vacuum for 2 hr. The mixture was extracted with ethanol until the ethanol washings became violet. Then it was washed with chloroform until the washings were colorless. The combined chloroform washings were evaporated to dryness to obtain black crystals. These were recrystallized from chloroform. *Anal.* Calcd. for $[Ru(C_{10}H_8N_2)_2Cl_2]\cdot CHCl_3$: C, 41.73; H, 2.83; N, 9.27. Found: C, 42.15; H, 3.11; N, 9.17.

Dichlorobis(bipyridine)ruthenium(III) Perchlorate.—The above compound (0.1 g.) was suspended in 50 ml. of water containing a few drops of concentrated hydrochloric acid. Chlorine was bubbled through the mixture until the crystals dissolved. Upon addition of 5 ml. of 7% perchloric acid, crystals formed. These were filtered, washed with cold water, then with ether, and air dried. *Anal.* Calcd. for $[Ru(C_{10}H_8N_2)_2Cl_2]ClO_4$: C, 41.10; H, 2.76; N, 9.59. Found: C, 41.08; H, 2.79; N, 9.62. The infrared spectrum of this compound was identical with that of the perchlorate obtained from the chlorination of oxalatobis(bipyridine)ruthenium(II).

Discussion

The present study describes a convenient method of preparation for bis(bipyridine)ruthenium compounds. Since the oxalato group is very easily oxidized off with chlorine the other compounds can be easily obtained from the dichloro derivative through substitution reactions. From the method of preparation the compounds are most likely of the *cis* configuration.

The oxalate ions serve the dual purpose of occupying two coordination positions and of reducing the ruthenium to the +2 state. The intermediate in the preparation is not known but it is quite likely that a bis- or even tris(oxalato)ruthenate is involved.[4]

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The Low Temperature Reaction of Sulfur Hexafluoride with Solutions of Sodium[1]

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Sulfur hexafluoride, SF_6, is a chemically unreactive material; it is not attacked by aqueous or fused alkali[2] and it does not react appreciably with sodium below 200°.[3] The lowest temperature at which SF_6 has previously been reported to undergo reaction is 180–250°. During 25 hr. at this temperature, it is incompletely decomposed by Al_2Cl_6 and also by SO_3 with the formation of sulfur chlorides and oxyfluorides, respectively.[4] Because of its lack of chemical reactivity, SF_6, and also some of its derivatives containing an SF_5 group, is difficult to analyze.

In the present study, it was found that SF_6 underwent rapid reaction with a solution of sodium in liquid NH_3 at −64°. The products were not identified. If, instead, a solution of sodium in a diphenyl–ethylene glycol dimethyl ether solution was used, complete reaction was found to occur within 15 hr. between −64 and −10°; at room temperature, quantitative reaction occurred within a few minutes according to the equation

$$8Na + SF_6 \rightarrow Na_2S + 6NaF$$

Both S^{-2} and F^- present in the resulting mixture could be determined quantitatively by standard procedures. It appears that this reaction offers a convenient method for analyzing SF_6 and it would probably be equally successful for quantitative sulfur and fluorine analyses of many species containing the relatively unreactive SF_5 group.

In view of the usual inertness of SF_6 to both nucleophilic and electrophilic reagents it appears that the rapidity of the above low-temperature reaction may be due to an electron transfer from a diphenyl radical-ion[5] to an SF_6 molecule as the first (and rate-controlling) step in the reaction. The relatively low-energy, empty, 3d orbitals of sulfur would be available to accommodate the added electron. It may be presumed that the resulting SF_6^- ion would be unstable since no compound containing this ion has been isolated. It could eliminate F^-, and the $\cdot SF_5$ species so formed would be expected to be sufficiently labile to react further with the sodium "solution" by one of several different mechanisms. It would seem likely that an analogous type of reaction could occur with a solution of sodium in liquid NH_3.

Experimental

All work was carried out using standard vacuum system techniques. Commercial SF_6 (minimum purity, 95%) was purified by repeated distillations through traps held at −134° in which it partially condensed. Pure material was obtained as a condensate in the −134° traps (mol. wt. found 146.8, calcd. 146.06; vapor pressure at −96.2° found 63.19 mm., calcd.[6] 62.80 mm.; at −112.0° found 13.53 mm., calcd.[6] 13.40 mm.; confirmed by infrared spectrum[7]). The approximately 1.5 *M* solution of sodium in the diphenyl–ethylene glycol dimethyl ether mixture, which also contained some added toluene, was prepared according to the method described by Ligget.[8]

Reaction of SF_6 with a Solution of Sodium in NH_3.—An excess of SF_6 was condensed into a flask containing a solution of sodium in predried NH_3. When the flask was placed in a −64° bath and gently shaken for a few minutes, the characteristic blue color of the sodium solution was completely discharged.

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Reaction of SF_6 with a Solution of Sodium in a Diphenyl–Ethylene Glycol Dimethyl Ether Mixture. A.—Excess SF_6 was distilled into a flask containing sodium solution. Slow reaction occurred at −78° during 75 min. between the SF_6 and the frozen solution. The flask was placed in a −64° bath and was allowed to warm slowly during 15 hr. to −10°. During this time, the color of the sodium solution was completely discharged.

B.—The weight of a sample of SF_6 (40–80 mg.) was accurately determined by measuring its pressure when present in a known volume at a given temperature. It was distilled into a 100-ml. flask containing approximately 20 ml. of the sodium solution. After warming the flask to room temperature, it was swirled gently for 2 or 3 min. and then cooled in liquid nitrogen and then rewarmed to room temperature. Approximately 5–10 ml. of water was added dropwise to destroy the unreacted sodium, and the contents of the flask were transferred to a 250-ml. separatory funnel. The flask was then washed three times with approximately 15 ml. of isopropyl ether and three times with approximately 15 ml. of water, and the washings were added to the separatory funnel. After vigorous shaking, the lower aqueous layer was allowed to pass through a filter into a 250-ml. volumetric flask. The ether was extracted three times with 25 ml. of water which was transferred to the volumetric flask. After diluting the solution to 250 ml., F^- was determined volumetrically by the thorium nitrate method[9] and S^{-2} was determined volumetrically by an iodometric method.[10] It was found in preliminary experiments that the fluoride and sulfide ions did not mutually interfere with their estimations by the analytical methods employed.

The values obtained for sulfur upon analyzing eight different samples of SF_6 by the above method were all within ±0.16% of the calculated value of 21.95%. In six different samples, the fluorine analyses all fell within ±0.66% of the calculated value of 78.05%.

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The Crystal Structure of 1,4-Diselenane Tetrachloride

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1,4-Diselenane tetrachloride ($Cl_2SeC_4H_8SeCl_2$), Fig. 1, is closely related to two organoselenium compounds for which crystal structures have been determined; these are the corresponding tetraiodide[1] and the parent compound, 1,4-diselenane.[2] In diphenylselenium dibromide and dichloride, selenium lies at the center of a distorted trigonal bipyramid with the X–Se–X bond angle approximately 180°. It was shown recently by Chao and McCullough[1,3] that iodine forms molecular complexes with 1,4-diselenane and 1,4-dithiane rather than true iodides.[4] The crystal and molecular structures of the compounds formed between diselenane and chlorine or bromine were not known and prompted this investigation of 1,4-diselenane tetrachloride.

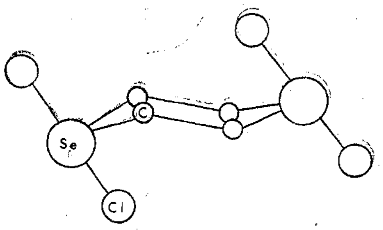

Fig. 1.—1,4-Diselenane tetrachloride.

Experimental

Single crystals of 1,4-diselenane tetrachloride (henceforth referred to as $DSCl_4$) were difficult to prepare; its solubility in common solvents is very limited and solutions had to be prepared at relatively low temperatures since $DSCl_4$ was found to decompose rapidly at temperatures close to 100°. Very thin platelets were obtained by passing chlorine gas over a solution of diselenane in *o*-dichlorobenzene. X-Ray patterns of single crystals obtained in this manner gave limited intensity data; the diffraction spots were weak and diffuse and it was clear that better crystals were needed. Some improvement occurred when less common solvents were used. $DSCl_4$ was found to be soluble in several inorganic liquid halides and attempts were made to recrystallize from $AsCl_3$, $POCl_3$, and $SeOCl_2$. The latter was found to be the most satisfactory and a single crystal was chosen from a mixture obtained by evaporating a solution of $DSCl_4$ in $SeOCl_2$ under reduced pressure. The diffraction patterns obtained from these crystals, though better than those previously recorded, were still poor, primarily because the material decomposed on exposure to X-rays. Nevertheless, enough reflections were recorded so that it was possible to proceed with the determination of the molecular configuration and approximate bond lengths.

Weissenberg and precession photographs were obtained using filtered Cu and Mo radiations. The unit cell is orthorhombic with $a = 12.12 \pm 0.02$, $b = 12.43 \pm 0.02$, and $c = 6.43 \pm 0.01$ Å. These cell dimensions were computed from a diffractometer record of powdered $DSCl_4$. Intensity data for the three principal zones were recorded and reflections of the following types were systematically absent: ($hk0$) and h odd; ($0kl$) with k odd; and ($h0l$) with l odd. Upper-layer Weissenberg photographs showed the cell to be primitive; the space group is therefore Pbca. Reflections of the type ($0kl$), though suitable for space group determination, were too diffuse to be useful in the structure determination. The intensities of 96 reflections, 65 ($hk0$) and the remainder ($h0l$), were measured and used in the subsequent analysis.

Measurements of the density by flotation in methylene iodide–carbon tetrachloride solutions indicated $\rho = 2.41$ g./cm.$^{-3}$; if we assume there are four molecules per unit cell, the calculated density is 2.44 g./cm.$^{-3}$. The linear absorption coefficient of $DSCl_4$ is 187 cm.$^{-1}$ for Cu Kα and 114 cm.$^{-1}$ for Mo Kα. It was clear that recorded intensity data were strongly affected by absorption, and corrections for this effect, based on the assumption that the crystal approximated a sphere with a radius of 0.35 mm., were applied to the measured intensities.[5] The crystal used was a well-formed parallelepiped with edges in the ratio of approximately 1:2:5. The usual Lorentz polarization corrections were applied to the measured intensities.

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