX97). All subsequent structure solutions and refinements were performed within the WinGX system. **Cs1**: $H_{44}Cs_{13}NaSiNb_{18}O_{76}$, tetragonal, $P4_2/ncm$, $a=16.8305(13)$, $b=16.8305(13)$, $c=28.914(2)$ Å, $V=8190.3(11)$ Å^3, $Z=4$, $M=4711.01$, $\rho_{calcd}=3.785$ Mg m^{-3}; $\mu(Mo_{K\alpha})=8.243$ mm^{-1}; $1.41\le\theta\le25.00°$. **Rb1**: $H_{50}Rb_{12}Na_2SiNb_{18}O_{79}$, triclinic, $P\bar{1}$, $a=14.045(5)$, $b=16.332(6)$, $c=20.579(8)$ Å, $\alpha=74.964(4)$, $\beta=73.149(4)$, $\gamma=69.597(4)°$, $V=4168(3)$ Å^3, $Z=2$, $M=4079.20$, $\rho_{calcd}=3.216$ Mg m^{-3}; $\mu(Mo_{K\alpha})=9.475$ mm^{-1}; $1.35\le\theta\le23.57°$. Compound **K1**: $H_{68}K_{10}Na_2SiNb_{18}O_{87}$, orthorhombic, $P2_12_12_1$, $a=18.540(2)$, $b=19.390(2)$, $c=24.774(3)$ Å, $\alpha=\beta=\gamma=90°$, $V=8906.1(17)$ Å^3, $Z=4$, $M=3595.99$, $\rho_{calcd}=2.585$ Mg m^{-3}; $\mu(Mo_{K\alpha})=2.824$ mm^{-1}; $1.52\le\theta\le28.16°$. **Rb2**: $H_{63}Rb_{13}SiNb_{12}O_{70}$, trigonal, $R3$, $a=21.1506(18)$, $b=21.1506(18)$, $c=12.2109(10)$ Å, $\alpha=\beta=90$, $\gamma=120°$, $V=3429.84$ Å^3, $Z=3$, $M=4036.09$, $\rho_{calcd}=3.553$ Mg m^{-3}; $\mu(Mo_{K\alpha})=12.217$ mm^{-1}; $1.93\le\theta\le27.44°$. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD -423225 (**Rb1**), -423226 (**Rb2**), -423227 (**Cs1**), and -423228 (**K1**).

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[1] a) M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, **1983**; b) M. T. Pope, A. Muller, *Angew. Chem.* **1991**, *103*, 56; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34.

[2] a) W. G. Klemperer, T. A. Marquart, O. M. Yaghi, *Angew. Chem.* **1992**, *104*, 51; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 49; b) A. Müller, P. Kogerler, A. W. M. Dress, *Coord. Chem. Rev.* **2001**, *222*, 193.

[3] a) U. Kortz, A. Muller, J. van Slageren, J. Schnack, N. S. Dalal, M. Dressel, *Coord. Chem. Rev.* **2009**, *253*, 2315; b) T. M. Anderson, W. A. Neiwert, M. L. Kirk, P. M. B. Piccoli, A. J. Schultz, T. F. Koetzle, D. G. Musaev, K. Morokuma, R. Cao, C. L. Hill, *Science* **2004**, *306*, 2074.

[4] a) Q. H. Luo, R. C. Howell, M. Dankova, J. Bartis, C. W. Williams, W. D. Horrocks, V. G. Young, A. L. Rheingold, L. C. Francesconi, M. R. Antonio, *Inorg. Chem.* **2001**, *40*, 1894; b) A. Dolbecq, P. Mialane, L. Lisnard, J. Marrot, F. Secheresse, *Chem. Eur. J.* **2003**, *9*, 2914; c) Y. V. Geletii, B. Botar, P. Koegerler, D. A. Hillesheim, D. G. Musaev, C. L. Hill, *Angew. Chem.* **2008**, *120*, 3960; *Angew. Chem. Int. Ed.* **2008**, *47*, 3896.

[5] M. H. Chiang, C. W. Williams, L. Soderholm, M. R. Antonio, *Eur. J. Inorg. Chem.* **2003**, 2663.

[6] M. Nyman, *Dalton Trans.* **2011**, *40*, 8049.

[7] a) M. Nyman, T. M. Alam, F. Bonhomme, M. A. Rodriguez, C. S. Frazer, M. E. Welk, *J. Cluster Sci.* **2006**, *17*, 197; b) T. M. Anderson, S. G. Thoma, F. Bonhomme, M. A. Rodriguez, H. Park, J. B. Parise, T. M. Alam, J. P. Larentzos, M. Nyman, *Cryst. Growth Des.* **2007**, *7*, 719; c) T. M. Anderson, M. A. Rodriguez, F. Bonhomme, J. N. Bixler, T. M. Alam, M. Nyman, *Dalton Trans.* **2007**, 4517.

[8] M. R. Antonio, M. Nyman, T. M. Anderson, *Angew. Chem.* **2009**, *121*, 6252; *Angew. Chem. Int. Ed.* **2009**, *48*, 6136.

[9] Y. Marcus, G. Hefter, *Chem. Rev.* **2006**, *106*, 4585.

[10] a) Y. F. Fang, I. A. Weinstock, *Dalton Trans.* **2010**, *39*, 6143; b) V. A. Grigoriev, D. Cheng, C. L. Hill, I. A. Weinstock, *J. Am. Chem. Soc.* **2001**, *123*, 5292; c) P. C. Yin, D. Li, T. B. Liu, *Isr. J. Chem.* **2011**, *51*, 191.

[11] M. Nyman, F. Bonhomme, T. M. Alam, M. A. Rodriguez, B. R. Cherry, J. L. Krumhansl, T. M. Nenoff, A. M. Sattler, *Science* **2002**, *297*, 996.

[12] M. Nyman, F. Bonhomme, T. M. Alam, J. B. Parise, G. M. B. Vaughan, *Angew. Chem.* **2004**, *116*, 2847; *Angew. Chem. Int. Ed.* **2004**, *43*, 2787.

[13] F. Bonhomme, J. P. Larentzos, T. M. Alam, E. J. Maginn, M. Nyman, *Inorg. Chem.* **2005**, *44*, 1774.

[14] M. Nyman, A. J. Celestian, J. B. Parise, G. P. Holland, T. M. Alam, *Inorg. Chem.* **2006**, *45*, 1043.

[15] M. Nyman, J. P. Larentzos, E. J. Maginn, M. E. Welk, D. Ingersoll, H. Park, J. B. Parise, I. Bull, F. Bonhomme, *Inorg. Chem.* **2007**, *46*, 2067.

[16] Z. Y. Zhang, Q. P. Lin, D. Kurunthu, T. Wu, F. Zuo, S. T. Zheng, C. J. Bardeen, X. H. Bu, P. Y. Feng, *J. Am. Chem. Soc.* **2011**, *133*, 6934.

[17] a) S. G. Mitchell, H. N. Miras, D.-L. Long, L. Cronin, *Inorg. Chim. Acta* **2010**, *363*, 4240; b) P. Ma, L. Chen, J. Zhao, W. Wang, J. Wang, J. Niu, *Inorg. Chem. Commun.* **2011**, *14*, 415; c) M. D. Ritorto, T. M. Anderson, W. A. Neiwert, C. L. Hill, *Inorg. Chem.* **2004**, *43*, 44; d) T. Ruizhan, L. Chen, Y. Liu, B. Liu, G. Xue, H. Hu, F. Fu, J. Wangb, *Inorg. Chem. Commun.* **2010**, *13*, 98.

[18] R. P. Bontchev, M. Nyman, *Angew. Chem.* **2006**, *118*, 6822; *Angew. Chem. Int. Ed.* **2006**, *45*, 6670.

[19] J. R. Black, M. Nyman, W. H. Casey, *J. Am. Chem. Soc.* **2006**, *128*, 14712.

