ments strongly suggests hydride ion transfer from the borohydride to decaborane, probably in a single step. It is possible that the reaction occurs by the formation of diborohydride-like BHB linkage[11] between the borohydride and the most positive[12] 6(9) decaborane atom, followed by loss of a borane group and possible rearrangement to the as yet undetermined $B_{10}H_{15}^-$ structure. The initial attack of borohydride ion would thus occur in a manner similar to the first step of a proposed mechanism[13,14] for reaction of acetonitrile with decaborane and would resemble the many other known examples of nucleophilic attack on decaborane. The formation of $NaB_{10}H_{13}$ in 18% yield (as judged by hydrogen evolution) during the early stages of the reaction between sodium borohydride and decaborane allows the possibility that a competing mechanism may operate to produce $NaB_{10}H_{13}$ directly by reaction 1 previously proposed.[3] The majority of the $B_{10}H_{13}^-$, however, was produced by the decomposition $B_{10}H_{15}^-$ according to eq. 3. The subsequent appearance of $NaB_{11}H_{14}$ in solution indicates that the over-all reaction of sodium borohydride with decaborane in ethylene glycol dimethyl ether solution is similar to the synthesis of $NaB_{11}H_{14}$ in dioxane solution.

Isotope studies of the decaborane–sodium borohydride system were concerned primarily with the exchange reaction of diborane with $NaB_{10}H_{13}$ after hydrogen evolution according to eq. 3 had taken place. An analysis of the diborane in the early stages of the exchange, however, indicated that after 2.5 hr. at 0° only 27% of the decaborane boron had exchanged with the diborane. In an experiment previously described in the literature,[15] diborane was mixed with preformed $NaB_{10}H_{13}$ and exchange of diborane with all ten boron atoms of the decaborane cage had reached completion within 1 hr. It is apparent that B_2H_6–$NaB_{10}H_{15}$ exchange and $NaB_{10}H_{15}$–$NaB_{10}H_{13}$ exchange either do not take place or are slow with respect to the diborane–$NaB_{10}H_{13}$ reaction. A more detailed study of isotope exchange in this system would be of interest.

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On the Nature of $SeCl_4 \cdot 2C_5H_5N$

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Present knowledge of the stereochemistry of selenium in its IV oxidation state reveals an interesting and rather unique situation concerning the role of the lone pair of electrons on selenium. The tetrahalides appear to be either molecular substances with structures based on a trigonal bipyramid shape $(:SeX_4)$[1,2] or ionic materials $(:SeX_3^+ + X^-)$ with pyramidal trihalide cations.[3] In each of these situations the lone pair of electrons appears to play a significant role in the geometry of the molecule or ion. In contrast to this, the hexahaloselenate ions (SeX_6^{-2}) are reported to be octahedral, and the lone pair of electrons is considered "stereochemically inert."[4]

The reported addition product of selenium tetrachloride with two molecules of pyridine is of interest with respect to this situation concerning the role of the lone-pair electrons. Several reports of this material have appeared in the literature,[5–7] and speculation as to the nature of the substance has included a molecular compound $SeCl_4 \cdot 2py$ isoelectronic with the hexahaloselenates, and a pyridine adduct of a chloroselenium cation such as $(SeCl_3py_2)^+$ or $(SeCl_2py_2)^{+2}$. In this communication we wish to report an investigation of this addition product which indicates the material is, in solution, a pyridine derivative of a trichloroselenium cation.

Experimental

Materials.—Anhydrous selenium tetrachloride was prepared by reaction of powdered black selenium and gaseous chlorine according to the method described in *Inorganic Syntheses*.[8]

Fisher reagent grade pyridine was distilled once through a 40-cm. Vigreux column. The acetonitrile used as the solvent for the dissociation study was purchased from Matheson Coleman and Bell.

General Experimental Procedures.—All of the selenium compounds investigated in this study decompose immediately when exposed to air of average humidity; therefore all of the work was performed in a plastic bag[9] filled with dry nitrogen.

Analytical Methods.—The selenium analysis was obtained by dissolving the sample in dilute sulfuric acid, adding starch indicator and sodium thiosulfate solution, and back-titrating the excess thiosulfate with iodine solution. Nitrogen analyses were obtained by the Kjeldahl method using a Pregl type microapparatus.[10] For the chlorine and bromine analysis the standard Volhard method was used; an acid solution of the sample was titrated with thiocyanate solution after the addition of excess standard silver nitrate.

X-Ray Powder Patterns.—Because the samples decomposed readily in air they were sealed in 0.3-mm. o.d. capillary tubing, and diffraction patterns were recorded photographically on a General Electric camera of radius 7.2 cm., using Cu Kα radiation obtained from a standard Norelco unit. The intensities were estimated visually.

Preparation and Characteristic of $SeCl_4 \cdot 2py$.—Newly prepared selenium tetrachloride was added gradually to freshly distilled

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pyridine. A yellow precipitate of the desired product formed immediately and considerable heat was evolved. The crystalline product was removed by filtration, washed with dry ether, dried in a stream of dry nitrogen, and stored in a desiccator over calcium chloride.

Anal. Calcd. for $SeCl_4 \cdot 2py$: Se, 20.8; Cl, 37.4; N, 7.4. Found: Se, 20.8; Cl, 36.7; N, 7.4.

The material melts with decomposition at 78–84° in a sealed capillary. The sample decomposes immediately on exposure to moist air. The Bragg spacings (Å.) and relative intensities of the prominent reflections of the X-ray powder pattern are: 6.33, 100; 8.51, 36; 5.47, 36; 5.07, 32; 3.79, 32; 3.08, 32; 2.54, 28; 1.96, 14; 1.84, 14; 4.62, 12; 2.47, 12; 1.47, 10; 2.32, 8; 2.75, 8; 4.44, 6; 2.13, 6; 2.07, 6; 1.68, 6; 1.91, 4.

The infrared spectra showed the following absorptions (given in $cm.^{-1}$): 1650 w, 1620 m, 1610 m, 1540 m, 1350 w, 1250 m, 1200 s, 1170 w, 1160 m, 1080 w, 1061 s, 1030 w, 1010 s, 930 s, 855 vw, 750 vs, 690 s, 650 s, and 430 m. The compound is soluble in acetonitrile (about 4.5 g./100 ml. of acetonitrile at 27°), slightly soluble in chloroform, and insoluble in carbon tetrachloride, carbon disulfide, benzene, ether, tetrahydrofuran, alcohols, dioxane, and dimethylformamide. It is decomposed by acid solutions.

Dissociation of $SeCl_4 \cdot 2py$ in Acetonitrile.—Dissociation of $SeCl_4 \cdot 2py$ in acetonitrile was measured by a Mechrolab Model 301A vapor pressure osmometer. Benzil was used to calibrate the instrument for the solvent. The results of ten measurements on two solutions which were 0.018 and 0.01334 *F* indicated 2.05 ± 0.06 particles formed per formula unit of $SeCl_4 \cdot 2py$.

Conductivity measurements were taken using a Jones bridge. The results are given in Table I.

TABLE I

CONDUCTANCE OF ACETONITRILE SOLUTIONS OF $SeCl_4 \cdot 2py$

Concn., *M*	Spec. cond., mhos/cm.	Equiv. cond., mhos $cm.^2$/equiv.
Solvent	3.23×10^{-6}	. . .
1.81×10^{-2}	1.164×10^{-3}	64.55
1.64×10^{-2}	1.029×10^{-3}	52.80
1.29×10^{-2}	8.62×10^{-4}	66.90
9.02×10^{-3}	6.40×10^{-4}	71.00
8.20×10^{-3}	5.94×10^{-4}	72.40
6.02×10^{-3}	4.38×10^{-4}	72.80
4.1×10^{-3}	3.37×10^{-4}	82.10
2.1×10^{-3}	2.44×10^{-4}	116.10

Discussion

The possibility of a chlorine atom bonded to the pyridine ring in $SeCl_4 \cdot 2py$ can be eliminated on the basis of the infrared spectra. All of the recorded absorption peaks for the compound are observed in the spectra for free pyridine. Especially noteworthy is the absence of any new absorption in the range 600–800 $cm.^{-1}$ which would be expected for a C–Cl or N–Cl bond. The Se–Cl bond absorptions are all lower than 400 $cm.^{-1}$ and thus were not observed.

The dissociation of $SeCl_4 \cdot 2py$ into two ions in acetonitrile is indicated by the osmometer measurements and is qualitatively supported by the magnitude of the extrapolated value of the equivalent conductance at infinite dilution.[11] This suggests that the reaction is best represented by the equation

$$SeCl_4 + 2py \longrightarrow SeCl_3py_2^+ + Cl^-$$

The resulting cation with one lone pair and five bonded pairs of electrons is comparable in central atom bonding to $SeOCl_2 \cdot 2py$ and IF_5. By consideration of the known structure of the isoelectronic $SeOCl_2 \cdot 2py$, which has an octahedral structure with the two chlorines in *trans* positions, the two pyridines in *trans* positions, and the oxygen atom bonded *trans* to the lone pair of electrons,[12] one might expect the pyridine rings in $SeCl_3py_2^+$ to be *trans* also. A single-crystal X-ray study of the material will be started in the near future in order to determine the bonding in the solid state.

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Dithiobenzoatotetracarbonylmanganese(I)

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Although a metal complex of dithiobenzoic acid has been used in the synthetic route to nickel tetracarbonyl,[1] no previous reference can be found to a metal carbonyl coordinated to the dithiobenzoate ion. We have isolated such a compound, $C_6H_5CSSMn(CO)_4$, from the reaction between C_6H_5CSSH and $Mn(CO)_5Br$. The product is a very stable red solid, monomeric in solution and with an infrared spectrum compatible with the C_{2v} symmetry required for a bidentate attachment of the dithiobenzoate group.[2]

Experimental

Dithiobenzoic Acid.[3]—K_2S (30 g.) was suspended in 200 ml. of boiling methanol and 50 g. of $C_6H_5CCl_3$ was slowly added. Upon starting, the reaction was exothermic and was cooled in an ice bath to retain control. The solution was then decanted and diluted with 500 ml. of ice water and made basic to litmus with NaOH. A clear oil separated from the dark red solution. This oil, assumed to be $C_6H_5CCl_3$, was returned to the excess sulfide with 200 ml. of fresh methanol and allowed to react again. The total water solution was acidified with HCl and extracted with ether. Removing the ether layer and distilling the ether left an oil which boiled at room temperature and 1 mm. pressure with $C_6H_5CCl_3$ condensing in a −78° trap. At 150° and 1 mm. pressure a red oil distilled to a room temperature trap with considerable H_2S collecting in a liquid nitrogen trap. The red oil was soluble in NaOH solutions and ether but decomposed rapidly. Within hours of its isolation it dissolved in ether but left a residue and in 2 or 3 weeks was insoluble in ether. The infrared absorption spectrum of the compound has strong bands at 1690 and 1270 $cm.^{-1}$.

Dithiobenzoatotetracarbonylmanganese(I).—Freshly prepared dithiobenzoic acid (2 g.) was dissolved in dry ether and filtered. The filtrate was added to 1.1 g. of $Mn(CO)_5Br$[4] in 175 ml. of dry ether. The flask was kept in the dark for 12 hr. at 25° during which a fine yellow powder was deposited. No attempt was

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