10.71. Found: C, 64.48; H, 10.85. Triiron dodecacarbonyl was prepared by the method of McFarlane and Wilkinson.[7] Benzene was dried before use.

Preparation of Tricarbonyl(dimethyldivinylsilane)iron.—The entire preparation was performed in an atmosphere of prepurified nitrogen. In a typical preparation triiron dodecacarbonyl (6.0 g, 0.012 mol) and dimethyldivinylsilane (4.4 g, 0.040 mol) were dissolved in 50 ml of benzene. The mixture was heated at 85° for 12 hr, cooled, and filtered under nitrogen. After all of the benzene and iron pentacarbonyl had been removed *in vacuo*, a sublimator probe, cooled with Dry Ice, was inserted into the flask. Tricarbonyl(dimethyldivinylsilane)iron sublimes to the cold surface at room temperature under high vacuum. The yellow crystalline product, which is formed in about 15% yield, melts at -13 to $-14°$ to a brown, air-sensitive oil. *Anal.* Calcd for $C_9H_{12}FeO_3Si$: C, 42.86; H, 4.76; Fe, 22.2. Found: C, 43.12; H, 4.70; Fe, 22.5.

The compound reacted with triphenylphosphine at room temperature to give the known *trans* isomer of tricarbonylbis(triphenylphosphine)iron (characterized by satisfactory ir spectrum and melting point).[8]

Infrared and Nmr Spectra.—Infrared spectra were recorded on a Beckman Model IR 10 spectrophotometer. Nmr spectra were obtained on a Varian Model A-60 spectrometer.

Results and Discussion

The nmr spectrum of the complex is that expected for a π-bonded divinylsilane. There is an upfield shift of the vinyl resonance multiplet of about 4 ppm from τ 3.5–4.6 ppm *vs.* TMS in the free ligand (neat liquid) to τ 7.6–8.7 ppm in the complex.[9] Such an upfield shift is characteristic of complexed olefins.[10] In both the free ligand and the complex the ratio of the integrated intensity of the vinyl proton signal to that of the methyl proton signal is 1:1. The methyl proton resonance signal occurs as a sharp singlet, τ 9.9 ppm, in the free ligand. The corresponding peak is observed to be split into two signals, τ 10.1 and 9.4 ppm, in the spectrum of the complex. This splitting is to be expected since the two methyl groups of the silane are not magnetically equivalent in the complex. Finally, the integrated intensities of the vinyl and two methyl peaks are observed to be in the expected ratio of 2:1:1.

The infrared spectrum of tricarbonyl(dimethyldivinylsilane)iron is consistent with its formulation as a π complex. The C=C stretching vibration, which occurs at 1600 cm^{-1} in dimethyldivinylsilane, is shifted to 1500 cm^{-1} in the complex. This shift is typical of π-bonded alkenes,[11] and it reflects the lowered bond order of a coordinated double bond.

The carbonyl region of the infrared spectrum of the complex shows stretching modes at 2065, 1982, and 1967 cm^{-1} (dilute cyclohexane solution). In addition to these bands all infrared spectra obtained also showed bands at 2012 and 1995 cm^{-1}. These bands could be attributed to iron pentacarbonyl formed through decomposition of the complex while handling the cyclohexane solutions (the complex was transferred in an atmosphere of prepurified nitrogen, and the solutions were prepared using nitrogen-saturated cyclohexane). An alternative explanation for the unusual spectrum in the carbonyl region could involve a type of tautomeric motion in which the silicon atom may occupy two positions in the molecule, one of which would require an iron–silicon interaction. Low-temperature nmr studies are planned to investigate this possibility.

In summary, our results show that stable acyclic polyene complexes of iron exist in which the π system of the polyene is interrupted by a heteroatom, silicon. We are currently investigating other vinylmetallics which may form similar iron tricarbonyl derivatives.

Acknowledgments.—The authors are grateful to the Robert A. Welch Foundation for financial support (Grant No. AI-306).

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[7] W. McFarlane and G. Wilkinson, *Inorg. Syn.*, **8**, 181 (1966).

[8] W. Reppe and W. J. Schweckendiek, *Justus Liebigs Ann. Chem.*, **560**, 104 (1948); F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960).

[9] The nmr spectrum was obtained on the neat liquid. Chemical shifts were measured from the vinyl peaks of uncomplexed dimethyldivinylsilane (resulting from a small amount of decomposition of the complex during handling). These results were confirmed by obtaining the nmr spectrum of the complex in cyclohexane solution and referencing peaks to the cyclohexane resonance.

[10] M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, **3**, 47 (1965).

[11] G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. 2, Methuen, London, 1968, p 16.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Electronic and Vibrational Spectra for *trans*-Dihydroxotetrachloroplatinate(IV)

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Several investigations pertaining to the thermal and photochemical aquation of hexachloroplatinate(IV) have been reported, and some information is available concerning the probable identities of the reaction products and the effects of acidity and of platinum(IV) and chloride concentrations on the extent of aquation.[1-4] Nevertheless, a complete picture of the reaction sequence is lacking, due at least in part to insufficient knowledge about the individual aquation products and about the reactions which these species undergo. As a means of probing this system, prior to any detailed kinetics studies, we are seeking to prepare and isolate various members of the family of aquation products and to determine their spectral and chemical characteristics. In the present communication, we have focused attention on the spectral properties of the tetragonal (D_{4h}) complex *trans*-dihydroxotetrachloroplatinate(IV). Of particular interest is the fact that the two observable ligand-field bands for this complex are found at lower wave numbers than those of hexachloroplatinate(IV), in contradistinction to the prediction based on the spectrochemical series. In addition, a comparison has been made of the ligand-field and charge-transfer spectra for *trans*-dihy-

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[1] R. Dreyer, J. Dreyer, and D. Rettig, *Z. Phys. Chem.* (Leipzig), 199 (1963).

[2] R. Dreyer and J. Dreyer, *Z. Chem.*, 151 (1963).

[3] R. Dreyer, K. König, and H. Schmidt, *Z. Phys. Chem.* (Leipzig), 257 (1964).

[4] C. M. Davidson and R. F. Jameson, *Trans. Faraday Soc.*, **61**, 2462 (1965).

droxotetrachloroplatinate(IV), *trans*-tetrachlorodiaquoplatinum(IV), *trans*-tetrachlorodiammineplatinum(IV), and hexachloroplatinate(IV).

Experimental Section

Preparation of *trans*-$K_2PtCl_4(OH)_2$.—This compound was prepared by means of a procedure similar to that reported by Babajeva.[5] Two grams of purified K_2PtCl_4 (Fisher) was treated with 20 ml of reagent grade 30% hydrogen peroxide, and the beaker containing the reaction mixture was placed in a water bath at about 15° until effervescence had ceased and no solid K_2PtCl_4 was visible (approximately 10 min). Next, the solution of *trans*-$K_2PtCl_4(OH)_2$ in hydrogen peroxide was cooled in an ice–salt bath, and to the solution was added 50 ml of ice-cold ethanol.[6] Finally, the resulting pinkish beige precipitate of *trans*-$K_2PtCl_4(OH)_2$ was collected by suction filtration of the mixture through a fine-porosity sintered-glass Büchner funnel and was washed with several 10-ml portions of absolute ethanol.[7] *Anal.* Calcd for $K_2PtCl_4(OH)_2$: Pt, 43.50; Cl, 31.60. Found: Pt, 44.00; Cl, 31.40.

Preparation of *trans*-$K_2PtCl_4(OD)_2$.—*trans*-$K_2PtCl_4(OH)_2$ was dissolved in a minimal volume of 98% D_2O, the solution was placed in a vacuum desiccator at room temperature, and the excess solvent was removed at a pressure of 0.5 Torr. After one such step, the resulting crystalline material consisted of approximately 50–60% of *trans*-$K_2PtCl_4(OD)_2$. Since the mixture of crystals was entirely satisfactory for the assignment of vibrational frequencies for *trans*-$K_2PtCl_4(OD)_2$, no effort was made to increase the yield of this compound by additional treatments with D_2O.

Preparation of *trans*-$Pt(H_2O)_2Cl_4$.—An aqueous solution of *trans*-$K_2PtCl_4(OH)_2$ was prepared and passed through a column containing strong-acid ion-exchange resin in the hydrogen form (Bio-Rad AG 50W-X4). In all experiments described in this paper, only the solution of *trans*-$Pt(H_2O)_2Cl_4$ was examined spectrally; a bright yellow solid can be isolated upon evaporation of this solution in a vacuum desiccator, but the material undergoes relatively rapid decomposition and was not characterized. By titration of an aliquot of the solution of *trans*-$Pt(H_2O)_2Cl_4$ with sodium hydroxide, the two acid dissociation constants for this compound were established. A computer program[8] was employed to fit a theoretical titration curve to the experimental titration data; pK_1 and pK_2 were found to be 1.9 and 5.5, respectively.

Commercially available (K & K Laboratories) $Pt(NH_3)_2Cl_4$ was used throughout the work discussed in this paper.

Spectral Measurements.—Infrared spectra were recorded with a Perkin-Elmer 621 grating spectrophotometer, all samples being examined as potassium bromide pellets. Raman spectra were obtained with a Cary 81 spectrophotometer equipped with a Spectra Physics helium–neon laser source. For all measurements the 6328-Å exciting line was employed, and Raman spectra of both powdered solid samples and aqueous solutions were observed. Visible and ultraviolet spectra were recorded with a Cary 14 spectrophotometer; sample and blank solutions were contained in matched 1.00-cm quartz cuvettes.

Results and Discussion

Vibrational Spectra.—Group theory predicts 10 normal modes of vibration for a seven-atom molecule of D_{4h} symmetry. Raman-active modes are 2 a_{1g} + b_{1g} + b_{2g} + e_g and those active in the infrared region are 2 a_{2u} + 3 e_u. Table I lists the Raman and infrared frequencies and assignments for *trans*-$K_2PtCl_4(OH)_2$, *trans*-$K_2PtCl_4(OD)_2$, and *trans*-$Pt(NH_3)_2Cl_4$. Of particular interest are the a_{1g} vibrational modes since they reflect most closely the force constants for stretching of the metal–ligand bonds, provided the masses of the in-plane and out-of-plane ligands are not too similar. Comparison of the a_{1g} frequencies for the complexes in Table I reveals two significant features. First, the platinum–chlorine stretching frequency is relatively insensitive to changes in the out-of-plane ligands. Data for a number of complexes with the general formula *trans*-PtX_2Y_4 with X = NH_3, $S(CH_3)_2$, $P(C_2H_5)_3$, and $As(C_2H_5)_3$ and Y = I, Br, and Cl lead to a similar conclusion.[9] Second, ligands exhibiting as profoundly different spectrochemical properties as do OH^- and NH_3 show nearly identical stretching frequencies with platinum. An absence of any straightforward relationship between bond strength and ligand-field strength is evident.

TABLE I

VIBRATIONAL FREQUENCIES (CM^{-1}) OF SOME PLATINUM(IV) COMPLEXES

Assignment		*trans*-$K_2PtCl_4(OH)_2$	*trans*-$K_2PtCl_4(OD)_2$	*trans*-$Pt(NH_3)_2Cl_4$
a_{1g}	ν(Pt–Cl)	338 s, pol[a]	338 s, pol	363
b_{1g}	ν(Pt–Cl)	317 m	317 m	336 m
a_{1g}	ν(Pt–O)	548 w	537 w	. . .
a_{1g}	ν(Pt–N)	. . .	. . .	545 w
b_{2g}	ν(Pt–Cl)	182 w	179 w	197 w
e_u	ν(Pt–Cl)	329 s	329 s	352[b]
a_{2u}	ν(Pt–O)	540 s	530 s	. . .
a_{2u}	ν(Pt–N)	. . .	. . .	554[b]
	δ(O–H)	998	. . .	. . .
	δ(O–D)	. . .	752	. . .
	ν(O–H)	3572	. . .	. . .
	ν(O–D)	. . .	2637	. . .
	Other	237 w	230 w	222 w, 379 w

[a] Abbreviations: s, strong; m, medium; w, weak; pol, polarized. [b] Data taken from ref 9.

Well known is the influence of hydrogen bonding on oxygen–hydrogen and nitrogen–hydrogen stretching frequencies.[10] In general, if the proton of a hydroxyl group is involved in hydrogen bonding, the stretching and bending bands are broadened and shifted to lower frequency. If the hydrogen bond is particularly strong, the ratios ν(O–H)/ν(O–D) and δ(O–H)/δ(O–D) may differ significantly from the harmonic oscillator approximation of $\sqrt{2}$. Hydroxyl deformation frequencies in several nitrosylruthenium complexes[11] have been interpreted in terms of hydrogen bonding involving NO (intermolecular) and NH_3 (intramolecular). On the other hand, the hydroxyl fre-

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(5) A. V. Babajeva, *Dokl. Akad. Nauk SSSR*, **24**, 145 (1939).

(6) Since most preparations of K_2PtCl_4 are contaminated with varying amounts of K_2PtCl_6, it is necessary to separate the latter prior to the precipitation of *trans*-$K_2PtCl_4(OH)_2$. This is accomplished by adding 5 ml of ice-cold ethanol to the solution of $PtCl_4(OH)_2{}^{2-}$ in hydrogen peroxide, cooling the mixture, and filtering off the K_2PtCl_6 before more ice-cold ethanol is introduced to obtain solid $K_2PtCl_4(OH)_2$.

(7) Several pieces of evidence have confirmed that this procedure yields a product of high purity, without appreciable amounts of platinum(II) contaminant. When aqueous perchloric acid solutions of *trans*-$K_2PtCl_4(OH)_2$ are examined by means of thin-layer voltammetry [J. C. Sheaffer and D. G. Peters, *Anal. Chem.*, **42**, 430 (1970); A. T. Hubbard and F. C. Anson, *ibid.*, **38**, 1887 (1966)], a small anodic wave is observed which indicates that this compound contains no more than 2–3% of platinum(II). When *trans*-$K_2PtCl_4(OH)_2$ is dissolved in hydrochloric acid, it is slowly (but quantitatively) converted to $PtCl_6{}^{2-}$; the ultraviolet spectrum of the resulting $PtCl_6{}^{2-}$ does not reveal (at 230 mμ) the presence of a detectable quantity of $PtCl_4{}^{2-}$ impurity.

(8) L. E. Cox, Ph.D. Thesis, Indiana University, 1970.

(9) D. M. Adams and P. J. Chandler, *J. Chem. Soc.*, 1009 (1967).

(10) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963.

(11) D. Scargill, *J. Chem. Soc.*, 4444 (1961).

quencies of *trans*-$K_2PtCl_4(OH)_2$ do not indicate hydrogen bonding. Furthermore, the oxygen–oxygen distance between adjacent $PtCl_4(OH)_2^{2-}$ ions in the potassium salt was found to be 3.89 Å,[12] much too great for significant interaction. The effect of hydrogen bonding on the π-donating ability, the orbital stabilities, and hence the ligand-field strength of hydroxide is not established. It is interesting to note, however, that most known hydroxide-containing complexes possess coordinated water or an amine *cis* to the hydroxide. Thus, the position of hydroxide in the spectrochemical series has been assigned on the basis of its behavior in these kinds of complexes.

Ligand-Field Spectra.—Visible and ultraviolet spectra for *trans*-$PtCl_4(OH)_2^{2-}$, *trans*-$PtCl_4(H_2O)_2$, and *trans*-$Pt(NH_3)_2Cl_4$ are shown in Figure 1. In each spectrum the two low-energy bands presumably correspond to one of the tetragonal components expected from the splitting of the $^3T_{1g}$ and $^1T_{1g}$ states in octahedral symmetry. Unfortunately, in no case are both components of either the singlet or the triplet state observable, so the assignment or calculation of spectral parameters is impossible. However, extended Hückel molecular orbital calculations (described briefly below and discussed in detail elsewhere[8]) have disclosed that for *trans*-$PtCl_4(OH)_2^{2-}$ the transitions $e_g \rightarrow b_{1g}$ and $e_g \rightarrow a_{1g}$ (Figure 2), both of which give rise to an E_g state, lie at lower energy than does the $b_{2g} \rightarrow b_{1g}$ transition for any reasonable value of the oxygen valence-state ionization energy (VSIE). In simple terms, this means that the difference between the π-antibonding influence of hydroxide and of chloride is larger than the difference in their σ-antibonding effects and that, consequently, hydroxide produces a weaker ligand field than chloride in *trans*-$PtCl_4(OH)_2^{2-}$.

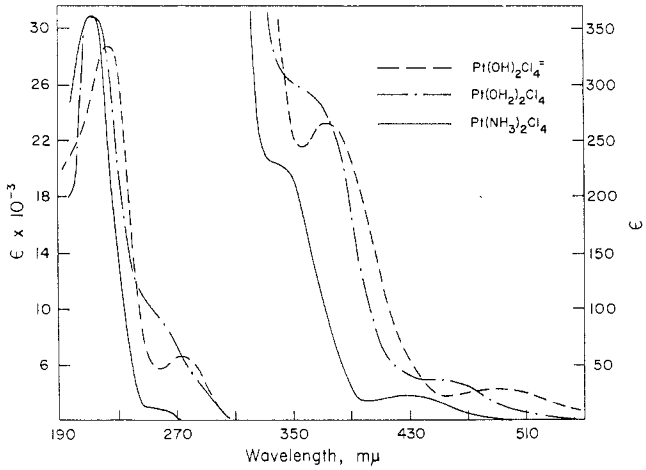

Figure 1.—Ultraviolet and visible spectra for *trans*-$Pt(OH)_2Cl_4^{2-}$, *trans*-$Pt(H_2O)_2Cl_4$, and *trans*-$Pt(NH_3)_2Cl_4$. Left-hand ordinate pertains to ultraviolet spectra, and right-hand ordinate pertains to visible spectra.

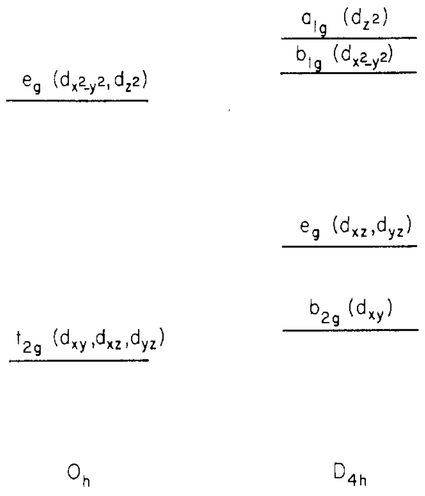

Figure 2.—Schematic one-electron energy levels involving the d orbitals for complexes of octahedral and tetragonal symmetry.

Therefore, the two ligand-field transitions for this compound can be assigned to $^1A_{1g} \rightarrow {}^3E_g$ (495 mμ, 20,200 cm^{-1}) and $^1A_{1g} \rightarrow {}^1E_g$ (375 mμ, 26,700 cm^{-1}), respectively. For hexachloroplatinate(IV) the corresponding ligand-field transitions appear at 452 mμ (22,100 cm^{-1}) and 353 mμ (28,300 cm^{-1}). Protonation of *trans*-$PtCl_4(OH)_2^{2-}$ to produce the diaquo complex causes the bands in the visible spectrum to shift approximately 1600 cm^{-1} toward shorter wavelength. This displacement is considerably larger than would be expected for a transition ($b_{2g} \rightarrow b_{1g}$) involving only in-plane orbitals. In fact, the magnitude of the shift is slightly greater than the 6% predicted for replacement of hydroxide by water.[13]

Probable assignments for the two low-intensity bands in the visible spectrum of *trans*-$Pt(NH_3)_2Cl_4$ are $^1A_{1g} \rightarrow {}^3A_{2g}$ for the band at 425 mμ (23,600 cm^{-1}) and $^1A_{1g} \rightarrow {}^1A_{2g}$ for the band at 340 mμ (29,400 cm^{-1}). These assignments are based on the fact that ammonia complexes generally exhibit values of $10Dq$ which are about 25% larger[13] than the corresponding aquo ion. This would place the lowest energy band for *trans*-$Pt(NH_3)_2Cl_4$ at approximately 360 mμ if the alternate assignment ($^1A_{1g} \rightarrow {}^1E_g$ or ^3E_g) were accepted.

Charge-Transfer Spectra.—Parity-allowed transitions for a number of second- and third-row hexahalo complexes have been discussed by Jørgensen.[14] Octahedral d^6 ions exhibit two intense absorption bands in the ultraviolet region which are assigned to $\pi \rightarrow \gamma_3$ ($t_{2u} \rightarrow e_g$) and $\sigma \rightarrow \gamma_3$ ($t_{1u} \rightarrow e_g$). For species of D_{4h} symmetry, the degeneracy of the T states is partially lifted, and four transitions are allowed on the basis of group theory: $a_{2u} \rightarrow a_{1g}$ ($A_{1g} \rightarrow A_{2u}$), $b_{2u} \rightarrow b_{1g}$ ($A_{1g} \rightarrow A_{2u}$), $e_u \rightarrow a_{1g}$ ($A_{1g} \rightarrow E_u$), and $e_u \rightarrow b_{1g}$ ($A_{1g} \rightarrow E_u$). Thus, assignment of the two charge-transfer bands for *trans*-$PtCl_4(OH)_2^{2-}$ is complicated by the possibility of configuration interaction between the two A_{2u} states and between the two states of E_u

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(12) From a study by members of the X-ray crystallography group at Indiana University; M. M. Cox, K. Folting, J. C. Huffman, and L. L. Merritt, Jr., submitted for publication. Uncertainties (one standard deviation) for the bond lengths in *trans*-$PtCl_4(OH)_2^{2-}$ are less than 0.006 Å for Pt–Cl and 0.017 Å for Pt–O.

(13) B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966, p 244.

(14) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley, Reading, Mass., 1962, pp 146–172.

symmetry. Although molecular orbital calculations are helpful in the semiquantitative description of these transitions, the validity of attempting to represent them as a difference between one-electron energy levels for ground-state equilibrium bond lengths is probably dubious.[15]

Comparison of the spectrum of *trans*-$PtCl_4(OH)_2^{2-}$ with that of *trans*-$PtCl_4(H_2O)_2$ is helpful in attaining a qualitative understanding of the bonding situation. The striking shift to higher energy of the band at 274 mμ for the dihydroxo complex which results from protonation of the hydroxide ligands suggests participation of oxygen π (e_u) orbitals in the originative molecular orbital. For the diaquo species the transition is probably best represented by $b_{2u} \rightarrow b_{1g}$. This assignment is substantiated by the fact that the diammine complex exhibits an absorption band at nearly the same energy. Platinum–chlorine bonding in these complexes is undoubtedly quite similar, although the energy of the a_{1g} antibonding orbital (Figure 2) is presumably somewhat higher in the *trans*-$Pt(NH_3)_2Cl_4$ species because of the greater σ-bonding ability of ammonia. Finally, the high-energy transition for each of the three complexes is much less sensitive to changes in the axial bonding and probably arises from an orbital comprised mainly of chlorine σ-type atomic orbitals; a reasonable assignment is $2e_u \rightarrow b_{1g}$.

As noted earlier, molecular orbital calculations have been performed in order to corroborate the conclusion reached about the relative ligand-field strengths of hydroxide and chloride in *trans*-$PtCl_4(OH)_2^{2-}$. Except for several modifications, the LCAO–MO theory which was employed closely followed that described by Ballhausen and Gray.[16] Numerical radial wave functions were calculated in the usual fashion.[17–19] For the platinum–chlorine and platinum–oxygen bond lengths in *trans*-$PtCl_4(OH)_2^{2-}$, values of 2.310 and 2.026 Å, respectively, were used.[12] Since appreciable ionicity exists for *trans*-$PtCl_4(OH)_2^{2-}$, a Madelung correction[20] was included to improve the results of the simple Wolfsberg–Helmholz calculations. Further information, including one-electron energy levels, linear combinations of ligand orbitals, group overlap integrals, and a complete set of eigenvectors, is on file with the American Society for Information Science;[21] other details about the computations are available upon request.

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[15] R. F. Fenske and D. D. Radtke, *Inorg. Chem.*, **7**, 479 (1968).

[16] C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, New York, N. Y., 1964, pp 92–132.

[17] F. Herman and S. Skillman, "Atomic Structure Calculations," Prentice-Hall, Englewood Cliffs, N. J., 1963.

[18] H. Johansen, "Algol Programs for Molecular Orbital Calculations," H. C. Orsted Institute, University of Copenhagen, 1965.

[19] E. Clementi, C. C. J. Roothaan, and M. Yoshimine, *Phys. Rev.*, **127**, 1618 (1962).

[20] C. K. Jørgensen, S. M. Horner, W. E. Hatfield, and S. Y. Tyree, Jr., *Int. J. Quantum Chem.*, **1**, 191 (1967).

[21] For supplementary material, order Document No. NAPS-00973 from ASIS National Auxiliary Publications Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022, remitting $2.00 for microfiche or $5.00 for photocopies. Advance payment is required. Make check payable to: CCMIC–NAPS.

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Reactions of Trifluoromethyl Hypofluorite with Sulfur and with Other Substances Containing Divalent Sulfur[1]

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Trifluoromethyl hypofluorite, CF_3OF,[2] is known to react in either of two ways: (1) as a fluorinating agent somewhat less active than elemental fluorine or (2) by addition of the O–F group across an unsaturated configuration.[3–6] The reactions of hypofluorites with substances containing divalent sulfur have not been previously examined, with the exception of Porter and Cady's exploratory work with elemental sulfur.[3] In the present work, the reactions of CF_3OF with thiophosgene, CCl_2S, carbonyl sulfide, O=C=S, and elemental sulfur have been studied.

Experimental Section

Trifluoromethyl hypofluorite was prepared by the usual method[7] and stored in glass tubes at 90°K. All manipulations were performed in a glass vacuum line equipped with a diffusion pump using Kel-F-3 oil (Minnesota Mining and Manufacturing Co.) and stopcocks lubricated with Kel-F-90 grease. Mixtures of products were separated by fractional codistillation.[8] Infrared spectra were obtained with a Beckman IR-10 spectrometer using a 10-cm cell with silver chloride windows. A Varian HR-60 spectrometer was used for the determination of nmr spectra with $CFCl_3$ as internal standard.

Reaction of CF_3OF with Thiophosgene.—A solution of 4 mmol of CCl_2S in 10 mmol of CF_2Cl_2 at $-78°$ was exposed to 4 mmol of CF_3OF initially at a pressure of 100 Torr while stirring with a Teflon-covered magnet. Reaction was complete in about 10 min as shown by the disappearance of the yellow color of CCl_2S. The most volatile products, COF_2, SOF_2, CF_2Cl_2, and SF_4 were then removed by distillation from the reactor, while held at $-78°$, into a trap at $-183°$. The remaining materials were then separated by fractional codistillation giving 0.8 mmol of CF_3OCFCl_2, 1 mmol of $CF_3OSCFCl_2$, and 0.1 mmol each of two unidentified products of about equal volatility.

$CF_3OSCFCl_2$.—The ^{19}F nmr spectrum consisted of two resonances with relative intensities 3:1. One was a doublet, ϕ^* $+61.4$ ppm, and the other a quartet, ϕ^* $+28.0$ ppm, with $J = 9.2$

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[1] Presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

[2] K. B. Kellog and G. H. Cady, *J. Amer. Chem. Soc.*, **70**, 3986 (1948).

[3] R. S. Porter and G. H. Cady, *ibid.*, **79**, 5625, 5628 (1957).

[4] J. A. C. Allison and G. H. Cady, *ibid.*, **81**, 1089 (1959).

[5] L. C. Duncan and G. H. Cady, *Inorg. Chem.*, **3**, 850, 1045 (1964).

[6] J. M. Shreeve, L. C. Duncan, and G. H. Cady, *ibid.*, **4**, 1516 (1965).

[7] G. H. Cady, *Inorg. Syn.*, **8**, 165 (1966).

[8] G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).