experiments were run on solutions of Co(HMPA)$_2$X$_2$ containing excess HMPA at −50° in which the ^{31}P nuclei in the HMPA in the bulk solvent site were electronically decoupled. These experiments showed the free HMPA signal to collapse to about half its original width upon decoupling of the ^{31}P nuclei. Thus, the apparent free HMPA singlet is actually a doublet which is unresolved owing to the small ^{31}P–^{1}H coupling constant (9.86 cps) and the broadness of the component peaks. Therefore, the HMPA molecules appear to be exchanging between a site where ^{31}P–^{1}H coupling exists (bulk solvent) and one where this interaction is decoupled (primary coordination sphere). In view of this fact that the Co(HMPA)$_2$X$_2$ system is not a simple two-site exchange problem, no line-shape calculations were carried out. The fact that ^{31}P–^{1}H coupling is present in the free HMPA site in no way affects the results obtained from the line-width measurements on the coordinated ligand signal (which behaves normally in all respects[2,7]) since in the slow-exchange temperature region the shape of the signal due to magnetic nuclei in each site is dependent only upon the properties characteristic to that site.

One interesting result of our study is the mixed first- and second-order kinetics observed for the Co(HMPA)$_2$X$_2$ complexes. This is in contrast to the purely second-order kinetics observed for the Co(2-pic)$_2$Cl$_2$[3] and Co(TTP)$_2$X$_2$[2] (TPP = triphenylphosphine) complexes. A possible explanation for this can be advanced by postulating that the first-order process observed for the Co(HMPA)$_2$X$_2$ complexes occurs *via* a dissociative-type (SN1) mechanism and, therefore, that the loss of an HMPA molecule is the rate-determining step. Courtauld atomic models of the three types of CoL$_2$X$_2$ complexes (L = HMPA, TPP, and 2-picoline) showed that, although all three ligands are quite bulky, there is decidedly more steric interference in the case of HMPA than for TPP or 2-picoline. Thus, the Co–O bond in the HMPA complex (which might normally be expected to be weaker than the Co–N or Co–P bonds in the other two types of complexes) would be made weaker by steric interference increasing the tendency for an HMPA molecule to dissociate from the complex. Therefore, the appearance of the first-order process in the HMPA complex and not in the others can be rationalized. This type of interpretation is also supported by the activation energies found for the first-order process for Co(HMPA)$_2$Cl$_2$ and Co(HMPA)$_2$Br$_2$. The E_a value for k_1 appears to be smaller when X$^-$ = Br$^-$ than when X$^-$ = Cl$^-$ as would be expected for a dissociative mechanism where steric effects are important. Thus, the evidence supports the postulate that the dissociation of an HMPA molecule is the rate-determining step for the first-order process and this constitutes the first evidence for a three-coordinate Co(II) species.

Among other interesting aspects of these results are the values obtained for the activation energies of the process which governs the transverse relaxation rates for both Co(HMPA)$_2$X$_2$ complexes. $E_a(1/T_{2M})$ was found to be −0.3 kcal/mol for the Co(HMPA)$_2$Cl$_2$ complex and −0.7 kcal/mol for the Co(HMPA)$_2$Br$_2$ complex. These small activation energies, which are similar to those found by previous workers[2,3,7] for Co(II) and Ni(II) complexes, suggest that T_{2M} is determined by the rate of electron-spin relaxation.[7] The fact, noted in this study and in previous studies, that $1/T_{2M}$ for Co(II) and Ni(II) complexes is independent of the viscosity of the solution also supports this conclusion.[8]

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The Crystal Structure of Trimethylplatinum Hydroxide[1a]

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In 1947 Rundle and Sturdivant[2] published the structure of "tetramethylplatinum." They found that the platinum occurs in tetrahedra, 3.44 Å to an edge. The methyl carbons could not be located with their limited set of film data, but on chemical and symmetry grounds three of them were attached to each platinum, pointing away from the tetrahedron. The fourth was allowed to bridge three platinums, four such bridging carbons forming another, interpenetrating tetrahedron.

Cowan, Krieghoff, and Donnay[3] have now shown that the crystals used by Rundle and Sturdivant were, in fact, trimethylplatinum hydroxide. Presumably the bridging methyl groups postulated by Rundle and Sturdivant are in fact hydroxides. This structure has been inferred[4] from nmr data on a benzene solution of (CH$_3$)$_3$PtOH and is also entirely analogous to the structure of (CH$_3$)$_3$PtCl, also determined by Rundle and Sturdivant.[2] The present study confirms this structure in the crystals and provides molecular parameters for the oxygens and carbons as well as the platinums.

Experimental Section and Crystal Data

Trimethylplatinum(IV) hydroxide was prepared by the method of Pope and Peachey.[5] Slow recrystallization from chloroform

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[1] (a) Work done under auspices of the Atomic Energy Commission. Supported in part by Public Health Service Research Grant GM 13498 to T. G. S. (b) Princeton University. (c) University of California.

[2] R. E. Rundle and J. H. Sturdivant, *J. Am. Chem. Soc.*, **69**, 1561 (1947).

[3] D. O. Cowan, N. G. Krieghoff, and G. Donnay, *Acta Cryst.*, **B24**, 287 (1968).

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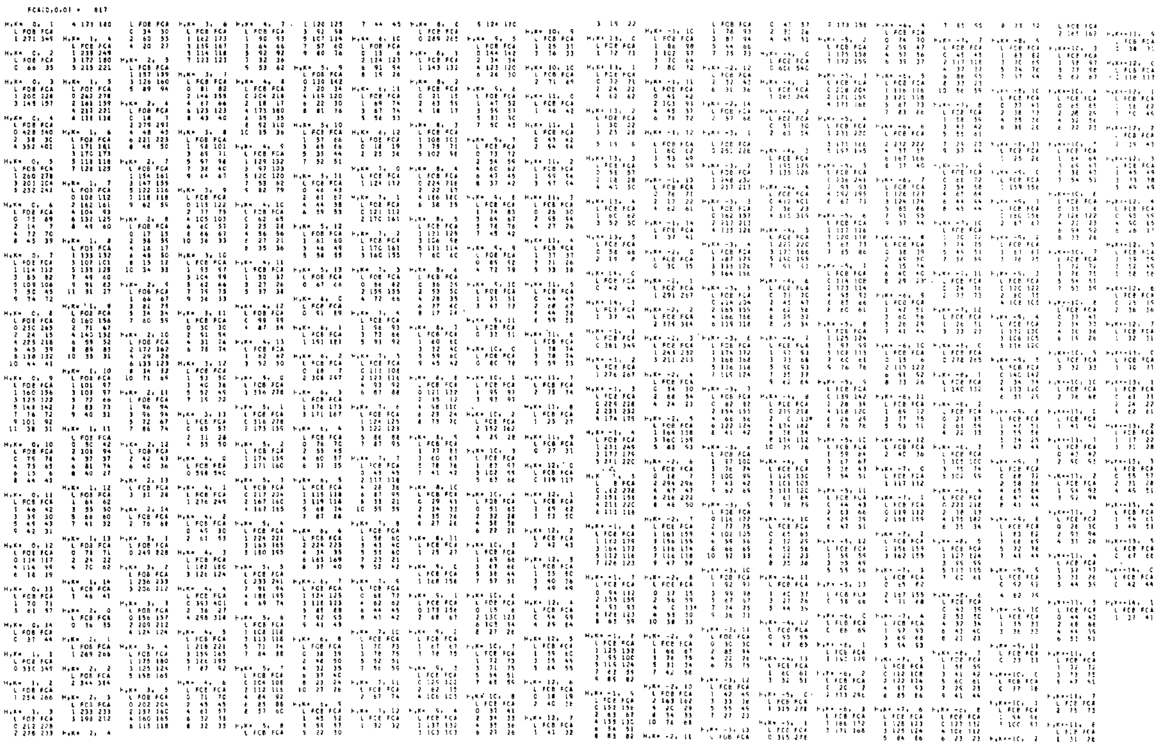
TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $(CH_3)_3PtOH$



gave colorless, well-developed rhombododecahedral crystals. Weissenberg films taken with copper radiation demonstrated their identity with the crystals studied by Rundle and Sturdivant[2] and by Cowan, *et al.*:[3] they are body-centered ($h + k + l = 2n$) cubic, with Laue symmetry m3m. Attempts to grind the crystals to spheres were unsuccessful, the material being too soft. A compact polyhedral fragment, 0.12 mm across, was chosen and mounted on a glass fiber, with the $01\bar{1}$ axis as the axis of rotation. The cell dimension and intensities were measured at 23° with a General Electric XRD-5 goniostat equipped with a scintillation counter, using Mo Kα radiation, $\lambda(K\alpha)$ 0.71069 Å. Our value for the cell edge, $a = 10.165 \pm 0.005$ Å is in agreement with that of Rundle and Strudivant,[2] 10.165 Å, while that of Cowan, *et al.*,[3] 10.179 ± 0.002 Å, is slightly higher. The experimental density,[2,3] 3.2 g/cm³, indicates eight molecules of $(CH_3)_3PtOH$ per unit cell ($d_{\text{calcd}} = 3.23$ g/cm³).

Of the space groups consistent with the Laue symmetry, Im3m, I432, and $I\bar{4}3m$, Rundle and Sturdivant chose the last, on relative intensity and chemical grounds. We accepted their reasoning and $I\bar{4}3m$, in fact, gave a satisfactory structure with Pt and O both in 8-fold positions (c) and C in 24-fold positions (g).[6]

A total of 1083 intensities were measured with 2θ values up to 60°. The reflections were divided equally between the hkl and $\bar{h}kl$ octants (which are equivalent in the Laue group but not in $I\bar{4}3m$). Because of the high symmetry there were only 169 nonequivalent reflections in each octant, so that the data set was overdetermined by a factor of 3. Although absorption was not inappreciable ($\mu R = 1.6$), no correction was attempted because of the irregular geometry of the crystal. However, the effects of variation in absorption with orientation were to some extent cancelled in the overdetermined data set.

Calculations were performed on a CDC-6600 computer using our own unpublished programs for Fourier series and interatomic distances and angles and our modified (unpublished) version of the Gantzel–Sparks–Trueblood full-matrix least-squares program, which minimizes $\Sigma w|\Delta F|^2/\Sigma w|F_o|^2$. The weights, w, were taken as unity. Atomic scattering factors were taken from the "International Tables."[7] The Pt scattering function was corrected for anomalous dispersion ($\Delta f'$) by subtracting 2.2, and at a later stage the out-of-phase correction $\Delta f'' = 9.0$ was included. The isotropic temperature factor was defined as $\exp(-B\lambda^{-2}\sin^2\theta)$. The anisotropic temperature factor was $\exp[-0.25(B_{11}b_1^2h^2 + B_{22}b_2^2k^2 + B_{33}b_3^2l^2 + 2B_{12}b_1b_2hk + 2B_{13}h_1b_3hl + 2B_{23}b_2b_3kl)]$, where b_i is the ith reciprocal axis.

Structure Determination

The platinum atom lies on a threefold symmetry axis and has only one independent coordinate. Rundle and Sturdivant's estimate of this coordinate, $x = 0.380$, was taken as a starting value and the Pt was refined isotropically using the full data set. Two cycles led to a residual, $R = \Sigma|\Delta F|/\Sigma|F_o|$, of 0.12. Anisotropic refinement (only two thermal parameters, B_{11} and B_{12}, are unrestricted) reduced R to 0.085. A fourier synthesis of ΔF, based on the Pt, showed only two prominent peaks. The higher, at $x = y = z = 0.100$, was assigned to oxygen, and the lower, at $x = y = 0.375$, $z = 0.175$, was assigned to carbon. The remaining peaks were at least ten times smaller than the oxygen peak. Further least-squares refinement, with O and C included isotropically, led to $R = 0.059$, and $\Sigma w|\Delta F|^2 = 176.4$.

The space group being noncentric, the imaginary part of the platinum anomalous dispersion ($\Delta f'' = 9.0$) was now included in the refinement. However R increased slightly and $\Sigma w|\Delta F|^2 = 178.6$. When the signs of all of the coordinates were reversed, the refinement lowered R to 0.058 and $\Sigma w|\Delta F|^2$ to 175.7, and the resulting coordinates are accepted. They differ from the results of the preceding calculation by less than 10^{-5} in the Pt co-

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(6) N. F. M. Henry, and K. Lonsdale, Ed., "International Tables of X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1962, p 326.

(7) See ref 6, Vol. III, pp 202, 212.

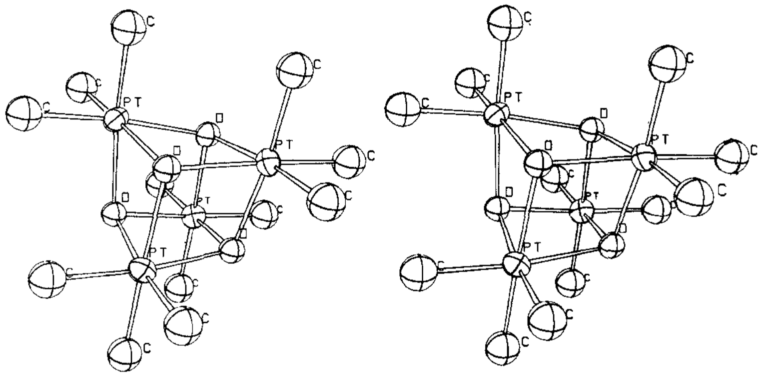

Figure 1.—Stereoscopic view of the tetrameric unit in $(CH_3)_3PtOH$. Bond distances and angles are given in Table II.

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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