J|A|C|S
COMMUNICATIONS

Crown Ether Complexes of $HPCl_6$

Zin-Min Tun, Matthew J. Panzner, Vincenzo Scionti, Douglas Medvetz, Chrys Wesdemiotis,
Wiley J. Youngs, and Claire Tessier*

Department of Chemistry, University of Akron, Akron, Ohio 44325-3601, United States

Received July 21, 2010; E-mail: tessier@uakron.edu

Abstract: The reactions of HCl, PCl_5, and a crown ether (12-crown-4 or 18-crown-6) in $CHCl_3$ under anaerobic conditions give complexes of the superacid $HPCl_6$: [H(12-crown-4)][PCl_6] and [H(18-crown-6)$_2$][PCl_6]. The crystal structures indicate that the proton lies roughly in the center of the 12-crown-4 molecule in [H(12-crown-4)][PCl_6] whereas it lies between two oxygen atoms of two different 18-crown-6 molecules in [H(18-crown-6)$_2$][PCl_6].

Superacids are Brønsted acids that are more acidic than 100% sulfuric acid ($H_o < -12$).[1] They exist in nonaqueous, weakly basic solvents. Superacids have found uses in important organic transformations such as hydrocarbon cracking and isomerization as well as Friedel−Crafts chemistry, and they appear to be involved in some cationic polymerization processes.[1,2]

An important class of superacids are the conjugate Brønsted−Lewis superacids.[1] These acids are generated from the reaction of a Brønsted acid HX (X = halide) and a Lewis acid MX_m, and the fluorinated systems are the most studied. Conceptionally, such superacids could be viewed as in eq 1 where the Lewis acid MX_m converts X^- into the more weakly coordinating anion $MX_{m+1}{}^-$, thereby increasing the Brønsted acidity of the system.

$$\mathrm{HX + MX_{\mathit{m}} \rightarrow [H^+][MX_{\mathit{m}+1}{}^-]} \tag{1}$$

However, eq 1 is an oversimplification.[1,3,4] Species other than H^+ and $MX_{m+1}{}^-$ usually also form from HX and MX_m, and the species formed are dependent on the stoichiometry.

Phosphazene polymers have many useful properties but are seldom used industrially.[5] A major problem in phosphazene chemistry concerns the difficulties and irreprodicibilities encountered in the synthesis and handling of the parent $[PCl_2N]_n$ polymer, from which most other polyphosphazenes are prepared. A number of the problems seem to involve unspecified Brønsted acids.[6−8] On the basis of our work on the reactions of Lewis acids and $[PCl_2N]_3$,[9] we suspect that at least some of these issues may be due to the presence of a strong acid or a superacid that is generated from the hydrolytically unstable, Lewis acid PCl_5 and HCl. PCl_5 is a reagent, catalyst, or initiator in all syntheses of $[PCl_2N]_n$ and thereby could be an impurity. Therefore, as suggested by eq 1, $HPCl_6$ or a related species could be generated from the reaction of PCl_5 and HCl, the latter of which is generated as a byproduct during some syntheses of chlorophosphazenes or from hydrolysis of P−Cl bonds. The effect of PCl_5 and HCl *separately* on the ring-opening polymerization synthesis of $[PCl_2N]_n$ has been considered, but their combined action has not.[10]

$HPCl_6$ salts of a few nitrogen bases are known.[11] Therefore, it appears that $HPCl_6$ is at least a strong acid. Herein, we describe some of our efforts to characterize the acidic compounds generated from the combination of HCl and PCl_5 in the presence of bases that are weaker than those already examined. Though there are very few references to $HPCl_6$ *per se*, a search of the Chemical Abstracts database showed that the combination of the reagents HCl and PCl_5 has been used in about 590 one-step reactions, most of which are syntheses of organic molecules. Therefore, an understanding of the chemistry HCl/PCl_5 has application to areas other than phosphazene chemistry.

Attempts to isolate $HPCl_6$ from the reactions of gaseous HCl and PCl_5 in hydrocarbon and chlorocarbon solvents were unsuccessful. The work of Andrianov and co-workers provided some inspiration.[10] They noted the polymer $[PCl_2N]_n$ was stable in air for over four years if it was stored in diglyme. They suggested that diglyme forms a complex with the acidic impurities that form in $[PCl_2N]_n$ on prolonged storage. Therefore, the HCl/PCl_5 system was examined in the presence of ethers, in particular crown ethers.

Equations 2 and 3 show the reactions of HCl, PCl_5, and two different crown ethers in $CHCl_3$.

$$\mathrm{HCl + PCl_5 + 12\text{-}crown\text{-}4 \rightarrow \underset{\mathbf{1}}{[H(12\text{-}crown\text{-}4)][PCl_6]}} \tag{2}$$

$$\mathrm{HCl + PCl_5 + 2(18\text{-}crown\text{-}6) \rightarrow \underset{\mathbf{2}}{[H(18\text{-}crown\text{-}6)_2][PCl_6]}} \tag{3}$$

The reaction with 12-crown-4 occurs in a 1:1:1 ratio whereas that with 18-crown-6 occurs in a 1:1:2 ratio, irrespective of the initial stoichiometry of the reagents. Complexes **1** and **2** were isolated as colorless crystals.

Complexes **1** and **2** are air-sensitive and have limited thermal stability. MS data of freshly prepared **1** and **2** show the $H[OCH_2CH_2]_n{}^+$ cation (n = 4 or 6, respectively) and lower molercular weight fragments. In addition, higher molecular weight $[OCH_2CH_2]_n$ and $H[OCH_2CH_2]_nH$ oligomers, indicative of degradation, are observed for freshly prepared **1**. Such oligomers were observed in MS studies of the free crown ethers.[12] After storage in an argon-filled glovebox for 3 days for **1** and 1−2 weeks for **2**, both degrade to form colorless oils. From NMR and mass spectral data, the oils largely consist of oligomers of formula $[OCH_2CH_2]_n$ and $H[OCH_2CH_2]_nH$. In air, **2** degrades to give crystals of the known $[H_3O(18\text{-crown-}6)][H_5O_2][Cl]_2$.[13]

The crystal structures of **1** and **2** have been obtained, and thermal ellipsoid plots of the cationic portions are shown in Figures 1 and 2, respectively. Disorder of an oxygen and two carbon atoms (O(5), C(8), and C(9)) in one of the two 18-crown-6 molecules of **2** was observed. In both **1** and **2**, the proton was found and it is two-coordinate. The proton of **1** lies in the center of the 12-crown-4 molecule, roughly midway between two oxygen atoms separated by 2.446 Å (Figure 1). The short O−O distance in **1** is consistent with a strong O−H−O hydrogen bond.[14] The proton of **2** is somewhat closer to one of the two oxygen atoms that are involved in a shorter *inter*molecular O−H−O hydrogen bond of 2.423 Å between two different 18-crown-6 molecules (Figure 2).

10.1021/ja1064697

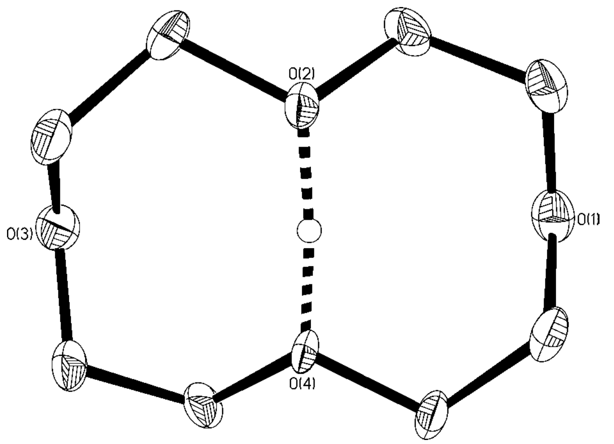

Figure 1. Thermal ellipsoid plot of the cation of **1** with ellipsoids at 50% and showing the position of the acidic hydrogen (unlabeled) in the O−H−O hydrogen bond (O--O = 2.446 Å). Carbon atoms are unlabeled and other hydrogen atoms are omitted for clarity.

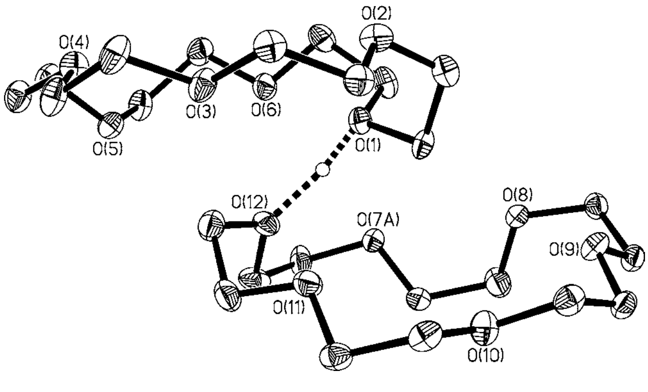

Figure 2. Thermal ellipsoid plot of the cation of **2** with ellipsoids at 50% and showing the position of the hydrogen atom (unlabeled) in the O−H−O hydrogen bond (O--O = 2.423 Å). Carbon atoms are unlabeled and other hydrogen atoms are omitted for clarity. O(5), C(8), and C(9) are slightly disordered, and only the predominant form is shown.

The structures of **1** and **2** show differences from the structures of the respective free or nearly free crown ethers. The crystal structure of free 12-crown-4, a liquid at room temperature, was not found. However, in structures where 12-crown-4 is involved only in weak noncovalent interactions, none of the oxygen atoms point toward the center of the ring.[15] In **2**, one end of each of the two 18-crown-6 molecules is cupped toward the proton in a conformation that is very different than that in the free 18-crown-6.[16] Some lengthening of the O−C bonds that involve the oxygen atoms bound to the proton relative to the other O−C bonds is observed in both **1** and **2**.

Superacid solutions often are a complex mixture of several species.[1] The NMR spectra of **1** and **2** in CD_2Cl_2 are in agreement with this expectation. The ^1H NMR spectra for the acidic protons show pairs of resonances at 6.05 and 5.99 for **1** and 6.00 and 5.96 ppm for **2**, respectively. The ^1H and ^{13}C NMR spectra show resonances for the CH_2 groups of the two crown ethers at 3.7 and 70.7 ppm, respectively for both compounds. Most of the resonances in the ^{31}P spectra of **1** and **2** in CD_2Cl_2 can be assigned to known species.[17] The ^{31}P spectrum of **1** showed signals at −80.7 (PCl_5), 85.1 and 92.4 (PCl_4^+), and 220.1 (PCl_3) ppm. The ^{31}P spectrum of **2** at 30 °C showed resonances at −296.9 (PCl_6^-), −80.7 (PCl_5), 5.2 ($OPCl_3$), 85.1 ($PCl_4^+Cl^-$), 92.4 ($\underline{P}Cl_4^+PCl_6^-$), and 220.1 ($PCl_3$) ppm. Apparently, PCl_6^- dissociates to PCl_5 and Cl^- and PCl_5 is known to be a source of PCl_4^+, PCl_6^-, Cl^-, and PCl_3.[18] Variable-temperature ^{31}P NMR spectra of **2** show that as the temperature is lowered to −20 °C, the resonances assigned to PCl_5 and PCl_6^- sharpen considerably, consistent with an equilibrium between PCl_6^-, PCl_5, and Cl^-.

In summary, we have synthesized and characterized two crown ether complexes of the little-known superacid $HPCl_6$. The coordination chemistry of the proton is a topic of recent interest.[19] Though numerous crown-ether complexes of oxonium ions have been isolated and characterized,[20] complexes **1** and **2** appear to be the first crystallographically characterized crown-ether complexes of otherwise uncomplexed protons. In a separate paper we will describe the reactions of $HPCl_6$ and chlorophosphazenes.

Acknowledgment. This material is based upon work supported in part by the National Science Foundation (NSF) under Grants CHE-0316944 and CHE-0616601. Instruments used in this work were obtained via NSF Grants CHE-9977144 and DMR-0821313. We thank the University of Akron and the Ohio Board of Regents for additional support; Stephanie Bilinovich for help with the crystallographic data; and Drs. Venkat Dudipala, Amy Heston (Walsh University), and John Rapko (St. Louis College of Pharmacy) for helpful discussions.

Supporting Information Available: Detailed synthetic and other experimental procedures and crystallographic and spectral data of **1** and **2** can be found in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Molnar, A.; Olah, G. A.; Surya Prakash, G. K.; Sommer, J. *Superacids*, 2nd ed.; Wiley: New York, 2009; Chapters 1−2.
(2) Some examples: (a) Kennedy, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2285–2293. (b) Kolishetti, N.; Faust, R. *Macromolecules* **2008**, *41*, 3842–3851. (c) Crivello, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 1825–1835.
(3) (a) Fărcaşiu, D. *Acc. Chem. Res.* **1982**, *15*, 46–51. (b) Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426–432.
(4) (a) Gillespie, R. J.; Liang, J. *J. Am. Chem. Soc.* **1988**, *110*, 6053–6057. (b) Culmann, J.-C.; Fauconet, M.; Jost, R.; Sommer, J. *New J. Chem.* **1999**, *23*, 863–867.
(5) Allcock, H. R. *Chemistry and Applications of Polyphosphazenes*; Wiley-Interscience: New York, 2003; Chapters 1−2.
(6) (a) Liu, H. Q.; Stannett, V. T. *Macromolecules* **1990**, *23*, 140–144. (b) Sayed, M. B. *Internet J. Chem.* **2002**, *5*, 6 Paper No. .
(7) (a) Emsley, J.; Udy, P. B. *Polymer* **1972**, *13*, 593–4. (b) Sulkowski, W. W. In *Phosphazenes: A Worldwide Insight*; Gleria, M., De Jaeger, R., Eds.; Nova Science: New York, 2004; Chapter 4.
(8) Andrianov, A. K.; Chen, J.; LeGolvan, M. P. *Macromolecules* **2004**, *37*, 414–420.
(9) (a) Heston, A. J.; Panzner, M.; Youngs, W. J.; Tessier, C. A. *Phosphorus, Sulfur Silicon Relat. Elem.* **2004**, *179*, 831–837. (b) Heston, A. J.; Panzner, M.; Youngs, W. J.; Tessier, C. A. *Inorg. Chem.* **2005**, *44*, 6518–6520.
(10) Allcock, H. R.; Gardner, J. E.; Smeltz, K. E. *Macromolecules* **1975**, *8*, 36–42.
(11) Examples of compounds of general form [H(base)][PCl_6] where "base" is a nitrogen containing compound: (a) Knachel, H. C.; Owens, S. D.; Lawrence, S. H.; Dolan, M. E.; Kerby, M. C.; Salupo, T. A. *Inorg. Chem.* **1986**, *25*, 4606–4608. (b) Rozinov, V. G.; Kolbina, V. E.; Dmitrichenko, M. Yu. *Russ. J. Gen. Chem.* **1997**, *67*, 483–484. (c) Kaupp, G.; Boy, J.; Schmeyers, J. *J. Prakt. Chem./Chem.-Zeitung* **1998**, *340*, 346–355. (d) Dillon, K. B.; Khabbass, N. D. A. H.; Ludman, C. J. *Polyhedron* **1989**, *8*, 2623–2626.
(12) (a) Selby, T. L.; Wesdemiotis, C.; Lattimer, R. L. *J. Am. Soc. Mass Spectrom.* **1994**, *5*, 1081–1092. (b) Lattimer, R. L. *J. Am. Soc. Mass Spectrom.* **1994**, *5*, 1072–1080.
(13) Atwood, J. L.; Bott, S. G.; Coleman, A. W.; Robinson, K. D.; Whetstone, S. B.; Means, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 8100–8101.
(14) (a) Emsley, J. *Chem. Soc. Rev.* **1980**, *9*, 91–124. (b) Perrin, C. L.; Nielson, J. B. *Annu. Rev. Phys. Chem.* **1997**, *48*, 511–544. (c) Gilli, P.; Pretto, L.; Bertolasi, V.; Gilli, G. *Acc. Chem. Res.* **2009**, *42*, 33–44.
(15) (a) Fonari, M. S.; Ganinb, E. V.; Wang, W.-J. *Acta Crystallogr.* **2005**, *C61*, o431–o433. (b) Babaian, E. A.; Huff, M.; Tibbals, F. A.; Hrncir, D. C. *J. Chem. Soc., Chem. Commun.* **1990**, 306–307.
(16) Dunitz, J. D.; Seiler, P. *Acta Crystallogr.* **1974**, *B30*, 2739–2741.
(17) (a) Kleeman, S. G.; Fluck, E.; Tebby, J. C. In *CRC Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*; Tebby, J. C., Ed.; CRC: Boca Raton, FL, 1991; p 54. (b) Germa, H.; Navech, J. In *CRC Handbook of Phosphorus-*

31 Nuclear Magnetic Resonance Data; Tebby, J. C., Ed.; CRC: Boca Raton, FL, 1991; p 185. (c) Brazier, J. F.; Lamandé, L.; Wolf, R. In *CRC Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*; Tebby, J. C., Ed.; CRC: Boca Raton, FL, 1991; p 508. (d) Lamandé, L.; Koenig, M.; Dillon, K. In *CRC Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*; Tebby, J. C., Ed.; CRC: Boca Raton, FL, 1991; p 556.

(18) (a) Suter, R. W.; Knachel, H. C.; Petro, V. P.; Howatson, J. H.; Shore, S. G. *J. Am. Chem. Soc.* **1973**, *95*, 1474–1479. (b) Dillon, K. B.; Lynch, R. J.; Reeve, R. N.; Waddington, T. C. *J. Inorg. Nucl. Chem.* **1974**, *36*, 815–817. (c) Wiberg, N. Hollerman, A. F.; Wiberg, E. *Inorganic Chemistry*; Academic: New York, 2001; pp 705 and 707.

(19) Chambron, J.-C.; Meyer, M. *Chem. Soc. Rev.* **2009**, *38*, 1663–1673.

(20) Junk, P. C. *New J. Chem.* **2008**, 762–773, and references cited therein.

JA1064697