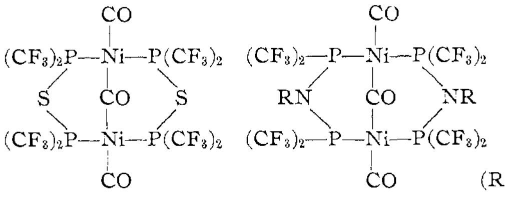

(R = H or $CH_3$)

continue to seem most reasonable for the sesquicarbonyls in the vapor phase: smaller molecules are not allowed by the empirical formulas; larger molecules would mean lower volatility; and less compact structures should be less stable. The mass spectra (by the Varian M66 instrument) of the compounds seemed confirmatory: although the parent molecule ions were absent, there were mass numbers corresponding to loss of CO therefrom, with greater intensities for more CO removed.

However, the curious solubility behavior of the sulfur compound suggests that the solid may be a higher polymer, subject to depolymerization during vaporization or solution, and then lacking stability because the relatively wide PSP bond angle would lead to strain in the six-atomic rings.

Also for the nitrogen compounds it is not certain that the suggested pattern represents the crystals, for good efforts at X-ray structure determination so far have failed, and change could occur on solution or vaporization. Indeed, the $^{19}F$ nmr spectra of their ether or acetone solutions (Figure 1) clearly show two environments for fluorine, as though the basic solvent were influencing one nickel or two phosphorus atoms differently from the others—still without destroying the Ni–(CO)–Ni bridge which the infrared spectra show for the solutions.

In summary, then, the suggested bicyclononane pattern seems supportable only for these complexes in the vapor phase and remains uncertain for other conditions.

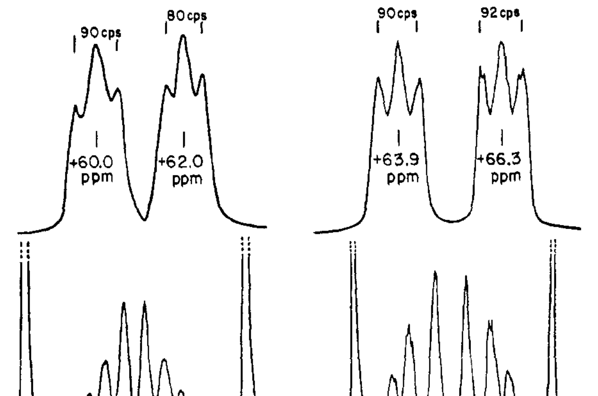

Figure 1.—Fluorine nmr spectra (at 94.1 Mc) of Ln (lower left), Lhn (lower right), and ether solutions of $Ln_2Ni_2(CO)_3$ (upper left) and $Lhn_2Ni_2(CO)_3$ (upper right). At far lower resolution, the Ln and Lhn bands have the appearance of 1:2:1 triplets. The upper figures represent the same "triplets," blurred by a larger number of nearby magnetic nuclei and doubled by a differential effect of the solvent. The different shapes and widths of these bands are quite real and repeatable. The chemical shifts are measured upfield from $Cl_3CF$.

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# Nuclear Magnetic Resonance Study of the Exchange of Hexamethylphosphoramide with Dihalobis(hexamethylphosphoramide)cobalt(II)[1]

BY STEVEN S. ZUMDAHL AND RUSSELL S. DRAGO

*Received February 29, 1968*

In two previous studies[2,3] of the exchange kinetics of pseudo-tetrahedral complexes of Co(II) the reactions were found to proceed by a mechanism giving purely second-order kinetics. In order to further explore the exchange reactions of the $CoL_2X_2$ complexes, we have studied $Co(HMPA)_2X_2$ complexes (where HMPA is hexamethylphosphoramide and $X^-$ is $Br^-$ or $Cl^-$) in deuteriochloroform with various concentrations of excess HMPA. The $Co(HMPA)_2X_2$ complexes enable us to study a very bulky ligand which is a poorer coordinating ligand than those previously investigated. These complexes have been previously prepared and characterized.[4]

## Experimental Section

**Complexes.**—The $Co(HMPA)_2X_2$ complexes were prepared as previously described.[4] *Anal.* Calcd for $Co(HMPA)_2Cl_2$: C, 29.52; H, 7.46; N, 17.22. Found: C, 29.31; H, 7.64; N, 16.74. Calcd for $Co(HMPA)_2Br_2$: C, 24.97; H, 6.30; N, 14.56. Found: C, 25.18; H, 6.53; N, 14.58.

**Nmr Spectra.**—The proton spectra were obtained in deuteriochloroform which was distilled from potassium carbonate just prior to use. A Varian Model A-60 nuclear magnetic resonance spectrometer equipped with a Model V-6040 temperature controller was used to record the spectra. The temperature was monitored by means of a YSI Model 42SL thermistor thermometer.

## Results

The present experiments were carried out on deuteriochloroform solutions of the $Co(HMPA)_2X_2$ complexes containing various concentrations of free HMPA. Preliminary studies on this system[5] have shown that below −25° separate pmr signals are observed for the free and complexed HMPA. At −61° the paramagnetic isotropic shift ($\Delta\nu_M$) between the signals due to protons in the coordinated and free ligand sites is −203 cps for $Co(HMPA)_2Cl_2$ and −621 cps for $Co(HMPA)_2Br_2$.

In order to study the ligand-exchange kinetics of the $Co(HMPA)_2X_2$ complexes, the slow-exchange line-width technique, which is applicable in the temperature region where $1/\tau_M \ll \Delta\nu_M$, was used. In the slow-exchange temperature region the line width of the signal due to protons in the coordinated ligand site is given by the expression[6,7]

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[1] Abstracted in part from the Ph.D. thesis of S. Zumdahl, University of Illinois, 1968.

[2] W. D. Horrocks and L. H. Pignolet, *J. Am. Chem. Soc.*, **88**, 5929 (1966).

[3] S. S. Zumdahl and R. S. Drago, *ibid.*, **89**, 4319 (1967).

[4] J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **2**, 572 (1963).

[5] M. Rosenthal, Ph.D. Thesis, University of Illinois, 1965.

[6] L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, **30**, 899 (1959).

[7] Z. Luz and S. Meiboom, *ibid.*, **40**, 1058, 1066 (1964).

$$\left(\frac{1}{T_2}\right)_M = \frac{1}{T_{2M}} + \frac{1}{\tau_M} = \pi(\Delta\nu_{1/2})_M \qquad (1)$$

where $T_2$ is the effective transverse relaxation time, $T_{2M}$ is the transverse relaxation time characteristic of protons in the coordinated ligand site in the absence of exchange, $\tau_M$ is the mean lifetime of a ligand in the primary coordination sphere of the metal ion, and $(\Delta\nu_{1/2})_M$ is the observed line width at half-height (cps) of the signal due to complexed ligand protons.

In order to study the role of the free ligand in the exchange process, several solutions of the Co(HMPA)$_2$X$_2$ complexes were prepared in which the concentration of excess HMPA was systematically varied. For Co(HMPA)$_2$Cl$_2$ all solutions were 0.100 *M* in complex and the concentration of excess HMPA was varied from 0.08 to 0.39 *M*. For Co(HMPA)$_2$Br$_2$ all solutions were 0.100 *M* in complex and the concentration of excess HMPA was varied from 0.10 to 0.61 *M*. The results for representative solutions are shown in Figures 1 and 2.

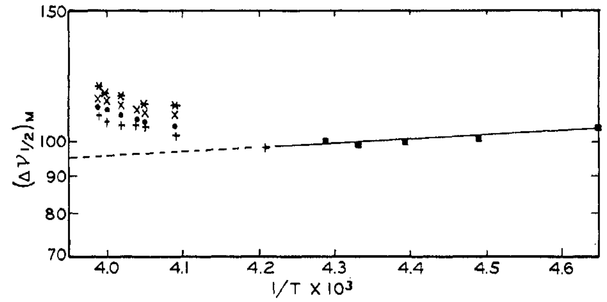

Figure 1.—Log of the observed line width of the signal due to the coordinated ligand protons *vs.* reciprocal absolute temperature for Co(HMPA)$_2$Cl$_2$ plus excess ligand. All solutions contain 0.10 *M* Co(HMPA)$_2$Cl$_2$ plus the following concentrations of excess HMPA: +, 0.0909 *M;* ●, 0.1748 *M;* ×, 0.2848 *M;* *, 0.3895 *M*. The points designated by ■ are average values.

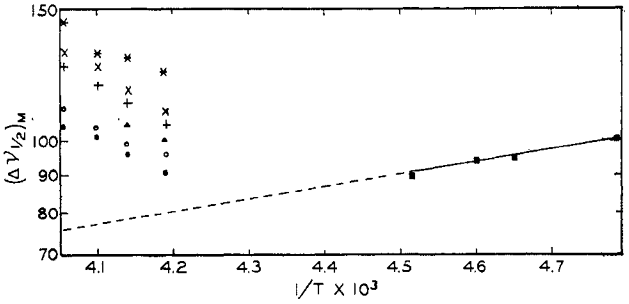

Figure 2.—Log of the observed line width of the signal due to the coordinated ligand protons *vs.* reciprocal absolute temperature for Co(HMPA)$_2$Br$_2$ plus excess ligand. All solutions contain 0.10 *M* Co(HMPA)$_2$Br$_2$ plus the following concentrations of excess HMPA: ●, 0.0995 *M;* ○, 0.1915 *M;* △, 0.2265 *M;* +, 0.2974 *M;* ×, 0.4450 *M;* *, 0.6140 *M*. The points designated by ■ are average values.

Figures 1 and 2 show plots of log $(\Delta\nu_{1/2})_M$ *vs.* $1/T$(°K) for solutions of Co(HMPA)$_2$Cl$_2$ and Co(HMPA)$_2$Br$_2$, respectively. These plots can be divided into two main temperature regions. At low temperatures the observed line width decreases with increasing temperature. This is characteristic of the case where the natural transverse relaxation rate ($1/T_{2M}$) controls the observed line width. Thus, in the low-temperature region exchange is essentially stopped and $T_2 = T_{2M}$.

Note that in the low-temperature region of Figure 1 only a single set of points is shown for $(\Delta\nu_{1/2})_M$. Measurements of the observed line widths for all of the solutions containing Co(HMPA)$_2$Cl$_2$ plus various concentrations of excess HMPA showed that, in the low-ture region, $(\Delta\nu_{1/2})_M$ is independent of the HMPA concentration. Since at low temperatures $(\Delta\nu_{1/2})_M = 1/\pi T_{2M}$, this means that $1/T_{2M}$ is independent of the viscosity of the solution. This result, which has been noted in the previous studies of pseudo-tetrahedral complexes of Co(II) and Ni(II),[2] is not unexpected since $1/T_{2M}$ for Co(II) and Ni(II) complexes is controlled by the rate of electron-spin relaxation and not the tumbling rate of the complex (see below). This lack of dependence of $1/T_{2M}$ for complexes of Co(II) and Ni(II) upon viscosity has been recently demonstrated quite convincingly by Frankel.[8] Thus, since $1/T_{2M}$ for Co(HMPA)$_2$Cl$_2$ is independent of viscosity, the values of $(\Delta\nu_{1/2})_M$ in the low-temperature portion of Figure 1 were obtained by averaging the observed line widths from all of the solutions not showing any exchange broadening at a given temperature. For example, the value of $(\Delta\nu_{1/2})_M$ shown at $10^3/T = 4.22$ was obtained by averaging the line widths from solutions containing 0.09 *M* HMPA and 0.08 *M* HMPA, since solutions with higher concentrations of HMPA show exchange broadening at this temperature.

The same procedure was followed for the Co(HMPA)$_2$Br$_2$ complex and the values of $(\Delta\nu_{1/2})_M$ given in the low-temperature region of Figure 2 are average values.

The second major temperature region found in Figures 1 and 2 is the region where $(\Delta\nu_{1/2})_M$ increases with increasing temperature. This behavior indicates that ligand exchange is significant, and, therefore, in this temperature region the observed line width contains contributions from $1/T_{2M}$ and $1/\tau_M$. By assuming that the mechanism controlling $1/T_M$ remains the same throughout the temperature region studied, one can obtain values of $1/T_{2M}$ in the exchange-controlled region by extrapolation of the low-temperature portion of the log $(\Delta\nu_{1/2})_M$ *vs.* $1/T_M$(°K) plot. Values of $1/\tau_M$ can then be obtained from eq 1.

Examination of Figures 1 and 2 shows that $1/\tau_M$ increases with increasing free-ligand concentration. Typical values for $1/\pi\tau_M$ at several temperatures for solutions of Co(HMPA)$_2$Cl$_2$ containing various concentrations of free ligand are given in Table I. Similar results were obtained for the Co(HMPA)$_2$Br$_2$ complex.

Experiments were also carried out in which the free-ligand concentration was held constant and the concentration of the Co(HMPA)$_2$X$_2$ complex was varied over the range from 0.05 to 0.10 *M*. These experiments showed that $1/\tau_M$ is not dependent upon the

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[8] L. S. Frankel, *J. Phys. Chem.*, **72**, 736 (1968).

Table I

Values of $1/\pi\tau_M$ at Several Temperatures for Solutions Containing $Co(HMPA)_2Cl_2$ and Various Concentrations of Free Ligand

| $10^3/T$(°K) | $1/\pi\tau_M$ for solutions containing $Co(HMPA)_2Cl_2$ and various concentrations of free ligand[a] 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| 3.99 | 13.5 | 13.0 | 16.0 | 17.0 | 19.5 | 22.5 |
| 4.00 | 12.3 | 11.8 | 14.3 | 15.3 | 18.8 | 21.3 |
| 4.02 | 10.0 | 9.0 | 13.0 | 14.0 | 18.0 | 18.5 |
| 4.04 | 8.7 | 8.7 | 11.0 | 11.7 | 15.5 | 17.7 |
| 4.05 | 7.7 | 8.2 | 9.7 | 11.2 | 12.7 | 15.7 |
| 4.08 | 5.5 | 7.0 | 9.0 | 8.5 | 11.0 | 13.3 |

[a] All solutions contain 0.100 *M* $Co(HMPA)_2Cl_2$ and the following excess HMPA concentrations: (1) 0.0844 *M*, (2) 0.0909 *M*, (3) 0.1748 *M*, (4) 0.1975 *M*, (5) 0.2848 *M*, and (6) 0.3895 *M*.

concentration of the complex for $Co(HMPA)_2Cl_2$ or $Co(HMPA)_2Br_2$.

Plots of $1/\tau_M$ *vs.* [L], the free-ligand concentration, for both the $Co(HMPA)_2Cl_2$ and $Co(HMPA)_2Br_2$ complexes yielded straight lines which were found not to pass through the origin within experimental error. Typical plots of $1/\pi\tau_M$ *vs.* [HMPA] for the $Co(HMPA)_2Cl_2$ complex at several temperatures are shown in Figure 3. Similar plots were obtained for the $Co(HMPA)_2Br_2$ complex. Thus, $1/\tau_M$ for the $Co(HMPA)_2X_2$ complexes can be described by

$$\frac{1}{\tau_M} = k_1 + k_2[L] \qquad (2)$$

and the exchange rate law can be written

$$\text{rate} = 2k_1[Co(HMPA)_2X_2] + 2k_2[Co(HMPA)_2X_2][HMPA] \qquad (3)$$

where $k_1$ and $k_2$ are first- and second-order rate constants, respectively.

Arrhenius activation energies were obtained for $k_1$ and $k_2$ for the $Co(HMPA)_2X_2$ complexes from studies at several temperatures in the exchange-controlled temperature region. Plots of $1/\pi\tau_M$ *vs.* [HMPA] were constructed at each temperature and $k_1$ and $k_2$ were obtained from the intercept and slope, respectively (see Figure 3). The activation energy plots for $Co(HMPA)_2Cl_2$ are shown in Figure 4. Similar plots were obtained for the $Co(HMPA)_2Br_2$ complex. The results of these studies are summarized in Table II.

## Discussion

The rather large error limits given in Table II for the $E_a$ values are mainly a result of the very small temperature range available for the study of the exchange kinetics of the $Co(HMPA)_2X_2$ complexes. This is due to the fact that the free and complexed ligand signals begin to overlap only 6–10° above the temperature where exchange becomes significant. Thus, eq 1 is applicable only in this narrow temperature region and the resulting activation energies are not expected to be of high quality. The obvious way to eliminate this difficulty would be to employ the complete line-shape technique[3] to study the exchange kinetics of these complexes. This proved to be infeasible for reasons given below. Another possible source of error which should be considered is that at the highest temperatures at which the exchange reactions of the $Co(HMPA)_2X_2$ complexes were studied there was a slight overlapping of the two signals leading to possible error in the use of eq 1 in this region. This could cause the $E_a$ values obtained for the first-order path to be a little on the high side.

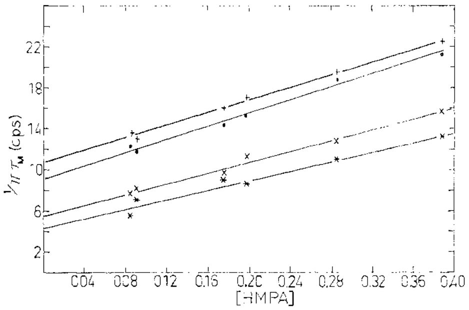

Figure 3.—Plots of $1/\pi\tau_M$ *vs.* the free HMPA concentration for $Co(HMPA)_2Cl_2$ at several temperatures in the exchange-controlled region. Plots are give for the following values of $10^3/T$(°K): +, 3.99; O, 4.00; ×, 4.05; *, 4.08.

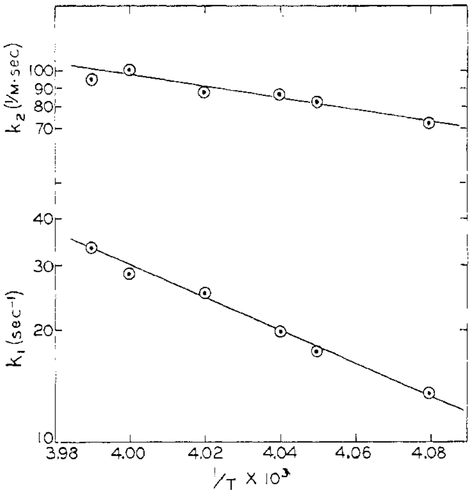

Figure 4.—Plots of log $k_1$ and log $k_2$ *vs.* $10^3/T$(°K) for the $Co(HMPA)_2Cl_2$ complex.

Table II

Summary of the Kinetic Data for the $Co(HMPA)_2X_2$ Complexes

| Complex | $k_1$ (−26°), $sec^{-1}$ | $E_a(k_1)$, kcal $mol^{-1}$ | $k_2$ (−26°), $M^{-1}$ $sec^{-1}$ | $E_a(k_2)$, kcal $mol^{-1}$ |
|---|---|---|---|---|
| $Co(HMPA)_2Cl_2$ | 25.1 | 20 ± 3 | 87.2 | 7 ± 2 |
| $Co(HMPA)_2Br_2$ | 57.4 | 15 ± 2 | 260.0 | 5 ± 1 |

Several previous studies[9-11] of paramagnetic complexes with ligands containing a phosphorus atom (including HMPA) have shown that, at least in these cases, the $^{31}P-^{1}H$ spin–spin coupling is apparently decoupled by the paramagnetic ion. At the concentrations of free ligand employed in this study it was found that the signal due to the free HMPA protons appears to be a singlet. Initially, it was felt that this was due to decoupling of the $^{31}P-^{1}H$ interaction in the "free" ligand by outer-sphere contact with the complex, thus giving a simple, noncoupled two-site system. However,

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(9) D. Shaw and E. W. Randall, *Mol. Phys.*, **10**, 41 (1965).

(10) D. Shaw and E. W. Randall, *Chem. Commun.*, **5**, 82 (1965).

(11) B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **87**, 2372 (1965).

experiments were run on solutions of $Co(HMPA)_2X_2$ 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 $Co(HMPA)_2X_2$ 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 $Co(HMPA)_2X_2$ complexes. This is in contrast to the purely second-order kinetics observed for the $Co(2\text{-pic})_2Cl_2$[3] and $Co(TTP)_2X_2$[2] (TPP = triphenylphosphine) complexes. A possible explanation for this can be advanced by postulating that the first-order process observed for the $Co(HMPA)_2X_2$ 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 $CoL_2X_2$ 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 $Co(HMPA)_2Cl_2$ and $Co(HMPA)_2Br_2$. 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 $Co(HMPA)_2X_2$ complexes. $E_a(1/T_{2M})$ was found to be $-0.3$ kcal/mol for the $Co(HMPA)_2Cl_2$ complex and $-0.7$ kcal/mol for the $Co(HMPA)_2Br_2$ 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]

**Acknowledgment.**—The authors wish to acknowledge the generous support of this research by the National Science Foundation through Grant GP-5498. We also wish to thank Dr. M. Crutchfield of Monsanto for carrying out the $^{31}P$ decoupling experiments.

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## The Crystal Structure of Trimethylplatinum Hydroxide[1a]

BY THOMAS G. SPIRO,[1b] DAVID H. TEMPLETON,[1c]
AND ALLAN ZALKIN[1c]

*Received April 26, 1968*

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 $(CH_3)_3PtOH$ and is also entirely analogous to the structure of $(CH_3)_3PtCl$, 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).

[4] G. L. Morgan, R. D. Rennick, and C. C. Soong, *Inorg. Chem.*, **5**, 372 (1966).

[5] W. J. Pope and S. S. Peachey, *J. Chem. Soc.*, **95**, 571 (1909).