proached down-the-steps. A similar observation has also been reported for the H_2–D_2 exchange reaction on platinum surfaces.[3]

The rates below 260 °C followed the Arrhenius behavior. The activation energy for this region was 11.7 ± 1.0 kcal/mol for the Zn-polar surface, 9.7 ± 1.0 kcal/mol for the nonpolar stepped surface, and 8.4 ± 1.0 kcal/mol for the O-polar surface. It should be noted that the activation energy for the stepped surface did not depend on the direction of approach, unlike the rates. Thus the enhanced rate in the "up" direction of approach must be due to a higher sticking coefficient of reactants in that direction, while the surface reaction probability remains the same.

The trends in the activation energy and the reaction rates follow those derived from temperature-programmed decomposition studies.[11,12] This trend has been explained by the different magnitudes of surface dipole, different hardness of the surface Zn ions, and different degrees of steric hindrance by the surrounding oxygen ions to the interaction of adsorbates with surface Zn ions on the different surfaces. It appears that these factors can be used to explain the trends in catalytic reactions as well.

First Electride Crystal Structure

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The crystal structure and optical, electrical, and magnetic properties of $Cs^+(18C6)_2 \cdot e^-$ (18C6 = 18-crown-6) show that each electron is trapped in a nearly spherical, otherwise empty, cavity of radius ~2.4 Å, surrounded by eight sandwich-complexed cesium cations. The shortest interelectron distance (8.68 Å) results in only weak coupling, so that this salt behaves as a localized electride.

When the first salt of an alkali metal anion was synthesized in 1974,[1,2] "blue, strongly paramagnetic solids" were also obtained by evaporation of ethylamine solutions that contained cryptated cations and solvated electrons.[2] This method permitted observation of the optical spectrum of a solvent-free electride[3] and led to intensive efforts to isolate crystalline electrides. Rapid autocatalytic decomposition of solutions frustrated these attempts until 1983, when crystals of the subject electride, $Cs^+(18C6)_2 \cdot e^-$, were isolated.[4,5]

Eight crystalline electrides have now been synthesized. The optical, electrical, and magnetic properties range from those of weakly interacting localized electrons,[4,6] to antiferromagnetism[7] and spin-paired states,[8,9] to electron delocalization.[9,10] This variability makes the nature of electron trapping in electrides a subject of great interest.

The electride, $Cs^+(18C6)_2 \cdot e^-$, crystallizes from dimethyl ether–trimethylamine mixtures as shiny black plates. The optical transmission spectrum of thin films consists of a single broad band with maximum absorbance at 1650 nm.[4] The low absorbance at wavelengths greater than 2000 nm indicates electron localization with a trap depth of at least 0.5 eV. The conductivity is consistent with electron localization since it shows semiconductor-like behavior with a band gap of 0.9 eV.[4,5]

Magnetic susceptibilities, down to ~2 K, nearly obey the Curie–Weiss law.[6] A single narrow EPR line (0.5 G down to 2 K) occurs at the free electron g value. The ^{133}Cs NMR spectrum of the solid exhibits a temperature-dependent chemical shift that corresponds to only 0.033% atomic character.[11] Thus, this electride has all of the characteristics expected of a compound in which all of the electrons are trapped at anion vacancies. This view is further strengthened by NMR evidence that up to three electrons around Cs^+ can be replaced by Na^- ions.[11] Since the crystal structure of $Cs^+(18C6)_2 \cdot Na^-$ shows that there are eight Na^- ions around each sandwiched cesium cation,[12] it seemed likely that the electride structure is similar to that of the sodide, with electrons occupying *all* of the anionic sites.

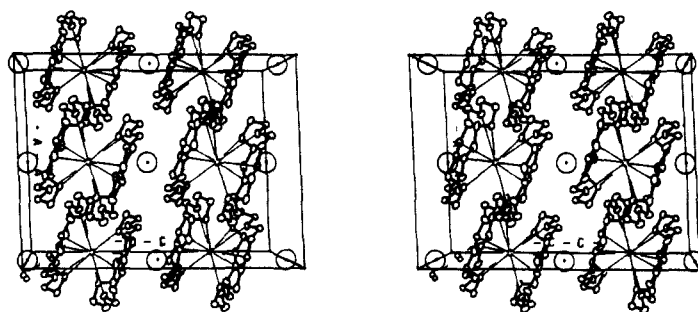The crystal structure of $Cs^+(18C6)_2 \cdot e^-$ [$CsC_{24}H_{48}O_{12}$] was

Figure 1. ORTEP stereo packing diagram of $Cs^+(18C6)_2 \cdot e^-$. The anionic hole centers are indicated by the symbol ⊙.
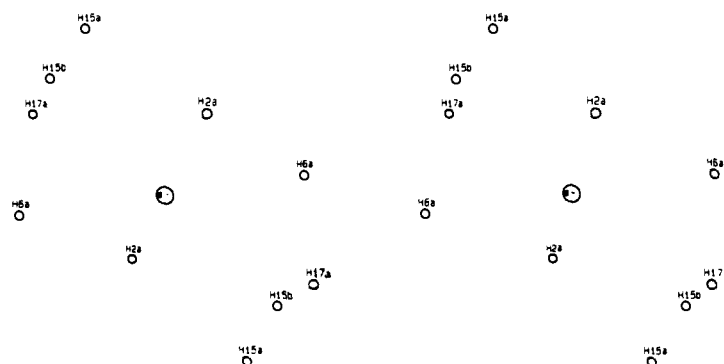

Figure 2. ORTEP stereodiagram of the anionic hole and surrounding atoms in $Cs^+(18C6)_2 \cdot e^-$ viewed along the *b* axis.

Table I. Selected Interatomic Distances in Cs⁺(18C6)·e⁻ᵃ

Cs⁺ to oxygen, Å		electronᵇ to surrounding atoms, Å	
Cs⁺–O₁	3.453 (8)	e⁻–H₆ₐᶜ	3.29
Cs⁺–O₄	3.296 (8)	e⁻–H₁₅ᵦᵈ	3.64
Cs⁺–O₇	3.305 (7)	e⁻–H₂ₐᵉ	3.76
Cs⁺–O₁₀	3.457 (8)	e⁻–H₁₇ₐᵈ	4.09
Cs⁺–O₁₃	3.296 (9)	e⁻–H₁₅ₐᵈ	4.17
Cs⁺–O₁₆	3.304 (8)	e⁻–C₆ᶜ	4.19
		e⁻–H₃ₐᵉ	4.24
		e⁻–H₈ᵦᶜ	4.29

ᵃMean C–C in crown, 1.49Å; mean C–O in crown, 1.42 Å. ᵇDistances from e⁻ are calculated from the inversion center at 0, ¹/₂, 0. ᶜIndicates atom at ¹/₂ - x, y + ¹/₂, ¹/₂ - z. ᵈAt -x - ¹/₂, ¹/₂ + y, ¹/₂ - z. ᵉAt -x, y, ¹/₂ - z.

determined at -57 °C in the monoclinic space group C2/c with a = 13.075 (5) Å, b = 15.840 (7) Å, c = 17.359 (8) Å, β = 92.30 (3)°, and Z = 4. The refinement began with the non-sodium parameters of the isostructural Cs⁺(18-crown-6)₂ Na⁻ structure.¹² Final agreement factors of R = 0.058 and R_w = 0.070 were obtained for 1306 observed unique reflections. An ORTEP stereo packing diagram is shown in Figure 1. The ions pack in alternate planes of cations and anionic holes perpendicular to the c axis with closest in-plane separation of 10.27 Å. The anionic holes are separated by 8.68 Å along the c axis. The cations, lying alternately ±0.42 Å from the c axis along the b direction, are separated by 8.72 Å. The size of the anionic hole, which lies at an inversion center, may be estimated by subtracting the van der Waal's radius for hydrogen from the distances to the surrounding hydrogen atoms from this center. The shortest hydrogen–hole center distances are listed in Table I and give a minimum hole radius of 2.1 Å and a mean hole radius of ~2.4 Å. A stereoview of the anionic hole down the b axis is shown in Figure 2. The hole appears to be nearly spherical with a slight elongation along the c axis toward the nearest-neighbor trapped electrons. The average calculated electron density throughout the anionic hole is only 0.026 e⁻/Å³, which is below the noise level on the final difference electron density map, thus precluding direct observation of the electride ion. That the cesium is a cation is shown by the Cs–O distances, which are nearly identical with those in the Cs⁺(18C6)₂·Na⁻ structure and only about 0.2 Å longer than those in the Cs⁺·(18C6)·SCN⁻ structure.¹³

Since the structure consists of only a complexed cation and noise level electron density at the usual anionic site, it supports the picture of a localized electride as a salt with electrons as the anions. This study is the first direct determination of the local structure around a trapped electron.

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Silox Hydrides (silox = t-Bu₃SiO⁻) of Group 5: Do [(silox)₂MH₂]₂ (M = Nb, Ta) Complexes Contain Unbridged M–M Bonds?

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Complexes containing M–H bonds are widely recognized as being important intermediates in numerous catalytic processes.¹ Investigations of early metal hydride reactivity have resulted in reagents² useful in organic synthesis and modeling studies³⁻⁵ relevant to the Fischer–Tropsch process.⁶

A variety of group 5 hydrides have been described; the majority contain ancillary phosphine⁷,⁸ and/or cyclopentadienyl ligands⁹⁻¹¹ that tend to electronically and sterically saturate the early metal center. By introducing an ancillary ligand system with electronic

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