

Table II. Energies^a for Stationary Points on the Reaction Surface $\text{SiH}_2 + \text{SiH}_3\text{OH} \rightarrow (\text{SiH}_3)_2\text{O}$

| molecule | HF ^b | $\epsilon^{(2)b}$ | $E(\text{rel})^c$ |
|--|-----------------|-------------------|-------------------|
| $\text{SiH}_3\text{OH} + \text{SiH}_2$ | -656.14223 | -366.08 | 0 |
| 4 | -656.266 63 | -372.75 | -75.7 |
| 5 | -656.162 45 | -375.63 | -12.8 |
| 6 | -656.107 47 | -397.78 | 4.9 |

^a Total energies in hartrees, correlation energies in mhartrees, and relative energies in kcal/mol. ^b Obtained with the 6-31G** basis. ^c Higher order effects of electron correlation, larger basis set effects, and vibrational corrections were taken from the first insertion reaction.

intermediate between that in **1** and **2**. The relative energy of **3** is very sensitive to the inclusion of electron correlation. The overall activation energy for the formation of silanol from SiH_2 and H_2O is calculated to be 11.3 kcal/mol at the highest theoretical level. The exothermicity of the reaction, 70.1 kcal/mol, is considerably lower than the value of 94.9 kcal/mol computed for the corresponding carbene-insertion reaction.⁸

We have also examined the second insertion reaction, viz., the reaction between silanol and SiH_2 to yield the ultimate reaction product disiloxane, **4** (Table II). This reaction proceeds in a manner qualitatively analogous to the first reaction, with the initial formation of a complex, **5**,¹⁸ between SiH_2 and the oxygen lone pair of silanol. The complexation energy of 12.8 kcal/mol is nearly the same value calculated for **2** at a similar level. However, the overall activation energy (4.9 kcal/mol) and the exothermicity (75.7 kcal/mol) of this step are calculated to be about 6 kcal/mol lower than the corresponding values for the initial insertion reaction. The key structural features of **1-3**, viz., the large variation in Si-O distance, wide angles at the oxygen bound to silicon,¹³ and the low symmetry of the rearrangement transition state, are also found in the structures **4-6**.¹⁸

We are currently examining the insertion of silylene in a variety of σ bonds to probe the general stability of zwitterionic structures involving silicon and other heteroatoms.¹⁴

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Registry No. SiH_2 , 13825-90-6; H_2O , 7732-18-5; SiH_3OH , 14475-38-8; $(\text{SiH}_3)_2\text{O}$, 13597-73-4.

Synthesis of Cesium 18-Crown-6: The First Single-Crystal Electride?

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A relatively stable crystalline compound between cesium metal and the crown ether 18-crown-6¹ has been synthesized. The optical, electrical, and magnetic properties suggest that it is an electride, $\text{Cs}^+18\text{C6}^-$, although the ceside, $\text{Cs}^+(18\text{C6})_2\text{Cs}^-$, cannot be ruled out. Electrides are salts in which the anion is a trapped electron.² They had previously been prepared only as films or powders by complete solvent evaporation from solutions that contained solvated electrons and alkali metal cations complexed by crown ethers or cryptands.³⁻⁸ Thin films had also been pre-

pared by direct vapor deposition.⁹ Characteristic of all electrides is an intense optical absorption band at 1250-1800 nm.³⁻⁶ Magnetic susceptibilities and EPR spectra of electride powders showed that they exhibit substantial spin pairing.⁶⁻⁸ Numerous attempts to crystallize electrides from solution have failed. In "good" solvents such as methylamine or ammonia the solubility is too high, while "poor" solvents such as isopropylamine or diethyl ether always led to rapid decomposition. The key to the present synthesis is stabilization of the solutions by dissolved lithium.

Extensive studies of films and powders prepared from methylamine solutions of cesium and 18-crown-6 in various proportions⁸ showed that when lithium was added the solutions were much more stable. In an attempt to prepare crystalline $\text{Cs}^+18\text{C6Li}$, analogous to the recently synthesized sodide salt $\text{Cs}^+18\text{C6Na}^-$,¹⁰ we dissolved equimolar amounts of Cs, Li, and 18C6 in methylamine in a fused silica apparatus. The solution was evaporated to near dryness, and the crystallization solvent, an approximately equimolar mixture of isopropylamine and diethyl ether, was added.¹¹ When the solution was cooled to -78 °C, a crystalline precipitate formed. Microscopic examination of the ether-washed crystals from this preparation and from a second identical synthesis showed the presence of well-formed dark blue crystals. Mixed with the crystals were numerous irregularly shaped dark particles.¹² Analysis of selected crystals showed the stoichiometry to be essentially $\text{Cs}18\text{C6}$. In a third preparation the final solution was passed through a coarse frit at ~ -10 °C before crystallization in order to retain any precipitated lithium. Well-formed crystals resulted that showed little contamination by noncrystalline particles. After removal of the supernatant solution, the crystals were repeatedly washed with diethyl ether, vacuum-dried at room temperature, and transferred through a graded seal to Pyrex storage tubes.

The crystals are stable in vacuo for days at room temperature and below. They melt at ~ 65 °C to yield an unstable deep blue liquid. Analysis of all three preparations showed the most likely stoichiometry to be simply $\text{Cs}18\text{C6}$. Surprisingly, lithium is not present in significant amounts, and that which was detected is probably adventitious lithium which adheres to the crystals. Complete analysis of a weighed sample from the third preparation was carried out as described elsewhere.¹⁰ Reaction with water produces 0.5 mol of H_2 and 1 mol of OH^- per mol of reducing species. Titration of the OH^- was followed by flame emission analysis for alkali metals. The residue was dissolved in D_2O and was analyzed for 18C6 by ^1H NMR integration with an internal standard of potassium hydrogen phthalate. Crystals were also reacted directly with D_2O and examined by ^1H NMR. The spectrum showed the complete absence of methylamine, isopropylamine, and diethyl ether. The number of millimoles obtained by analysis of a mass equivalent to 0.246 mmol of $\text{Cs}18\text{C6}$ from the third synthesis were 0.124 (H_2), 0.252 (OH^-), 0.253 (Cs), 0.0033 (Li), and 0.258 (18C6). These results confirm the stoichiometry $\text{Cs}18\text{C6}$. Preliminary X-ray diffraction studies of three crystals yielded only diffuse spots, showing that the crystal quality was too poor for a structure determination.

Lithium seems to act as a scavenger for radicals produced by solvent and/or crown ether decomposition (possibly by forming lithium alkyls). When crystals were dissolved in isopropylamine in the absence of lithium in an attempt to recrystallize them, immediate decomposition occurred. Subsequent experiments have shown that lithium also stabilizes other alkali metal-crown ether

(6) Landers, J. S.; Dye, J. L.; Stacey, A.; Sienko, M. J. *J. Phys. Chem.* **1981**, *85*, 1096.

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(9) Le, L. D.; Issa, D.; Van Eck, B.; Dye, J. L. *J. Phys. Chem.* **1982**, *86*, 7.

(10) Van Eck, B.; Le, L. D.; Issa, D.; Dye, J. L. *Inorg. Chem.* **1982**, *21*, 1966.

(11) Pure isopropylamine can also be used, but the yields are lower.

(12) The low lithium content of the crystals and the low solubility of lithium in the crystallization solvent make it likely that these particles are precipitated lithium.

(1) IUPAC: 1,4,7,10,13,16-hexaoxacyclooctadecane; abbreviation, 18C6.
(2) The trapped electrons may undergo spin pairing or even "dielectron" formation. Thus, the name "electride" refers to the stoichiometry, not the structure of the salt. The essential features are substantial electron localization and the absence of electron attachment to individual atoms or molecules to form conventional anions.

(3) Dye, J. L.; Yemen, M. R.; DaGue, M. G.; Lehn, J.-M. *J. Chem. Phys.* **1978**, *68*, 1665.

(4) DaGue, M. G.; Landers, J. S.; Lewis, H. L.; Dye, J. L. *Chem. Phys. Lett.* **1979**, *66*, 169.

(5) Dye, J. L.; DaGue, M. G.; Yemen, M. R.; Landers, J. S.; Lewis, H. L. *J. Phys. Chem.* **1980**, *84*, 1096.

solutions in isopropylamine–diethyl ether mixtures. The magnetic susceptibility of Cs₁₈C₆ crystals was measured from 1.7 to 270 K with an SHE Corp. Model VTS Squid susceptometer. The compound is essentially diamagnetic, with only about 1% unpaired spins. Single-crystal EPR spectra show the presence of two overlapping lines. One has $g = 2.0023$ and a line width of ~ 0.75 G, independent of temperature from -135 to $+51$ °C. The other line has a smaller g value (~ 2.0016) and shows g anisotropy upon rotation. It has a line width that broadens from ~ 1.25 G at -135 °C to ~ 3.5 G at $+31$ °C.

The stoichiometry suggests two possibilities for this compound, Cs⁺18C₆e⁻ and Cs⁺(18C₆)₂Cs⁻. The former interpretation is favored for three reasons: (1) Previous optical spectra of 1:1 Cs₁₈C₆ films did not show the characteristic peak of Cs⁻ at ~ 1000 nm^{3,5} but rather a single peak at 1500 nm attributed to trapped electrons.⁵ When crystals of Cs₁₈C₆ were dissolved in methylamine, dry annealed films produced by solvent evaporation also showed only the electride peak at 1500 nm. (2) Crystals of Cs⁺18C₆Na⁻ have been synthesized and analyzed.¹⁰ Therefore, if a ceside were to form, one might expect it to have the stoichiometry Cs⁺18C₆Cs⁻ rather than Cs⁺(18C₆)₂Cs⁻. (3) Polycrystalline samples of Cs₁₈C₆ have dc powder conductivities that vary logarithmically with $1/T$. The band gap over the temperature

range -54 to $+10$ °C is ~ 0.6 eV, thus verifying localization of the electron (or electron pair). This gap appears to be too small for a ceside salt.

These results show that it is possible to prepare stable crystalline samples of stoichiometry Cs₁₈C₆. Although the compound could be a ceside salt (if so, this is the first stable ceside), it is more reasonably described as an electride in which the electrons are trapped in potential wells at ~ 0.6 eV, below the conduction band. Electron spin pairing leads to a diamagnetic ground state. Although the concentration of unpaired spins is high enough to be easily measured, we cannot be certain at this time whether this is an intrinsic bulk property of the pure compound or is the result of defects. Work is in progress to grow better crystals for diffraction studies and to carry out quantitative single-crystal EPR studies.

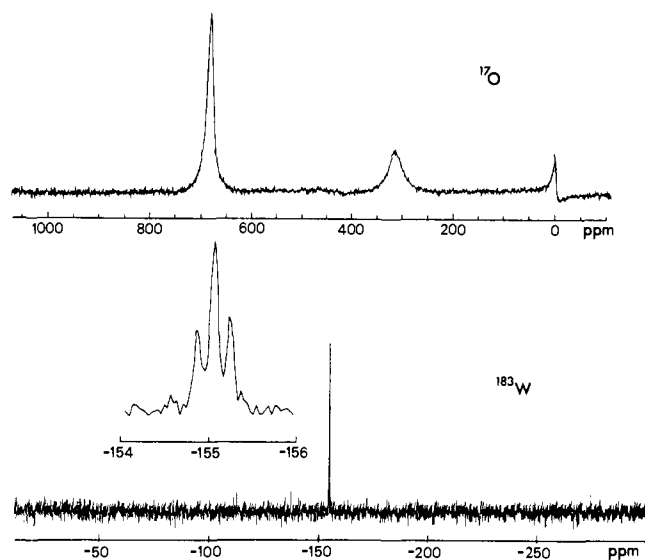
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Registry No. Cs⁺18C₆e⁻, 82065-73-4.

Additions and Corrections

Heteropolytungstobisphosphonates. Cyclopentane-Like Pseudorotation of an Oxometalate Structure [*J. Am. Chem. Soc.* 1981, 103, 7665–7666]. P. R. SETHURAMAN, M. A. LEPARULO, M. T. POPE,* F. ZONNEVILLE, C. BRÉVARD, and J. LEMERLE.

Page 7665: In Figure 2 the line in the ¹⁸³W NMR spectrum was not reproduced. Figure 2 below shows the missing line.



New Multidentate Ligands. X. Chelating Tendencies of *N,N'*-Diglycylethylenediamine-*N'',N''',N''',N''''*-tetraacetic Acid and Ethylenediamine-*N,N'*-di(acetylglycine)-*N,N'*-diacetic Acid [*J. Am. Chem. Soc.* 1970, 92, 4223]. R. J. MOTEKAITIS and A. E. MARTELL.*

It has come to our attention that Figure 3 in this paper was omitted in the final printing process and that the figure that appeared as Figure 3 is a duplicate of Figure 1. Because of this error the results described in our paper have been misinterpreted and our conclusions have been questioned.

EDDAG-DA by the Fe(III) ion to form a very stable Fe(III) chelate compound. This is the first example of the formation

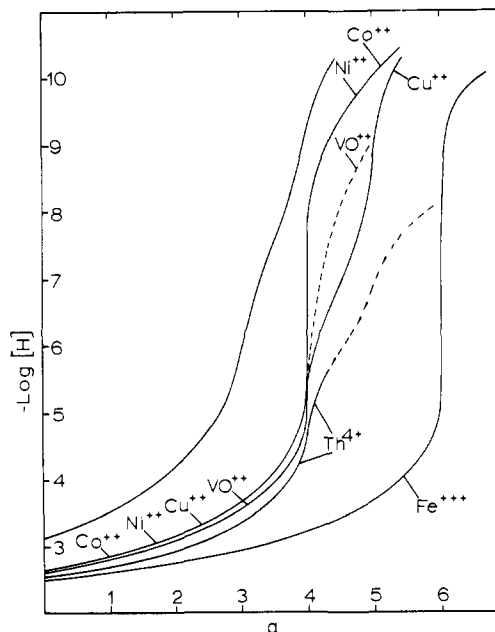


Figure 3. Potentiometric equilibrium curves for 1:1 molar ratios of metal ions to EDDAG-DA: the unlabeled curve represents the titration of pure ligand; broken lines represent precipitation; a = moles of 0.10 M base added per mole of ligand; concentration is 0.0010 M in ligand and metal ion; solution contains 0.10 M KNO₃; $t = 25$ °C.

The correct Figure 3, presented here, provides experimental proof for the displacement of two amide protons from the ligand

