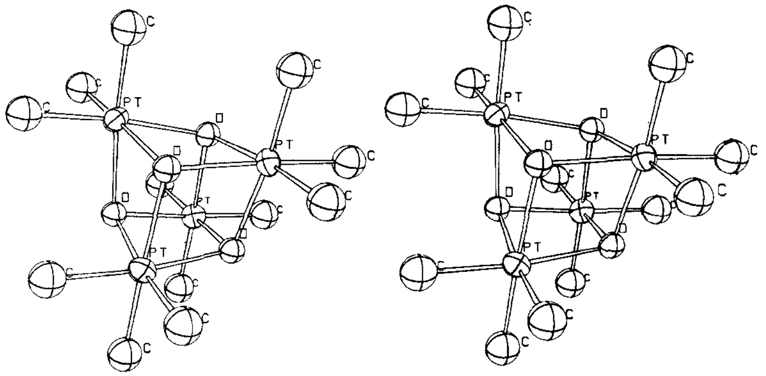

Figure 1.—Stereoscopic view of the tetrameric unit in $(CH_3)_3PtOH$. Bond distances and angles are given in Table II.

ordinate, 0.0005 in the O coordinate, and 0.0008 in the C coordinates. The very small effect of including anomalous dispersion is presumably a consequence of the overwhelming contribution of platinum to the structure factors.

The final parameters (standard deviations given in parentheses) are: for Pt: $x = y = z = 0.6193$ (0.0001), $B_{11} = B_{22} = B_{33} = 2.62$ (0.02), $B_{12} = B_{13} = B_{23} = -0.28$ (0.02); for O: $x = y = z = 0.903$ (0.001), $B = 2.6$ (0.4); for C: $x = y = 0.624$ (0.002), $z = 0.819$ (0.002), $B = 4.4$ (0.4). Preliminary low-temperature X-ray results of Truter[8] are consistent with these coordinates. The observed and calculated structure factors are given in Table I.

## Discussion

The structure of the tetrameric unit in $(CH_3)_3PtOH$ is shown in Figure 1. It is the same as that proposed by Rundle and Sturdivant[2] for "tetramethylplatinum." Although they were unable to extract the light-atom positions from their intensity data, Rundle and Sturdivant assigned them coordinates which were in fact quite accurate, the misidentification of carbon for oxygen notwithstanding.

The interatomic distances and angles are given in Table II. The platinum is in near-octahedral coordination, although the O–Pt–O angles are significantly lower than 90°. The Pt–C and Pt–O distances are in good agreement with those reported by Truter, *et al.*,[9,10] for other compounds containing trimethylplatinum groups bridged by oxygen atoms. The Pt–Pt distances in these dimeric species, 3.38[9] and 3.41 Å,[10] are nearly the same as that found here, 3.43 Å. The internuclear distance in metallic platinum is significantly shorter, 2.77 Å.[11]

TABLE II

INTERATOMIC DISTANCES AND ANGLES IN $[(CH_3)_3PtOH]_4$[a]

| Distance | Å | Angle | Deg |
|---|---|---|---|
| Pt–C | 2.04 (2) | O–Pt–O | 77.6 (6) |
| Pt–O | 2.22 (1) | C–Pt–C | 87 (1) |
| Pt–Pt | 3.430 (2) | Pt–O–Pt | 101.2 (6) |

[a] Standard deviations in parentheses refer to the least significant digits.

**Acknowledgment.**—We wish to thank Dr. Michael G. B. Drew and Dr. Barry DeBoer for valuable assistance during the course of this work. We also thank Dr. Gabrielle Donnay for communicating her results[3] in advance of their publication.

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# Trifluoromethylpyrosulfuryl Fluoride

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Compounds containing the pyrosulfuryl group, $-SO_2OSO_2-$, may be regarded as derivatives of pyrosulfuric acid, $HOSO_2OSO_2OH$, in which both OH groups have been replaced. Such materials have been known for some time,[1,2] but recently there has been renewed interest in the synthesis and study of compounds incorporating the pyrosulfuryl group.[3-6] This paper reports the preparation of $CF_3SO_2OSO_2F$ which completes the series from $CF_3SO_2OSO_2CF_3$[7,8] to $FSO_2OSO_2F$[9] and allows some comparisons to be made.

## Experimental Section

**Materials.**—Peroxodisulfuryl difluoride, $S_2O_6F_2$, was prepared by electrolysis of $HOSO_2F$ as described by Dudley.[10] The crude product was purified by fractional condensation. The fraction retained in a trap held at −78° was pure $S_2O_6F_2$ as shown by infrared spectral[11] and vapor density measurements.

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Bromine(I) fluorosulfate was prepared by allowing $Br_2$ (dried over $P_4O_{10}$) to react with a slight excess of $S_2O_6F_2$.[12,13] No further purification was attempted.

Trifluoromethylsulfuryl chloride was synthesized by oxidation of $CF_3SCl$ with $Cl_2$ in aqueous solution.[14] The crude product was fractionated under vacuum; $CF_3SO_2Cl$ was retained in a trap held at −85°. The material was dried over anhydrous $Na_2SO_4$, and its purity was checked by infrared analysis[14] and vapor density measurements.

**Preparation of $CF_3SO_2OSO_2F$.**—In a typical procedure, $BrOSO_2F$ (0.8365 g, 4.66 mmol) was condensed in a 250-ml Pyrex reaction vessel. $CF_3SO_2Cl$ (0.7766 g, 4.62 mmol) was added and the mixture was allowed to warm slowly to room temperature and remain for 12 hr. The crude product mixture was separated by fractional condensation under high vacuum. $CF_3SO_2OSO_2F$ remained in a trap held at −78° but was contaminated with $Br_2$ and BrCl produced in the reaction. The contaminants were easily removed by shaking the mixture with clean, dry mercury, and the product was obtained in 85% yield (0.9191 g, 3.95 mmol). (In a separate experiment it was determined that the reaction of $CF_3SO_2OSO_2F$ with Hg at 25° was negligible in a short time.) All of the other volatile products ($Br_2$, $Cl_2$, BrCl, and $CF_3OSO_2F$) were found in a trap held at −198°. $CF_3OSO_2F$ was identified by infrared analysis.[3] BrCl, $Cl_2$, and $Br_2$ were identified by gas chromatography and their characteristic colors.

In preliminary experiments involving small amounts of material, separation was effected by gas chromatography employing a 10 ft × 0.25 in. Al column packed with 20% Kel-F No. 3 polymer oil on 30–60 acid-washed Chromosorb W. At an He flow rate of 70 $cm^3$/min the components were eluted from the column in the following order: $Cl_2$ (small amount), $SiF_4$ (small amount), $CF_3OSO_2F$, BrCl, $Br_2$ (small amount), $CF_3SO_2Cl$, and $CF_3SO_2OSO_2F$. Authentic samples of $Cl_2$, $Br_2$, and a mixture of $Br_2$ and $Cl_2$ (BrCl)[15] gave identical $R_t$ values. $Cl_2$ and $Br_2$ were present owing to decomposition of BrCl.[15]

**Characterization of $CF_3SO_2OSO_2F$.**—The molecular weight of $CF_3SO_2OSO_2F$ was determined by the vapor density method. *Anal.* Calcd: 232 g/gmv. Found: 230 ± 1 g/gmv.

The $^{19}F$ nmr spectra were obtained with a Varian A56/60 nmr spectrometer operating at 56.4 MHz. All measurements were taken relative to $CCl_3F$ as an external reference. For $CF_3SO_2OSO_2F$ (pure): $\delta_{SF}$ −49.6 ppm (quartet), $\delta_{CF_3}$ +68.3 ppm (doublet), $J_{FF}$ = 2.1 Hz, relative area = 1:2.9. Spectra taken on a crude sample indicated the presence of $CF_3OSO_2F$ as well as $CF_3SO_2OSO_2F$. For $CF_3OSO_2F$: $\delta_{SF}$ −45.6 ppm (quartet),[16] $\delta_{CF_3}$ +56.2 ppm (doublet), $J_{FF}$ = 6.8 Hz.

Infrared spectral analysis of the mixture confirmed the presence of $CF_3OSO_2F$.[3] Trace resonances also appeared which could be ascribed to the presence of $S_2O_5F_2$[16] and $S_3O_8F_2$[16] at −47.4 and −48.8 ppm, but these materials were not present in sufficient amount to permit more definitive identification. No additional resonances were observed in the C–F region.

Mass spectra were recorded using a Consolidated Engineering Model 21103C mass spectrometer operating at 70 eV. Mass spectral analysis of pure $CF_3SO_2OSO_2F$ revealed the presence of the following fragments in order of decreasing intensity: $CF_3^+$, $SO_2^+$, $SO^+$, $CF_2^+$, $S^+$, $SO_2F^+$, $CF^+$, $COF^+$, $SOF^+$, $COF_2^+$, $CO_2^+$, $SO_3^+$, $CF_3SO_2^+$, $CF_3SO^+$, and $CF_3SO_3^+$. The last four species were present at an intensity level not much above the background level of the mass spectrometer. In addition, the usual fragments corresponding to $SiF_4$ and air impurities were present. No peak corresponding to the molecule ion was noted. These data resemble those obtained for another compound containing the $-OSO_2CF_3$ group, $CF_3SO_2OCF_3$.[17]

A sample of $CF_3SO_2OSO_2F$ was purified by gas chromatography for chemical analysis.[18] *Anal.* Calcd for $CF_3SO_2OSO_2F$: C, 5.17; S (hydrolyzable), 13.81; F, 32.76. Found: C, 4.73; S, 14.38; F, 30.57.

Vapor pressure measurements for $CF_3SO_2OSO_2F$ were obtained using the method of Kellogg and Cady.[19] Data were refined by a least-squares treatment.[20] The vapor pressure–temperature data in the range 35–65° are represented by $\log p_{mm} = 7.918 - (1721/T)$, from which may be derived the boiling point of 68.4° at which temperature the molar heat of vaporization is 7.83 kcal/mol. These values yield a Trouton constant of 22.9 eu.

Infrared spectra were recorded using Beckman IR-5 and Perkin-Elmer Model 621 infrared spectrophotometers. All samples were in the gas phase held in a 10-cm cell equipped with either NaCl or AgCl windows. The infrared spectrum of $CF_3SO_2OSO_2F$ (5 mm) showed absorption bands at 1497 (s), 1468 (s), 1242 (vs), 1138 (vs), 862 (s), 810 (vs), 778 (m), and 713 (m) $cm^{-1}$.

A weighed amount of the moisture-sensitive compound was hydrolyzed with excess 0.2 *N* NaOH in a sealed ampoule at 100° for 18 hr. The unconsumed base was titrated with standard 0.1 *N* HCl to the phenolphthalein end point. The material apparently hydrolyzed according to

$$CF_3SO_2OSO_2F + 4OH^- = CF_3SO_2O^- + SO_4^{2-} + F^- + 2H_2O$$

Data calculated for this reaction are: 4.00 mequiv of $OH^-$ consumed/mmol of $CF_3SO_2OSO_2F$; 1.00 mmol of $SO_4^{2-}$ produced/mmol of $CF_3SO_2OSO_2F$; the values found for these respective quantities were 4.17 and 1.05. Various metal salts of the trifluoromethanesulfonate ion have been prepared in aqueous media,[21] and the ion has been identified as a product in the basic hydrolysis of $(NO)OSO_2CF_3$.[22] Presumably the fluorosulfate ion was also formed as a product initially but was hydrolyzed in basic solution to fluoride and sulfate ions.[23]

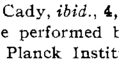
## Discussion

$CF_3SO_2OSO_2F$ is formed in good yield by the reaction of trifluoromethylsulfuryl chloride, $CF_3SO_2Cl$, with bromine(I) fluorosulfate, $BrOSO_2F$

$$CF_3SO_2Cl + BrOSO_2F = CF_3SO_2OSO_2F + BrCl$$

Some fission of the carbon–sulfur bond of $CF_3SO_2Cl$ occurs producing $CF_3OSO_2F$[3] as a minor product. Previous attempts to synthesize $CF_3SO_2OSO_2F$ by other methods resulted in degradation of the reactants without detectable production of the desired material.[24] Des Marteau[25,26] has shown that $BrOSO_2F$ has great utility as an O-fluorosulfurylating agent in cases where other methods of O-fluorosulfurylation lead to destruction of the reactants by vigorous oxidation reactions. The small amount of degradation observed in this work further illustrates this fact.

The proposed dianhydride structure of the material



$$\begin{matrix} & O & O & \\ CF_3S & & O & SF \\ & O & O & \end{matrix}$$

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is supported by all of the physical and chemical evidence.

Stepwise replacement of a fluorine atom on the pyrosulfuryl structure by a trifluoromethyl group increases the boiling point in a roughly linear manner: $S_2O_5F_2$, 51°;[27] $CF_3S_2O_5F$, 68.4°; $(CF_3)_2S_2O_5$, 84, 80.5°.[7,8]

Comparison of the infrared spectrum of $CF_3SO_2$-$OSO_2F$ with that of similar compounds allows tentative assignments of group frequencies to be made. The strong bands at 1497 and 1473 $cm^{-1}$ are assigned to the S=O asymmetric stretching modes of the fluorosulfuryl and trifluoromethylsulfuryl groups, respectively. These vibrational modes occur at 1513 $cm^{-1}$ in $S_2O_5F_2$[27] and 1471 and 1460 $cm^{-1}$ (doublet) in $(CF_3)_2S_2O_5$.[7] The band at 1242 $cm^{-1}$ is assigned to the S=O symmetric stretching mode on the basis of arguments advanced by Robinson.[28] This band occurs at 1248 $cm^{-1}$ in $S_2O_5F_2$[27] and 1239 $cm^{-1}$ in $(CF_3)_2$-$S_2O_5$.[7] The strong absorption at 1138 $cm^{-1}$ is ascribed to the C–F stretching mode which occurs at 1131 $cm^{-1}$ in $(CF_3)_2S_2O_5$[7] and 1150 $cm^{-1}$ in $CF_3SO_2F$.[29]

Resonances appearing in the $^{19}F$ nmr spectrum of $CF_3SO_2OSO_2F$ are assigned to $CF_3SO_2$– (+68.3 ppm) and –$OSO_2F$ (−49.3 ppm) on the basis of chemical shift data,[16] fine structure, and relative areas. The chemical shift for the $CF_3$ group in $(CF_3)_2S_2O_5$ occurs at +74.02 ppm.[24] The relatively small coupling constant of 2.1 Hz (that for $CF_3OSO_2F$ is 6.8 Hz) is consistent with that observed for coupling of nonequivalent fluorine atoms over a somewhat related four-atom bond and space system in the compound $FC(O)N(OCF_3)SO_2F$ for which $J_{CF_3\text{–}SO_2F} = 1.8$ Hz.[30]

**Acknowledgment.**—The author gratefully acknowledges support of this work by a grant from the Penrose Fund of the American Philosophical Society. The nmr spectrometer was purchased with funds provided by NSF Grant GP-3631. The author is indebted to Professor Harry B. Miller for the $^{19}F$ nmr spectra and to Mr. George Young, R. J. Reynolds Tobacco Co., for the mass spectral data.

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# Nickel(II) Complexes with the Two Isomers of 1,3,5-Triaminocyclohexane

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The recent reports[1-3] describing the coordination complexes of 1,3,5-triaminocyclohexane prompt us to communicate our results with this ligand system. Wentworth[2,3] has described the metal ion complexes of *cis,cis*-triaminocyclohexane (*cis,cis*-tach) in which the three amino groups rotate into axial ring positions in order to occupy the trigonal face of an octahedral coordination geometry. In addition, evidence was presented for the existence of a second ligand isomer, *cis,trans*-1,3,5-triaminocyclohexane (*cis,trans*-tach), but no coordination compounds of this isomer were reported. We have investigated the coordinating ability of 1,3,5-triaminocyclohexane with nickel(II) ions and have isolated two isomeric bis(triaminocyclohexane)-nickel(II) complexes. This note describes the synthesis and characterization of these isomeric complexes.

### Experimental Section

**Preparation of the Complexes.**—A methanol solution (25 ml) containing 0.9 g (3.8 mmol) of nickel(II) chloride hexahydrate was added dropwise to 1.0 g (7.7 mmol) of 1,3,5-triaminocyclohexane[4] in 10 ml of anhydrous methanol. Pink crystals separated almost immediately and continued to form until approximately half of the nickel chloride solution had been added. These crystals were removed, recrystallized (anhydrous methanol), and dried *in vacuo* at 79° for 12 hr. *Anal.* Calcd for $C_{12}H_{30}N_6Cl_2Ni$: C, 37.14; H, 7.79; N, 21.66; Cl, 18.27. Found: C, 37.34; H, 7.80; N, 21.23; Cl, 18.50; magnetic moment, $\mu_{eff} = 3.1$ BM.

Continued addition of the nickel chloride solution to the filtrate led to an orange solution which deposited a yellow microcrystalline precipitate upon cooling. This hygroscopic precipitate could not be recrystallized and gave nonreproducible analytical results. Substitution of 95% ethanol as the solvent after the removal of the pink isomer was found to yield a highly crystalline yellow complex upon standing after the further addition of nickel(II) chloride. The complex was recrystallized from 95% ethanol and dried *in vacuo* at 100° for 12 hr. The dried crystals were extremely hygroscopic. *Anal.* Calcd for $C_{12}H_{30}N_6Cl_2Ni$: C, 37.14; H, 7.79; N, 21.66; Cl, 18.27. Found: C, 36.90; H, 7.93; N, 21.36; Cl, 17.82; magnetic moment, $\mu_{eff} = 0.5$–0.6 BM.

**Physical Measurements.**—Solution absorption spectra and solid-state diffuse transmittance spectra of Nujol mulls supported on filter paper were obtained with a Cary Model 14 recording spectrophotometer. Magnetic susceptibilities were measured by the Faraday method. The infrared spectra were obtained with Nujol mulls using a Beckman IR-8 spectrophotometer. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

## Results and Discussion

Characterization of the pink and yellow isomers indicates that they are the nickel(II) complexes of *cis,cis*-tach and *cis,trans*-tach, respectively. The physical properties of each of the isomers which lead to this conclusion will be discussed separately.

**Pink Isomer, [Ni(*cis,cis*-tach)$_2$]Cl$_2$.**—Our results for this isomer are in agreement with those reported previously[3] and it is concluded that this isomer is the bis-nickel(II) complex of *cis,cis*-tach with both ligands functioning as tridentate chelates. The solution electronic spectrum of this complex ion is presented in Table I. The low values of the molar absorptivities for the

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