sulfonyloxaziridines is energetically destabilized relative to the transition state for nitrogen inversion where the nitrogen is trigonal and its p-type lone pair can interact well with sulfur via an $n-\sigma^*$ π-bond.[11]

The kinetic data for **4a–c** can be extrapolated[12] to give estimated half-lives for racemization at 25 °C of ~70 s (**4a**), ~40 s (**4b**), and ~20 s (**4c**). While one should in principle be cautious in extending these results to other *N*-sulfonyloxaziridines, data for *N*-alkyloxaziridines indicate that changing the 3-substituents from alkyl to aryl has little effect on the inversion barrier.[3] Accordingly, it is likely that attempts to obtain symmetrically 3-substituted *N*-sulfonyloxaziridines in optically active form[5] may only be successful if the reaction and workup are performed at low temperature where racemization by nitrogen inversion is slow. Additionally, the reported[2] exclusive formation of a single (trans) diastereoisomer of unsymmetrically 3-substituted *N*-sulfonyloxaziridines **1** may reflect thermodynamic product control rather than a kinetic preference since cis → trans isomerization in these compounds by nitrogen inversion could also be fairly fast at ambient temperature.[14] The trans configuration should be favored on thermodynamic grounds for oxaziridines of type **1** as it minimizes steric interactions. Nevertheless, the present observations suggest that the possibility of configurational inversion at nitrogen should be borne in mind when considering reactions performed at, or above, ambient temperature.

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(10) Forni, A.; Moretti, I.; Torre, G.; Bruckner, S.; Malpezzi, L. *J. Chem. Soc., Perkin Trans. 2* **1987**, 699.

(11) For a discussion of N–S $n-\sigma^*$ bonding as an alternative to the traditional concepts of $p_\pi-d_\pi$ bonding and negative hyperconjugation, see: Raban, M.; Kost, D. *J. Am. Chem. Soc.* **1972**, *94*, 3234. Kost, D.; Raban, M. *J. Am. Chem. Soc.* **1982**, *104*, 2960.

(12) The extrapolation assumes that $\Delta G^{\ddagger}$ remains essentially constant over the temperature range 62 → 25 °C. This is a reasonable assumption bearing in mind the relatively small temperature range of the extrapolation and the fact that $\Delta S^{\ddagger}$ has been shown to be very small for nitrogen inversion in oxaziridines (ref 3a). The rate of racemization is twice that for nitrogen inversion.

(13) Dahlquist, F. W.; Longmuir, K. J.; Du Vernet, R. B. *J. Magn. Reson.* **1975**, *17*, 411.

(14) We would concur with the suggestion by a referee that the trans → cis inversion barriers in *N*-sulfonyloxaziridines **1** derived from aldehydes could be somewhat higher than those determined in **4**, due to reduced steric interactions in trans **1** where the sulfonyl group is syn to a ring hydrogen atom.

The H_3O^+ Cation in Aromatic Solvents. Synthesis, Structure, and Solution Behavior of $[H_3O^+\cdot 18\text{-crown-6}][Cl-H-Cl]$

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The interaction of the oxonium ion, H_3O^+, with polar solvents has been extensively reviewed in the broader context of hydrogen bonding.[1] The first report of a complex of H_3O^+ and a macrocycle was an infrared spectroscopic study in 1972.[2] More recently, several reports have appeared.[3-8] This has proved to be a method of isolation of H_3O^+ from higher hydrated species, $H_3O^+(H_2O)_n$.[9] The structures of two complexes of H_3O^+ coordinated to macrocycles have been reported, one which lends strong support for pyramidal H_3O^+,[10,11] and one which may be interpreted in terms of planar H_3O^+.[12] In the extensive literature of the oxonium ion, evidence for the species in aromatic solution has not been presented. Here we report that the oxonium ion coordinated to 18-crown-6 does indeed have a stable existence in aromatic media.

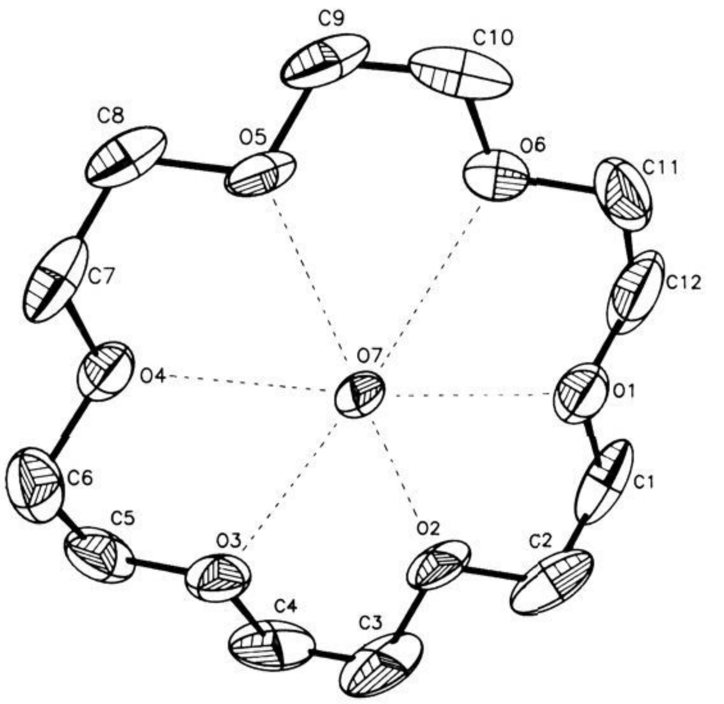

Figure 1. Structure of the $[H_3O^+\cdot 18\text{-crown-6}]^+$ cation. The hydrogen atoms of the oxonium ion could not be located. The O(7)···O separations range from 2.70 to 2.85 Å.

We have long been interested in the interaction of salts with aromatic solvents. The formation of two liquid layers by such systems has been the subject of recent reviews.[13,14] Since this "liquid clathrate effect" has been shown to provide extra stabilization for ionic species in aromatic solutions,[15] we initially attempted to protonate 18-crown-6 by bubbling HCl(g) through an aromatic suspension of the macrocycle.[16] Under anhydrous conditions no reaction was observed. However, when HCl(g) was passed through a vessel open to the atmosphere, two liquid layers quickly resulted. Colorless crystals were collected and the complex was found to be $[H_3O^+\cdot 18\text{-crown-6}][Cl-H-Cl]$.[17] Subsequently,

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(1) *The Hydrogen Bond*; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North Holland: Amsterdam, 1976; Vol. I–III.

(2) Izatt, R. M.; Haymore, B. L.; Christensen, J. J. *J. Chem. Soc., Chem. Commun.* **1972**, 1308.

(3) Behr, J.-P.; Dumas, P.; Moras, D. *J. Am. Chem. Soc.* **1982**, *104*, 4540.

(4) Heo, G. S.; Bartsch, R. A. *J. Org. Chem.* **1982**, *47*, 3557.

(5) Kolthoff, I. M.; Wang, W.-J.; Chantooni, M. K., Jr. *Anal. Chem.* **1983**, *55*, 1202.

(6) Jagur-Grodzinski, J. *Isr. J. Chem.* **1985**, *25*, 39.

(7) Buschmann, H.-J. *Inorg. Chim. Acta* **1986**, *118*, 77.

(8) Chenevert, R.; Rodrigue, A.; Chamberland, D.; Ouellet, J.; Savoie, R. *J. Mol. Struct.* **1985**, *131*, 187.

(9) Kochanski, E. *J. Am. Chem. Soc.* **1985**, *107*, 7869 and references therein.

(10) The structure of $[H_3O^+\cdot 18\text{-crown-6}(COOH)_4]Cl^-$ is reported in ref 3. The oxonium oxygen atom resides 0.61 Å out of the plane of the three crown oxygen atoms to which it is hydrogen bonded. (The X-ray diffraction data yielded the positions of the hydrogen atoms.)

(11) This Journal has hosted several manuscripts, both experimental and theoretical, which have been concerned with pyramidal versus planar geometry for H_3O^+. See: Rodwell, W. R.; Radom, L. *J. Am. Chem. soc.* **1981**, *103*, 2865 and references therein.

(12) Shoemaker, C. B.; McAfee, L. V.; Shoemaker, D. P.; DeKock, C. W. *Acta Crystallogr.* **1986**, *C42*, 1310. The oxonium oxygen atom lies within 0.1 Å of the plane of the crown oxygen atoms, although disorder of the oxonium oxygen atom was not ruled out.

(13) Atwood, J. L. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic: London, 1984; pp 395–405.

(14) Atwood, J. L. In *Chemical Separations*; Navratil, J. D., King, C. J., Eds.; Litarvan: Arvada, Colorado, 1986; pp 335–354.

(15) For example, the superoxide ion, O_2^-, is stable in refluxing toluene in the complex $[K\cdot 18\text{-crown-6}][O_2(AlMe_3)_2]$: Hrncir, D. C.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 4277.

(16) Protonation of simple crown ethers in more polar solvents such as 1,2-dichloroethane has been studied: see ref 6. Protonation of pyridine-containing crown ethers has also been investigated: Gokel, G. W.; Garcia, B. J. *Tetrahedron Lett.* **1977**, 317. Grootenhuis, P. D. J.; Uiterwijk, J. W. H. M.; Reinhoudt, D. N.; vanStaveren, C. J.; Sudholter, E. J. R.; Bos, M.; van Eerden, J.; Klooster, W. T.; Kruise, L.; Harkema, S. *J. Am. Chem. Soc.* **1986**, *108*, 780.

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the reaction was carried out as in (1) with the H_2O added stoichiometrically and the atmosphere excluded. The yield was quantitative based on the macrocycle. The reaction is done in the presence of an aromatic solvent, and liquid clathrates of composition $[H_3O^+\cdot 18\text{-crown-6}][Cl\text{–}H\text{–}Cl]\cdot 4.8C_6H_6$ and $[H_3O^+\cdot 18\text{-crown-6}][Cl\text{–}H\text{–}Cl]\cdot 3.6C_6H_5Me$ have been prepared.[18]

$$18\text{-crown-6} + H_2O + HCl(g) \rightarrow [H_3O^+\cdot 18\text{-crown-6}][Cl\text{–}H\text{–}Cl] \quad (1)$$

The structure of the $[H_3O^+\cdot 18\text{-crown-6}]^+$ cation is shown in Figure 1. The hydrogen atoms could not be located with certainty, presumably because of disorder.[19] The O(oxonium)···O(crown) separations range from 2.70 to 2.85 Å, and they all are well within the range for hydrogen bonding.[20] The six crown oxygen atoms are planar to 0.20 Å, and the oxonium oxygen atom lies 0.29 Å from this plane. However, it is noteworthy that the oxonium oxygen atom lies only 0.09 Å from the plane of the three nearest crown oxygen atoms. A distance of 0.61 Å from the plane of the hydrogen bonded oxygen atoms was found for the pyramidal oxonium oxygen atom in $[H_3O^+\cdot 18\text{-crown-6}(COOH)_4]Cl$,[3] while a distance of 0.1 Å from the plane of the six oxygen atoms of the ring was observed in $[H_3O^+\cdot 18\text{-crown-6}]_2[Mo_6O_{19}]$.[12] The title compound lends a measure of support for planar H_3O^+, but determination of the proton positions from low-temperature data will provide conclusive proof of the geometry about the oxonium oxygen atom.

The anion $[Cl\text{–}H\text{–}Cl]^-$ was first observed in 1909,[21] and its structure has been determined in several salts.[22-25] The Cl···Cl separation in the title compound, 3.11 Å, is at the low end of the range which stretches up to 3.315 Å.[25] The hydrogen atom was clearly located 1.60 and 1.57 Å from the two chlorine atoms, and the angle at the hydrogen atom is 157°. Although the $[Cl\text{–}H\text{–}Cl]^-$ anion has been studied rather extensively,[26] to our knowledge this is the first instance of it in an aromatic solution. Studies of the chemical reactivity of both $[H_3O^+\cdot 18\text{-crown-6}]^+$ and $[Cl\text{–}H\text{–}Cl]^-$ in aromatic solutions are in progress.

Acknowledgment. We are grateful to the National Science Foundation, the Department of Energy, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, and thermal parameters (3 pages); listing of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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[17] In a typical experiment 1.32 g of 18-crown-6 (0.005 mol) was moistened with 0.09 mL of distilled water (0.005 mol) and ca. 30 mL of toluene was layered over the mixture which was contained in a Schlenk tube. Anhydrous HCl(g) was bubbled through the solvent. The evolution of heat was noted immediately, and in 5 min the formation of two liquid layers was apparent. The passage of HCl(g) was continued until the lower liquid layer reached constant volume (ca. 30 min). Large, colorless crystals of the title compound were obtained from the lower layer by allowing the reaction mixture to cool to room temperature. The crystals are hygroscopic and decompose quickly upon exposure to the atmosphere. Those for the X-ray diffraction study were examined under toluene and transferred while wet with toluene to thin-walled glass capillaries. The space group is the monoclinic $P2_1/c$ with $a = 10.455$ (7) Å, $b = 20.701$ (9) Å, $c = 8.552$ (7) Å, $\beta = 96.21$ (3)°, and $D_c = 1.28$ g cm^{-3} for $Z = 4$. Least-squares refinement based on 1100 observed reflections led to a final R value of 0.065. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the crown ether were placed in calculated positions and were not refined. The hydrogen atom of the anion was located on a difference Fourier map and was not refined. The details of data collection and refinement are given in Holton et al.: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45.

[18] The stoichiometry of the liquid clathrates was established by ^1H NMR integration. In addition to the toluene, two resonances result: 3.07 ppm (18-crown-6), and 10.36 ppm ($[H_3O^+]$), referenced to the toluene methyl at 2.30 ppm. A resonance due to the proton of the $[Cl\text{–}H\text{–}Cl]^-$ ion was not observed.

[19] Data were collected on two different crystals, and $(\sin\theta)/\lambda$ cut-offs were employed, but the hydrogen atoms of the oxonium group could not be unequivocally located.

[20] Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; Benjamin: New York, 1968; p 16.

[21] Kaufler, F.; Kunz, E. *Chem. Ber.* **1909**, *42*, 385, 2482.

[22] Schroeder, L. W.; Ibers, J. A. *Inorg. Chem.* **1968**, *7*, 594 ($CsCl\cdot{}^1/_3(H_3O\cdot Cl\text{–}H\text{–}Cl)$).

[23] Williams, J. M.; Peterson, S. W. *Am. Cryst. Assoc. Prog. Abstr.*, Ottawa, Canada, 1970 ($[NMe_4][Cl\text{–}H\text{–}Cl]$).

[24] Mootz, D.; Poll, Wolfgang; Wunderlich, H.; Wussow, H.-G. *Chem. Ber.* **1981**, *114*, 3499 ([phosphonium][Cl–H–Cl]).

[25] Atwood, J. L.; Bott, S. G.; Coleman, A. W.; Zhang, H.; Means, C. M., unpublished results ($[K\cdot 18\text{-crown-6}][Cl\text{–}H\text{–}Cl]$, $[Mg\cdot 18\text{-crown-6}][Cl\text{–}H\text{–}Cl]_2$).

[26] Emsley, J. *Chem. Soc. Rev.* **1980**, *9*, 91.

Pentaammineosmium(II)-η^2-2,6-Lutidine: An Intermediate for C-H Activation

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Though a few transition-metal complexes featuring η^2-bound arene ligands are known,[1] no reports on η^2-nitrogen heterocycles are available to date. The role of η^2-bound ligands as intermediates for arene C-H activation has been established,[2] but such intermediates have heretofore not been isolated. Our interest in the reactivity of pentaammineosmium(II) with aromatic molecules has led to the discovery of a stable η^2-bound 2,6-lutidine complex. We have found that this complex is a precursor for the activation of the para carbon-hydrogen bond.

When $[(NH_3)_5Os(TMB)]^{2+}$[3] reacts with 2,6-lutidine (lu), a new species characterized as $[(NH_3)_5Os(\eta^2\text{-lu})]^{2+}$ (**1**) can be isolated as a triflate salt.[4] The ^1H NMR spectrum[5] of **1** at −60 °C reveals inequivalent ring proton resonances at 6.68 (d, 1 H), 5.28 (m, 1 H), and 5.22 (d, 1 H) ppm. The latter two frequencies are shifted ~2 ppm upfield from free ligand values, characteristic of protons that are adjacent to the metal coordination site.[6] Spin saturation exchange was observed between the doublets, indicating a fluxional process where the metal migrates between the [3,4] and [4,5] positions. Upon warming to room temperature, the doublets and methyl resonances broaden significantly but do not coalesce, indicating a specific rate $k < 1.3 \times 10^3$ s^{-1} for tautomerization, corresponding to $\Delta G^\ddagger > 13$ kcal mol^{-1}.[7]

Protonation of the lutidine nitrogen leads to the formation of $[(NH_3)_5Os(\eta^2\text{-luH})]^{3+}$ (**2**).[8] By arguments analogous to those outlined above, it was established that **2** also exists as the [3,4] isomer. For

$$[(NH_3)_5Os(\eta^2\text{-luH})]^{3+} \rightleftarrows [(NH_3)_5Os(\eta^2\text{-lu})]^{2+} + H^+ \quad (1)$$

a pK_a of 7.4 was obtained at room temperature.

A cyclic voltammogram of **1** displays a chemically irreversible oxidation wave at +0.45 V.[9] Upon return scan a new, also

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[1] Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883-1885, and references therein.

[2] (a) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650-1663. (b) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 305-306.

[3] TMB = 1,2,3,4-tetramethylbenzene, see: Harman, W. D.; Taube, H. *Inorg. Chem.* **1987**, *26*, 2917.

[4] Preparation of **1**: Pure 2,6-lutidine (0.5 mL) is added to 0.15 mmol of $[(NH_3)_5Os(TMB)]^{2+}$[3] in 8 mL of DME solution. After 1 h cold CH_2Cl_2 (15 mL) is added, and the precipitate is filtered and washed with Et_2O.

[5] (a) All NMR spectra recorded in acetone-d_6. (b) Additional peaks: *cis*- and *trans*-ammines, 3.65 (12 H), 4.97 (3 H) ppm; methyl groups, 2.24 (3 H), 2.48 (3 H) ppm.

[6] Harman, W. D. Ph.D. Thesis, Stanford University, 1987. Sekine, M., unpublished results.

[7] Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; pp 79, 96.

[8] Full characterization of **2** will be reported separately.

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