



Dihydrogen Tetrametaphosphate, $[P_4O_{12}H_2]^{2-}$: Synthesis, Solubilization in Organic Media, Preparation of its Anhydride $[P_4O_{11}]^{2-}$ and Acidic Methyl Ester, and Conversion to Tetrametaphosphate Metal Complexes via Protonolysis

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S Supporting Information

ABSTRACT: Dihydrogen tetrametaphosphate $[P_4O_{12}H_2]^{2-}$ (**1**) can now be synthesized and isolated as its PPN salt ($[PPN]^+ = [N(PPh_3)_2]^+$) via treatment of $[PPN]_4[P_4O_{12}]$ with trifluoroacetic anhydride in wet acetone; this simple procedure affords the oxoacid salt in 94% yield. A pK_a of 15.83 ± 0.11 in acetonitrile was determined. $[P_4O_{12}H_2]^{2-}$ reacts with the dehydrating agent *N,N'*-dicyclohexylcarbodiimide to afford tetrametaphosphate anhydride $[P_4O_{11}]^{2-}$ (**2**) in 82% yield, also as the PPN salt. From **2** a monohydrogen tetrametaphosphate ester $[P_4O_{10}(OH)(OMe)]^{2-}$ (**3**, 96%) was derived by addition of methanol, illustrating that **2** can function as a reagent for chemical phosphorylation. Addition of water to **2** regenerates **1** quantitatively. Deprotonation of **1** by metal amides in the +2 oxidation state led to the unconventional monomeric tin(II) κ^4 tetrametaphosphate $[Sn(P_4O_{12})]^{2-}$ (**4**, 78%, a molecular analog of SnO) and binary dimeric chromium(II) bis($\mu_2, \kappa^2, \kappa^2$) derivative $[Cr_2(P_4O_{12})_2]^{4-}$ (**5**, 82%). Structural data stemming from single-crystal X-ray diffraction studies for the PPN salts of anions **1–5** are also reported.

The study of cyclic phosphates was initially undertaken almost two centuries ago coinciding with the advent of modern chemistry.¹ The early interest in this fundamentally important research area² has not yet translated into a modern field of vigorous activity, although applications in materials science and conventional coordination chemistry have been reported sporadically.³ This class of molecules, the cyclic phosphates, is also strongly implicated in prebiotic chemistry.⁴ Recognizing that a significant opportunity for the expansion of cyclic phosphate chemistry could be realized by synthesizing an organic-media soluble acid form of tetrametaphosphate,⁵ we set out to investigate if a convenient entry point into this domain could be identified. Herein, we report a simple and high-yielding procedure for the preparation of a previously unknown organic-soluble form of dihydrogen tetrametaphosphate,⁶ which is demonstrated to be a potent precursor not only to its

corresponding anhydride and methyl ester but also to metal tetrametaphosphates. This is a powerful new strategy in cyclic phosphate chemistry: the synthesis of tetrametaphosphate metal complexes via protonolysis.

In their work identifying the key intermediate in ATP synthetic routes developed by Todd and Khorana,⁷ Glonek, Kleps, and Myers (GKM) definitively characterized cyclic adenosine triphosphate which rapidly decomposed to ATP upon contact with water.⁴ GKM concluded that “it is likely that trimetaphosphate esters including that of adenosine will be found only in a nonaqueous milieu, such as the lipid portions of cell organelles”.⁴ The requirement of anhydrous media for the preparation of cyclic phosphate esters⁸ is universal not only in the synthesis of phosphate nucleosides but also in previous attempts to access the acid forms of cyclic phosphates. In 1956, Griffith reported that under furnace conditions the reaction of phosphoric acid with sodium dihydrogen phosphate afforded cyclic phosphate acids.⁹ However, an unrefined structure was reported,¹⁰ and there was an ensuing debate on the composition of the obtained polycrystalline form.¹¹ Structurally well-characterized cyclic phosphate acids are a tetrakis(3,5-xylydinium) dihydrogen cyclohexaphosphate dihydrate¹² and a sodium monohydrogen trimetaphosphate.¹³

Why are the acid forms of metaphosphate rings so rare? One reason could be associated with their essentially strong acidity, as implicated by the titration of sodium tri- and tetrametaphosphate with nitric acid.¹⁴ Following the “anhydrous principle”, we investigated whether a lipophilic organic cation, such as $[PPN]^+$ ($[PPN]^+ = \text{bis}(\text{triphenylphosphine})\text{iminium}$), could facilitate access to dihydrogen tetrametaphosphate in nonaqueous media by protonation of its tetrametaphosphate salt with a strong acid. Treatment of $[PPN]_4[P_4O_{12}] \cdot 5H_2O^{3f}$ with 1 equiv of trifluoroacetic anhydride in acetone at 23 °C resulted in the formation of a single new cyclic phosphate species **1**, which exhibits a singlet resonance at -25.6 ppm in its $^{31}P\{^1H\}$ NMR spectrum. Upon addition of a dehydrating agent such as DCC (DCC = *N,N'*-dicyclohexylcarbodiimide) to the reaction mixture, the $^{31}P\{^1H\}$

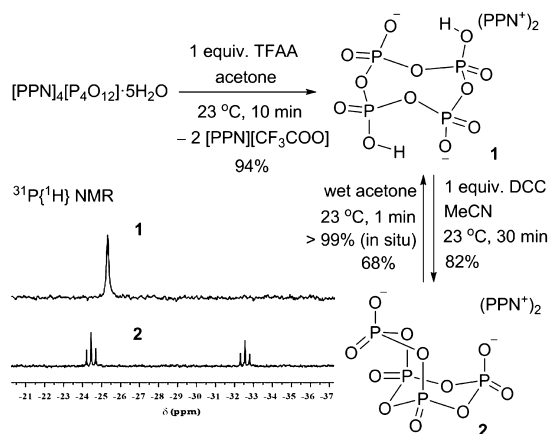
Received: June 10, 2014

Published: August 7, 2014



NMR spectrum displayed two triplet signals at -24.4 and -32.5 ppm in an A_2X_2 spin system, characteristic for the small ultraphosphate $[P_4O_{11}]^{2-}$ (**2**, Scheme 1).¹⁵ These results suggest

Scheme 1. Synthetic Route to the PPN Salts of Dihydrogen Tetrametaphosphate **1 and Tetrametaphosphate Anhydride **2****



that **1** is the oxoacid dianion dihydrogen tetrametaphosphate $[P_4O_{12}H_2]^{2-}$. Indeed, we were able to isolate the PPN salt of **1** as an analytically pure solid in 94% yield. The presence in **1** of acidic P–OH groups is evidenced by a broad singlet at 14.03 ppm in the 1H NMR spectrum recorded in CD_3CN at 23 °C. However, in solution these terminal acidic hydrogens are mobile; this being a general property of hydrogen-bonded oxoacids.¹⁶ The fluxional behavior of **1** is reflected in its $^{31}P\{^1H\}$ NMR spectrum which displays a single singlet resonance.

It should be emphasized that the synthesis of **1** is so facile that the reaction can be carried out on gram scales under open air conditions using commercial solvents and reagents as received. Trifluoroacetic anhydride reacts with H_2O from either the solvent or $[PPN]_4[P_4O_{12}] \cdot 5H_2O$ to in situ generate trifluoroacetic acid (TFA), which can then protonate $[P_4O_{12}]^{4-}$. Acetone was identified as the most convenient solvent as it delivers a simple purification process. The simplicity of the purification procedure in acetone is primarily attributed to the lower solubility of $[PPN]_2[1]$ (this precipitates out of or crystallizes from the reaction mixture) relative to the byproduct $[PPN][CF_3COO]$. It should be noted that strong Brønsted acids such as TFA, triflic acid, and triflic anhydride also react with $[P_4O_{12}]^{4-}$ to afford **1** in good isolated yields. In comparison, no formation of **1** was observed when $[P_4O_{12}]^{4-}$ was treated with a weaker Brønsted acid such as acetic acid.

The solid-state structure of $[PPN]_2[1]$ was established using single-crystal X-ray diffraction, and the resulting model of the dianion in C_i symmetry is depicted in Figure 1. The hydrogen

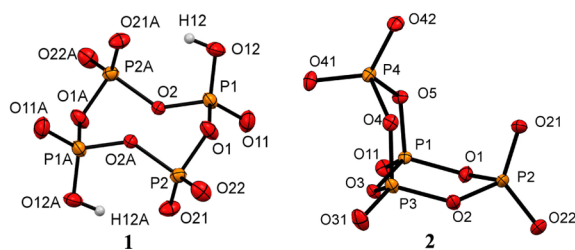


Figure 1. Solid-state molecular structures of $[P_4O_{12}H_2]^{2-}$ (**1**) and $[P_4O_{11}]^{2-}$ (**2**) with ellipsoids at the 50% probability level.

atoms (placed at calculated positions and refined using a riding model) are arranged in a mutual 1,5 disposition. The most prominent feature is the presence of intramolecular hydrogen bonds between the protons and neighboring P–O[−] hydrogen-bond acceptors showing a short O21...O12A distance of 2.731(5) Å.¹⁷ Such hydrogen-bonding interactions may contribute to the stability of **1** in both the solid state and in organic solvents. The P–OH bond length of 1.5096(19) Å is intermediate between the long bridging P–O distances and the short external P–O distances.

Dihydrogen tetrametaphosphate **1** is not stable in aqueous solution in that it generates an acidic medium in which the formation of linear phosphates and phosphoric acid can be detected by $^{31}P\{^1H\}$ and 1H NMR spectroscopy. However, **1** shows significant stability toward H_2O in organic solvents such as acetonitrile and acetone, as no decomposition was detected after 48 h at 23 °C for an acetone solution of **1** containing 50 equiv of H_2O . The dianionic character of **1** serves to inhibit nucleophilic attack at the phosphorus atoms. Such an anion stabilization effect is commonly observed in the chemistry of general anionic phosphate diesters.¹⁸

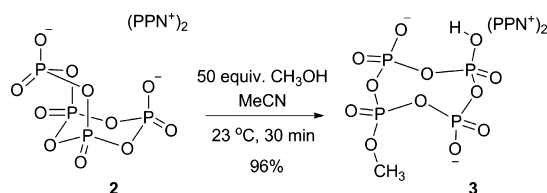
The instability of **1** in aqueous solution hampers measurement of its acidity in water. Nevertheless, the pK_a of **1** in acetonitrile was determined by UV–vis spectrophotometric titration of $[PPN]_2[P_4O_{12}H_2]$ coupled with 2,4-dinitrophenol ($pK_a = 16.66$ in MeCN) as a chromophore.¹⁹ A pK_a value of 15.83 ± 0.11 was thereby obtained for **1** in acetonitrile, corresponding to an intermediate acidity between that of TFA ($pK_a = 12.65$ in MeCN) and acetic acid ($pK_a = 23.51$ in MeCN);²⁰ this being in agreement with the experimental observation that **1** can be prepared by protonation of tetrametaphosphate with TFA but not with acetic acid.

We further pursued the isolation of the observed small ultraphosphate **2**.¹⁵ It was reported to be an important intermediate in the hydrolysis of P_4O_{10} ²¹ and a key phosphorylating precursor to esters of orthophosphate and linear polyphosphate.²² However, neither an isolation procedure nor structural characterization was available until now.²³ The reaction of **1** with a stoichiometric amount of DCC in acetonitrile led to the quantitative formation of **2** (as its PPN salt), which was isolated as an analytically pure solid in 82% yield after removing the byproduct dicyclohexylurea (DCU) that precipitated from the reaction mixture. Since ultraphosphate was originally defined as “an infinite cross-linked polymer of high viscosity”,^{15,24} **2** would be more aptly described as the anhydride of dihydrogen tetrametaphosphate.

The solid-state structure of **2** was established via an X-ray diffraction study and is shown in Figure 1. The two negatively charged terminal phosphates are bent away from each other probably due to electrostatic repulsion making the two six-membered rings of the bicyclic structure that share a P1–O3–P3 bridge adopt boat and chair conformations.

Treatment of **2** with acetone (H_2O content ≤ 0.5 w/w%) at 23 °C regenerates **1** in quantitative in situ yield and in a 68% isolated yield. The reaction likely occurs via nucleophilic attack of H_2O with concomitant rupture of the phosphoanhydridic P1–O3–P3 bridge. In a similar manner, the P1–O3–P3 bridge of **2** can also be cleaved by other hydroxy nucleophiles such as methanol, in that case yielding an acidic tetrametaphosphate methyl ester (Scheme 2). The reaction of **2** with 50 equiv of methanol at 23 °C afforded within 30 min the quantitative formation of methanolysis product $[P_4O_{10}(OH)(OMe)]^{2-}$ (**3**). The $^{31}P\{^1H\}$ NMR spectrum of **3** revealed a triplet at -24.6 ppm

Scheme 2. Methanolysis of 2 to Monohydrogen Tetrametaphosphate Methyl Ester 3



for the methoxyl-bonded phosphorus and multiplet signals from -25.3 to -26.4 ppm for the other three phosphorus atoms due to the fast migration of the proton. Collecting the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** at -30 °C resolved the multiplet signal into two triplets at -26.2 and -27.2 ppm in a 1:2 ratio corresponding to the P–OH and P–O $^-$ moieties, respectively. In the ^1H NMR spectrum, a broad signal at 13.2 ppm is assigned to the hydroxyl group and a doublet at 3.78 ppm ($^3J_{\text{HP}} = 12$ Hz) to the methoxy protons. This assignment was further supported by a doublet at 54.4 ppm ($^2J_{\text{CP}} = 6$ Hz) observed by ^{13}C NMR spectroscopy. Notably when 1 equiv of methanol was employed the quantitative conversion of **2** to **3** could still be achieved at room temperature within 24 h. Although the existence of the so-called “ethyl metaphosphate” (Langheld ester) has been reported,²⁵ compound **3** now represents the first example of a structurally characterized metaphosphate ester (See Figure 2).

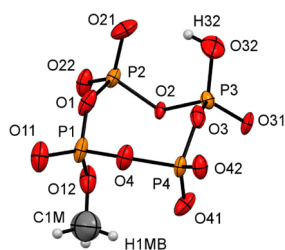


Figure 2. Solid-state molecular structure of $[\text{P}_4\text{O}_{10}(\text{OH})(\text{OMe})]^{2-}$ (**3**) with ellipsoids at the 30% probability level.

In the structure of **3** (Figure 2), the hydroxyl and methyl residues are located on opposing phosphoryl residues and intramolecular O–H \cdots O hydrogen bonding¹⁷ between the hydroxyl and neighboring P–O $^-$ bond is indicated, with a O32 \cdots O21 distance of 2.617(9) Å.

Since **1** can be delivered in anhydrous form and is soluble in organic solvents, it is uniquely suitable for synthesizing metal tetrametaphosphate complexes by protonolysis leading to replacement of simple basic ligands. Moreover, due to its diacidic nature **1** is commensurate for reaction with metals in the +2 oxidation state. Herein we tested the reactivity of **1** with a pair of metal(II) bis(hexamethyldisilazide) complexes leading to exemplary binary metal(II) tetrametaphosphate systems.

The reaction of $[\text{PPN}]_2[\text{1}]$ with 1 equiv of $\text{Sn}(\text{HMDS})_2$ (selected as a representative p-block metal amide, HMDS = hexamethyldisilazide) in acetonitrile at 23 °C afforded within 15 min a new species **4** showing a singlet in its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at -23.54 ppm, which is slightly downfield from that of **1** (Scheme 3). ^{119}Sn NMR spectroscopy revealed a singlet at 800.57 ppm, consistent with the coordination of the cyclic phosphate to the tin center. As the reaction generates only the volatile $\text{HN}(\text{SiMe}_3)_2$ as byproduct, the PPN salt of **4** was easily isolated as analytically pure solid with the formula $[\text{PPN}]_2[\text{Sn}(\text{P}_4\text{O}_{12})]^{2-}$ in 78% yield. The structure of anion **4** was established

Scheme 3. Protonolysis Route to Anionic $(\text{P}_4\text{O}_{12})^{4-}$ Complexes of Tin(II) and Chromium(II)

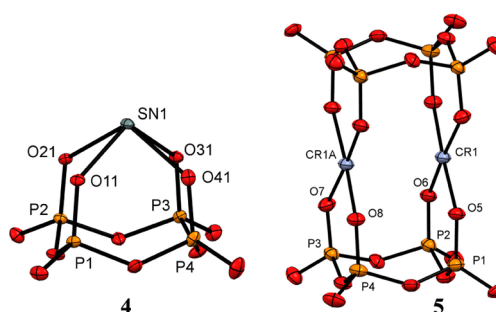
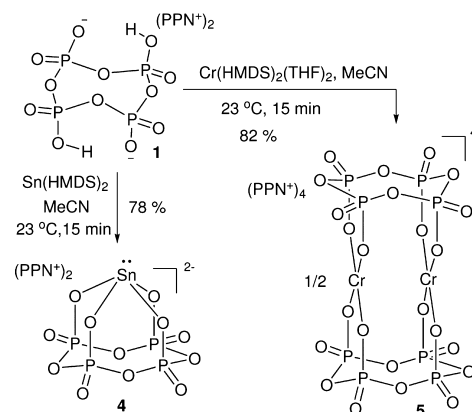


Figure 3. Solid-state molecular structures of $[\text{Sn}(\text{P}_4\text{O}_{12})]^{2-}$ (**4**) and $[\text{Cr}_2(\text{P}_4\text{O}_{12})_2]^{4-}$ (**5**) with ellipsoids at the 50% probability level.

by an X-ray diffraction study to be the C_{4v} symmetric tin(II) κ^4 tetrametaphosphate (Figure 3). The tin vertex is centered above the four-membered face consisting of four oxygen atoms, resulting in a tetragonal pyramidal geometry. The Sn–O distances were found to be in the range of 2.1876(17) to 2.2240(16) Å. The O–Sn–O angles between neighboring phosphates are quite similar to each other varying from 74.65(3) to 75.90(4)°.

Previous reports of tin(II) in a similar C_{4v} all-oxygen binding site were focused upon tungstostannate(II) heteropolyanions²⁶ and tridentate alkoxyl tin(II) clusters.²⁷ In fact, the solid-state tin(II) oxide SnO has tin(II) in nearly an identical C_{4v} environment consisting of four oxide ions as reported by Moore and Pauling,²⁸ making **4** an excellent molecular mimic of a known solid oxide material. To the best of our knowledge, **4** also represents the first example of κ^4 tetrametaphosphate coordination to a metal. The lone pair electrons at the tin(II) center are expected to be localized in an orbital very rich in s character in view of Bent's rule considerations.²⁹

We further examined the reactivity of **1** toward the d-block metal(II) amide $\text{Cr}(\text{HMDS})_2(\text{THF})_2$.³⁰ Addition of 1 equiv of $[\text{PPN}]_2[\text{1}]$ to a purple-brown solution of $\text{Cr}(\text{HMDS})_2(\text{THF})_2$ at 23 °C rapidly afforded a pale-green solution. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this new species is silent in the phosphate region, suggesting that the tetrametaphosphate is coordinated to a paramagnetic chromium(II) center. After workup, a pale-gray solid was isolated in 82% yield. The solid-state structure of **5** was identified as a binary chromium(II) tetrametaphosphate dimer $[\text{Cr}_2(\text{P}_4\text{O}_{12})_2]^{4-}$ (**5**, Scheme 3, Figure 3) by X-ray diffraction. Each chromium adopts a square planar configuration. The Cr \cdots Cr distance of 2.9020(13) Å suggests a very weak Cr \cdots Cr

interaction.³¹ Compound **5** represents the first example of a binary metal(II) tetrametaphosphate dimer. In the case of most other κ^2 tetrametaphosphate complexes, such as those bearing d^8 Rh and Ir centers, typically only one tetrametaphosphate ligand is involved with two metal moieties bonded on either side of the P_4O_{12} mean plane.^{3f} However, an example of the $M_2(P_4O_{12})_2$ configuration observed here for anion **5** with approximate D_{2h} symmetry has been reported previously for titanium.^{3g}

We have described a simple preparative procedure for an organic-media soluble salt of the strong Brønsted acid dihydrogen tetrametaphosphate $[P_4O_{12}H_2]^{2-}$ (**1**). This diacid dianion serves as precursor to numerous derivatives. The use of anhydride **2** as a reagent to effect phosphorylation (along the lines of our demonstrated synthesis of methyl ester **3**) might be adapted to access tetrametaphosphate amino acids or nucleosides, etc. The reaction with metal amides results in monomeric κ^4 and dimeric κ^2 species **4** and **5** and suggests the possible existence of a broad family of p- and d-block metal tetrametaphosphate materials to be accessed by the protonolysis method illustrated herein.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental details, spectroscopic data, and X-ray diffraction studies (CCDC codes 998201–998205). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare the following competing financial interest(s): A provisional patent containing the material in this paper has been filed by MIT.

■ ACKNOWLEDGMENTS

Drs. Peter Müller and Daniel Tofan are acknowledged for crystallographic assistance. Y.J. and N.M. acknowledge Fellowship support respectively from SNSF and FSE, Calabria Region. X-ray diffraction data were collected on an instrument supported via NSF CHE-0946721. This material is based upon work supported by NSF CHE-1305124.

■ REFERENCES

- (1) "The development of the chemistry of cyclophosphates was very slow, spreading along almost two centuries". Quote from André Durif, ref 32; see also references therein.
- (2) Van Wazer, J. R. *Phosphorus and its Compounds*. Vol. 1: Chemistry; Interscience: New York, 1958.
- (3) (a) Trojan, M.; Šulcová, P. *Dyes Pigm.* **2000**, *47*, 291–294. (b) Onoda, H.; Okumoto, K.; Nakahira, A.; Tanaka, I. *Materials* **2009**, *2*, 1–9. (c) Besecker, C. J.; Day, V. W.; Klemperer, W. G. *Organometallics* **1985**, *4*, 564–570. (d) Klemperer, W. G.; Main, D. J. *Inorg. Chem.* **1990**, *29*, 2355–2360. (e) Day, V. W.; Klemperer, W. G.; Main, D. J. *Inorg. Chem.* **1990**, *29*, 2345–2355. (f) Kamimura, S.; Kuwata, S.; Iwasaki, M.; Ishii, Y. *Inorg. Chem.* **2004**, *43*, 399–401. (g) Kamimura, S.; Matsunaga, T.; Kuwata, S.; Iwasaki, M.; Ishii, Y. *Inorg. Chem.* **2004**, *43*, 6127–6129. (h) Ikeda, Y.; Yamaguchi, T.; Kanao, K.; Kimura, K.; Kamimura, S.; Mutoh, Y.; Tanabe, Y.; Ishii, Y. *J. Am. Chem. Soc.* **2008**, *130*, 16856–16857. (i) Montag, M.; Clough, C. R.; Müller, P.; Cummins, C. C. *Chem. Commun.* **2011**, *47*, 662–664. (j) Kanao, K.; Ikeda, Y.; Kimura, K.; Kamimura, S.; Tanabe, Y.; Mutoh, Y.; Iwasaki, M.; Ishii, Y. *Organometallics* **2013**, *32*, 527–537. (k) Manna, C. M.; Nassar, M. Y.; Tofan, D.; Chakarawet, K.; Cummins, C. C. *Dalton Trans.* **2014**, *43*, 1509–1518.
- (4) Glonek, T.; Kleps, R. A.; Myers, T. C. *Science* **1974**, *185*, 352–355.
- (5) The term "metaphosphate" is defined^{2,9,32} as PO_3^- (phosphorus analog of nitrate) which exists as cyclic oligomers $(PO_3)_n^{n-}$.
- (6) See ref 9 for a preparation of $Na_2H_2P_4O_{12}$.
- (7) (a) Baddiley, J.; Michelson, A. M.; Todd, A. R. *Nature* **1948**, *161*, 761–762. (b) Smith, M.; Khorana, H. G. *J. Am. Chem. Soc.* **1958**, *80*, 1141–1145.
- (8) (a) Sood, A.; Kumar, S.; Nampalli, S.; Nelson, J. R.; Macklin, J.; Fuller, C. W. *J. Am. Chem. Soc.* **2005**, *127*, 2394–2395. (b) Han, Q.; Gaffney, B. L.; Jones, R. A. *Org. Lett.* **2006**, *8*, 2075–2077.
- (9) Griffith, E. J. *J. Am. Chem. Soc.* **1956**, *76*, 3867–3870.
- (10) Dornberger-Schiff, K. *Acta Crystallogr.* **1964**, *17*, 482–491.
- (11) (a) Gryder, J. W.; Donnay, G.; Ondik, H. M. *Acta Crystallogr.* **1957**, *10*, 820–821. (b) Jarchow, O. H. *Acta Crystallogr.* **1964**, *17*, 1253–1262.
- (12) Marouani, H.; Rzaigui, M. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2010**, *66*, o233.
- (13) Averbuch-Pouchot, M. T.; Guitel, J. C.; Durif, A. *Acta Crystallogr.* **1983**, *C39*, 809–810.
- (14) Watters, J. I.; Kalliney, S.; Machen, R. C. *J. Inorg. Nucl. Chem.* **1969**, *31*, 3817–3821.
- (15) (a) Glonek, T.; Myers, T. C.; Han, P. Z.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 7214–7216. (b) Glonek, T.; Van Wazer, J. R.; Mudgett, M.; Myers, T. C. *Inorg. Chem.* **1972**, *11*, 567–570.
- (16) Tolstoy, P. M.; Schah-Mohammed, P.; Smirnov, S. N.; Golubev, N. S.; Denisov, G. S.; Limbach, H.-H. *J. Am. Chem. Soc.* **2004**, *126*, 5621–5634.
- (17) Brown, I. D. *Acta Crystallogr.* **1976**, *A32*, 24–31.
- (18) (a) Westheimer, F. H. *Science* **1987**, *235*, 1173–1178. (b) Bowler, M. W.; Cliff, M. J.; Waltho, J. P.; Blackburn, G. M. *New J. Chem.* **2010**, *34*, 784–794.
- (19) (a) Leito, I.; Kaljurand, I.; Koppel, I. A.; Yagupolskii, L. M.; Vlasov, V. M. *J. Org. Chem.* **1998**, *63*, 7868–7874. (b) Leito, I.; Rodima, T.; Koppel, I. A.; Schwesinger, R.; Vlasov, V. M. *J. Org. Chem.* **1997**, *62*, 8479–8483.
- (20) Eckert, F.; Leito, I.; Kaljurand, I.; Kuett, A.; Klamt, A.; Diedenhofen, M. *J. Comput. Chem.* **2009**, *30*, 799–810.
- (21) Henry, W.; Nickless, G.; Pollard, F. J. *Inorg. Nucl. Chem.* **1967**, *29*, 2479–2480.
- (22) Glonek, T.; Kleps, R. A.; Van Wazer, J. R.; Myers, T. C. *Bioinorg. Chem.* **1976**, *5*, 283–310.
- (23) Glonek, T.; Van Wazer, J. R.; Kleps, R. A.; Myers, T. C. *Inorg. Chem.* **1974**, *13*, 2337–2345.
- (24) Thilo, E. *Angew. Chem., Int. Ed.* **1965**, *4*, 1061–1071.
- (25) Burkhardt, G.; Klein, M. P.; Calvin, M. *J. Am. Chem. Soc.* **1965**, *87*, 591–596.
- (26) Chorghade, G. S.; Pope, M. T. *J. Am. Chem. Soc.* **1987**, *109*, 5134–5138.
- (27) Boyle, T. J.; Segall, J. M.; Alam, T. M.; Rodriguez, M. A.; Santana, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 6904–6913.
- (28) Moore, W. J.; Pauling, L. *J. Am. Chem. Soc.* **1941**, *63*, 1392–1394.
- (29) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275–311.
- (30) (a) Bradley, D. C.; Hursthouse, M. B.; Newing, C. W.; Welch, A. J. *Chem. Commun.* **1972**, 567–568. (b) Frazier, B. A.; Wolczanski, P. T.; Lobkovsky, E. B. *Inorg. Chem.* **2009**, *48*, 11576–11585.
- (31) (a) Pyykkö, P.; Atsumi, M. *Chem. Eur. J.* **2009**, *15*, 12770–12779. (b) Cotton, F. A.; Extine, M. W.; Rice, G. W. *Inorg. Chem.* **1978**, *17*, 176–186.
- (32) Durif, A. *Solid State Sci.* **2005**, *7*, 760–766.