

of the gel (in this case, strontium chloride). Diffusion into the gel takes place and under the proper conditions of pH, concentration of the active ingredients, density of the gel, and temperature, crystals grow in the gel (strontium tartrate in this example). We report here the results of an X-ray study of gel-grown strontium tartrate tetrahydrate ($\text{SrC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$).

No available X-ray data on this crystal were known to us, but a similar material, calcium tartrate, is reported to be orthorhombic (Donnay & Nowacki, 1954), having the space group $P2_12_12_1$ with four molecules per unit cell and lattice constants (a, b, c) equal to 9.62, 10.54, and 9.20 Å, respectively. Electron spin resonance (e.s.r.) data (Murphy & Bohandy, 1967) of Cu^{2+} in strontium tartrate indicated that this crystal was probably isomorphous with calcium tartrate with four molecules per unit cell as expected. However, for the purpose of further e.s.r., optical, and piezoelectric measurements on this material, we needed to know the space group and lattice constants with certainty.

Zero, first, and second level X-ray precession pictures were taken with Mo $K\alpha$ radiation. Interpretation of these photographs showed that the strontium tartrate lattice is orthorhombic with the lattice constants:

$$\begin{aligned} a &= 9.48 \pm 0.04 \text{ \AA} \\ b &= 10.96 \pm 0.04 \\ c &= 9.46 \pm 0.04 \end{aligned}$$

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Reinvestigation of the reaction of trimethylplatinum(IV) iodide with methylsodium. By DWAIN O. COWAN and NILDE G. KRIEGHOFF,* *Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218, U.S.A.*, and GABRIELLE DONNAY, *Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C. 20008, U.S.A.*

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The product from the reaction of trimethylplatinum(IV) iodide and methylsodium is shown to be identical with that previously obtained from this reaction and subsequently characterized as tetramethylplatinum. However, the supposed tetramethylplatinum is now shown to be trimethylplatinum(IV) hydroxide.

Gilman & Lichtenwalter (1938, 1953) have reported the synthesis of tetramethylplatinum in 46% yield by reacting trimethylplatinum(IV) iodide with methylsodium in benzene-free hexanes. They based their identification of the compound primarily upon combustion analysis. The true composition of this substance could be questioned since the compound explodes when heated. The authors reported that tetramethylplatinum did not react with iodine in chloroform when refluxed for 24 hours nor did it react with benzoyl chloride in benzene when refluxed for 100 hours, but it did react with dry hydrogen chloride gas when the gas was bubbled through a refluxing solution of tetramethylplatinum in light petroleum (b.p. 60–68°) producing white crystals of trimethylplatinum(IV) chloride. Tetramethylplatinum was reported to be readily soluble in organic solvents and was said to crystallize from light petroleum in large hexagonal plates.

Rundle & Sturdivant (1947) described the crystals of tetramethylplatinum supplied by Gilman as rhomb-dodecahedra. They found the cell edge to be 10.165 Å (10.145

The diffraction symbol was determined to be $mmmP2_12_12_1$. This diffraction symbol unambiguously implies the space group $P2_12_12_1$ for strontium tartrate. Although a and c are nearly equal, the intensity of zero level reflections indicates that the crystal is not tetragonal. The crystals are elongated in the c direction and the principal faces are the prismatic ones (110) and ($\bar{1}10$), with their symmetry equivalents. (101) and ($\bar{1}01$), with their symmetry equivalents, are present as the principal, if not the only, end faces. The density of the crystal was measured and found to be 2.05 with the use of standard techniques. A computation of the density of $\text{SrC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ with the measured lattice constants gave the value 2.08, in good agreement with the measured value.

Powder photographs of calcium tartrate and strontium tartrate were taken. Complete isomorphism to calcium tartrate is highly probable but cannot be claimed as certain without further intensity comparisons.

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kX) long. They determined the density of the crystals to be 3.16 g.cm⁻³, from which they deduced that the cell contains eight molecules giving a calculated density of 3.23 g.cm⁻³. Qualitative intensity considerations combined with symmetry information obtained from the known Laue class, $4/m\bar{3}2/m$, led to a structure with 2 tetramers per cell.

Tetramethylplatinum is unique not only in that it is the first molecule reported in which a platinum(IV) atom is bonded only to four organic ligands, but also in that the tetramer bonding requires the application of the concept of four-center two-electron bonds (Rundle & Sturdivant, 1947).

We have repeated the Gilman–Lichtenwalter synthesis of tetramethylplatinum. A suspension of methylsodium was prepared from sodium and dimethylmercury in benzene-free 2,3-dimethylbutane under a nitrogen atmosphere after the method of Schlenk & Holtz (1917). To the resulting black suspension were added trimethylplatinum(IV) iodide crystals which had either been recrystallized from benzene and vacuum dried to remove all the solvent molecules or had been recrystallized from chloroform and then air dried. The methylsodium–trimethylplatinum(IV) iodide mixture was stirred for 24 hours at room temperature and then

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hydrolyzed with n-pentyl alcohol, ethanol, and, finally, water. The hexane layer was then separated and filtered to remove the pasty black precipitate composed mainly of amalgamated sodium and platinum metal from decomposition. The filtrate was dried, and the solvent evaporated. A white residue was obtained in all cases. To extract any possible tetramethylplatinum from the white residue, the residue was covered with 20 ml light petroleum (b.p. 30–60°) for 30 minutes, the suspension was filtered, and the solvent removed. From 1 g of trimethylplatinum(IV) iodide, we usually obtained about 10 mg (1.4%) of a white solid whose nuclear magnetic resonance spectrum in benzene solution gave a single sharp peak at $\tau 9.05$ with satellites due to platinum 195 showing a $J(^{195}\text{Pt}-\text{CH}_3) = 78$ Hz. The reaction gave the same result when performed at different temperatures and in different solvents.

The white solid product from the above reaction gave a combustion analysis of C 14.33, H 4.08%; calc. for $\text{Pt}(\text{CH}_3)_4$: C 18.8, H 4.7%; for $\text{Pt}(\text{CH}_3)_3\text{OH}$: C 14.01, H 3.92%. (The combustion analysis was performed by J. Walters of the Johns Hopkins University.) From 100% ethanol solution, the compound crystallizes in transparent, colorless rhomb-dodecahedra which are stable in air but decompose slowly when subjected to strong fluorescent light. Precession and Weissenberg X-ray photographs of these crystals, taken with zirconium-filtered Mo radiation, show reflections for which the sum of the Miller indices is even with Laue class $4/m\bar{3}2/m$ for which space groups $Im\bar{3}m$, $I432$, or $I\bar{4}3m$ are possible. The cell edge was refined by means of a back-reflection Weissenberg photograph taken with nickel-filtered Cu radiation ($\lambda_{\text{Cu}} K\alpha_1 = 1.54051$, $\lambda_{\text{Cu}} K\alpha_2 = 1.54434$ Å) and the Burnham least-squares program LCLSQ to give $a = 10.179 \pm 0.002$ Å at 21°C. We obtained an experimental density of 3.2 ± 0.2 g.cm⁻³ for the crystals by the flotation method in methylene iodide–methyl iodide. Assuming that eight molecules of $\text{Pt}(\text{CH}_3)_3\text{OH}$ are contained in the cell, we calculate a density of 3.29 g.cm⁻³. Thus, our crystal habit, density, cell edge and Laue class agree, within experimental accuracy, with the values reported by Rundle & Sturdivant.

Because of the similarity between the reported values (Kite, Smith & Wilkins, 1966) for the nuclear magnetic resonance (n.m.r.) spectrum of trimethylplatinum(IV) hydroxide and those obtained for 'tetramethylplatinum', we decided to investigate the possibility that the Gilman–Lichtenwalter synthesis yields trimethylplatinum(IV) hydroxide and that Rundle & Sturdivant may have determined the structure of trimethylplatinum(IV) hydroxide instead of tetramethylplatinum. The X-ray intensities of the diffraction maxima, which were obtained by them from a rotation pattern, could not have given any indication of the mistaken identity of their crystals, since the scattering curves f of OH and CH₃ are indistinguishable in the presence of the heavy atom platinum. But although the tetramethylplatinum and trimethylplatinum(IV) hydroxide, if isostructural, would give similar X-ray intensities, their cell edges should differ measurably: the hydroxide should have a smaller cell than the tetramethyl compound. A comparison of the cell dimension with that of the isostructural trimethylplatinum(IV) chloride (10.57 Å) indicates that the order of magnitude of the change to be expected is several per cent.

We synthesized trimethylplatinum(IV) hydroxide by the method of Pope & Peachey (1909) and recrystallized the product ten times from light petroleum (b.p. 30–60°) to remove any unreacted trimethylplatinum(IV) iodide. The n.m.r. spectrum of the final product in a saturated benzene solution shows a sharp singlet peak at $\tau 9.04$ flanked by two satellite peaks due to platinum 195 with a $J(^{195}\text{Pt}-\text{CH}_3) = 79$ Hz. X-ray powder patterns taken of the hydroxide compound and the unknown white compound previously presumed to be $\text{Pt}(\text{CH}_3)_4$ are identical. Thus since the n.m.r. spectra, powder patterns, and combustion analyses are identical for the two materials, we conclude that they are one and the same compound.

The one and only other product isolated by fractional recrystallization from the trimethylplatinum(IV) iodide reaction is another white solid whose n.m.r. spectrum in benzene consists of a sharp singlet peak at $\tau 8.46$ with $J(^{195}\text{Pt}-\text{CH}_3) = 78$ Hz. This material recrystallizes easily from benzene also giving transparent rhomb-dodecahedra which remain colorless and clear when exposed to air. Combustion analysis (by J. Walters) gave C 13.48, 14.17; H 3.50, 3.67%; calc. for $\text{Pt}(\text{CH}_3)_3\text{Cl}$: C 13.07; H 3.29%. The combustion analysis is difficult to execute since this material also explodes upon heating. Precession and Weissenberg X-ray photographs using zirconium-filtered Mo radiation show an I lattice ($h+k+l=2n$). The X-ray patterns obtained are exactly the same as those of the hydroxide crystal, only the cell dimension is different, namely 10.59 ± 0.03 Å. Rundle & Sturdivant (1947) obtained $a = 10.57$ Å (10.55 kX) for trimethylplatinum(IV) chloride. The experimental density determined by the flotation method using methylene iodide and methyl iodide was found to be 3.08 g.cm⁻³, which agrees with the published value of 3.1 g.cm⁻³. The material is trimethylplatinum(IV) chloride which, as an impurity, survived the reaction conditions of the methylsodium–trimethylplatinum(IV) iodide synthesis.

From the above considerations, it appears that tetramethylplatinum has not been synthesized and that Rundle & Sturdivant studied trimethylplatinum(IV) hydroxide. No new bonding concept is needed to explain the hydroxide tetramer.

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