Anal. Calcd. for $[Pt(C_3H_{10}N_2)_3]Cl_4$: C, 19.32; H, 5.41; N, 15.03; Pt, 34.89; Cl, 25.35. Found: C, 19.5; H, 5.64; N, 15.16; Pt, 34.94; Cl, 25.2.

D-Bis-(*d*-propylenediamine)-*l*-propylenediamine-platinum (IV) Chloride.—The more soluble portion of the mixture of isomers above was converted to the *d*-tartrate in the usual manner and combined with the filtrate remaining after the crystallization of the less soluble diastereoisomer. The solution was then concentrated to 60 ml. and the less soluble diastereoisomer, which crystallized, was removed. The more soluble diastereoisomer in solution was treated with concentrated hydrochloric acid and the mixture evaporated to dryness. The *d*-tartaric acid was completely removed by washing with warm alcohol, and the complex chloride transformed with silver sulfate and then barium *l*-tartrate to the *l*-tartrate. Fractional crystallization of the latter material gave the pure diastereoisomer, D-$[Pt\text{-}d\text{-}pn_2\text{-}l\text{-}pn](l\text{-tart.})_2 \cdot 7H_2O$; in the least soluble fractions.

Anal. Calcd. for $[Pt(C_3H_{10}N_2)_3](C_4H_4O_6)_2 \cdot 7H_2O$: C, 24.30; H, 6.24; Pt, 23.24. Found: C, 24.40; H, 6.14; Pt, 23.45.

The chloride obtained in the usual way, after recrystallization from water gave $[\alpha]_D$ +83°, $[\alpha]_{5461}$ +100°. The recovered propylenediamine gave $[\alpha]_D$ +11.80° in benzene, whence $d\text{-pn}/l\text{-pn} = 1.96 \pm 0.1$.

Anal. Found: C, 19.16, H, 5.36; N, 15.06; Pt, 34.92; Cl, 25.1.

D-Bis-(*l*-propylenediamine)-ethylenediamine-platinum-(IV) Chloride.—The intermediate substances $[Pten\ Cl_2]$ and $[Pten\ Cl_4]$ have been described previously.[5] The former is best prepared in the same manner as $[Ptpn\ Cl_2]$ above, using potassium tetrachloroplatinate(II), (10 g.) and ethylenediamine dihydrochloride (4 g.) yield 6.5 g., 82%). Levopropylenediamine (6.6 g.) was added to a solution of tetrachloro-(ethylenediamine)-platinum(IV) (15.8 g.) in dimethylformamide (250 ml.). A gel gradually formed and, after 3 hr., dry hydrogen chloride gas was passed until the mixture was acid and coagulation effected by the addition of acetone (70%), alcohol (30%) mixture (1 l.). The white solid (17.5 g., 80%) gave $[\alpha]_D$ +85°. The substance was dissolved in hot water and evaporated until approximately half of the complex separated on cooling. This portion was then converted to the *d*-tartrate as above, in boiling solution. The diastereoisomer *d*-$[Pt\text{-}l\text{-}pn_2en](d\text{-tart})_2 \cdot 5H_2O$ that separated on cooling was recrystallized from hot water. *Anal.* Calcd. for $[Pt(C_3H_{10}N_2)_2 \cdot C_2H_8N_2](C_4H_4O_6)_2 \cdot 5H_2O$: C, 24.33; H, 5.87; Pt, 24.71. Found: C, 24.62; H, 6.03; Pt, 24.6.

The chloride, obtained with hydrochloric acid and alcohol, after three recrystallizations from water, gave $[\alpha]_D$ +176°, $[\alpha]_{5461}$ +210° (0.25% soln.). *Anal.* Calcd. for $[Pt(C_3H_{10}N_2)_2 \cdot C_2H_8N_2]Cl_4$: C, 17.62; H, 5.17; Pt, 35.79; Cl, 26.00; molar ratio pn/en, 2.00. Found: C, 17.65; H, 5.24; Pt, 35.74, Cl, 25.86; molar ratio pn/en, 2.06.

L-Bis-(*l*-propylenediamine)-ethylenediamine-platinum-(IV) Chloride.—The more soluble portion of the mixture of isomers was converted as before to the *d*-tartrate, combined with the mother liquors from the less soluble diastereoisomer and concentrated gradually to 50 ml. Small amounts of the less soluble diastereoisomer, that separated, were removed. The *d*-tartrate was removed from the remaining sirup by the addition of hydrochloric acid, followed by evaporation to dryness and extraction with warm alcohol. The complex chloride was then transformed to the *l*-tartrate, as before, and the solution concentrated. A small amount of the diastereoisomer D-$[Pt\text{-}l\text{-}pn_2 \cdot en](l\text{-tart.})_2$ that separated was removed, and finally a gum was left. The *l*-tartrate was then replaced by chloride and the substance fractionally crystallized from aqueous methanol. The least soluble fractions gave the pure levo form, $[\alpha]_D$ −29°; $[\alpha]_{5461}$ −35°, (0.5% solution). *Anal.* Calcd. for $[Pt(C_3H_{10}N_2)_2 \cdot C_2H_8N_2]Cl_4 \cdot H_2O$: C, 17.06; H, 5.37; Pt, 34.64; Cl, 25.17, molar ratio pn/en, 2.00. Found: C, 17.46; H, 5.33; Pt, 34.62; Cl, 24.9; molar ratio pn/en, 2.01.

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CANBERRA, AUSTRALIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY, KAISER ALUMINUM & CHEMICAL CORPORATION]

Preparation of Pure Anhydrous Aluminum Fluoride by Vacuum Sublimation

BY JACK L. HENRY AND S. H. DREISBACH

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Laboratory quantities of pure anhydrous aluminum fluoride have been prepared by vacuum sublimation of a calcined hydrated salt in a simple and easily constructed apparatus. By proper selection of condenser temperature and retort-condenser temperature differential, a dense pad of well-defined crystals can be produced. Individual crystals up to four millimeters in diameter are observed in the product. The purity is greater than 99% with no detectable oxyfluorides.

For many chemical and physical applications the level of impurities in technical grade aluminum fluoride and the water of hydration in reagent grade product cannot be tolerated. Technical grade aluminum fluoride may contain up to 15% alumina together with minor impurities such as cryolite, aluminum sulfate, silica and iron oxide. Reagent grade aluminum fluoride contains only traces of impurities but is a hydrated salt or mixture of hydrates containing up to 40% water of crystallization. Attempts to remove this water inevitably result in the loss of fluoride and formation of alumina by thermal hydrolysis. Removal of the last traces of water requires calcination temperatures from 500 to 800°.[1] Thermal hydrolysis takes place at temperatures as low as 150 to 200°.[2]

Pure anhydrous aluminum fluoride has been prepared by some investigators by sublimation techniques. Batashev[3] states that it may be prepared by distillation of the dry impure salt in a hydrogen fluoride atmosphere. Zhivov[4] suggests sublimation of technical aluminum fluoride from an Alundum crucible at not less than 1100° using a second Alundum crucible as a condenser. To avoid basic fluoride formation, it is necessary to employ an atmosphere of hydrogen fluoride or inert gas. The sublimation of aluminum fluoride from a mixture of fluorspar and kaolin is the subject of a Russian patent.[5]

The method described here was developed for the purpose of preparing laboratory quantities of high

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[1] T. R. Scott, Council for Scientific and Industrial Research, Bulletin 230, Melbourne, Australia, 1947.

[2] A. J. Edwards, British Patent 656,374 (August 22, 1951).

[3] K. P. Batashev, *Trans. Leningrad Ind. Inst. No. 1, Sect. Met.*, No. 1, 40 (1939).

[4] V. G. Zhivov, *Khim. Referat. Zhur.*, **6**, 98 (1940).

[5] G. S. Morozov and N. A. Ivanov, Russian Patent 52,597 (February 28, 1938).

purity product for use in fused salt studies. Approximately fifty grams can be prepared in six hours.

The starting material employed was a grade of anhydrous aluminum fluoride whose purity ranged from 93 to 95%. The principal impurities were chiolite and alumina together with small amounts of SiO_2, MgO, Fe_2O_3, CaO, TiO_2, Ga_2O_3 and V_2O_5. The material was calcined at 800° for 30 minutes prior to carrying out the sublimation. There is no reason that reagent grade aluminum fluoride trihydrate would not be as good or better as a starting material provided all the water is removed with a minimum degree of hydrolysis by calcination at 600 to 800° in a stream of dry air.

The vacuum sublimation is conducted in a graphite system consisting of two high density graphite crucibles, each measuring 2.5 inches outside diameter, 1.75 inches inside diameter, and 2.5 inches deep. The lips of the two crucibles are machined in such a manner that the lip of one seats snugly about $^{1}/_{8}$ to $^{1}/_{4}$ inch into the lip of the second, providing a reasonably tight seal. Sitting vertically, the lower crucible serves as a retort to contain the starting material, and the top inside surface of the upper crucible serves as the condenser.

The crucible assembly is fitted into a type 86 Nichrome cylindrical heating element so that the windings are symmetrical about the mid-point of the assembly. The element is seated directly on a circular block of Insulbrick 4.5 inches in diameter and 2.5 inches thick. A similar Insulbrick block is used for insulation of the top of the assembly. This block is altered by removing a circular section the same diameter as the graphite crucible and 1 inch deep from the center surface. This "cup" is then placed open end down over the top surface of the graphite condenser crucible. The purpose of the removal of this cylinder of insulation is to provide a greater rate of heat loss to maintain a temperature gradient between retort and condenser.

Measurement of temperature gradient during operation is accomplished by two chromel–alumel thermocouples, one in contact with the center of the outside end of the condenser and one at the center of the outside end of the retort. About $^{3}/_{4}$ inch of fiber insulation is placed around the sides of the heating element but not on the end nor around the Insulbrick blocks. The furnace can be conveniently contained in a steel or aluminum cylinder 4.5 inches in diameter and 8 to 10 inches long. The geometry of the insulation block over the condenser can be altered slightly if necessary to achieve the correct temperature differential. The entire assembly is then placed into any suitable container which can be evacuated to about 500 μ pressure. A good product and substantial yield can be obtained at a pressure of 500 μ and with a temperature differential of 25 to 30° between the retort and condenser ends. Larger retort–condenser assemblies up to 3 inches diameter and 7 inches over-all length have been used successfully. It is important that the starting material and the entire assembly be bone dry before starting the sublimation.

About 80 g. of the anhydrous starting material is placed into the lower crucible, and the system is assembled. The entire assembly is then pumped down to about 500 μ and the temperature raised until the condenser is at 900° and the retort at approximately 925°. Sublimation is allowed to continue for three to six hours. At the completion of the run the power is turned off and the assembly is cooled to below 100° prior to releasing the vacuum. The product will consist of a dense pad of well-defined crystals on the underside of the top surface of the condenser. No product should be found on the sidewalls.

The pressure may be allowed to vary by $\pm 200\ \mu$ and the retort and condenser temperature by ±25°. The 25–30° differential should be maintained. The condenser temperature should not rise above about 925°. At 950° the yield is greatly reduced, the product being lost from the system.

The purity of the product varies slightly from batch to batch. A typical spectrographic analysis shows: Si, 0.008; Mn, <0.002; Fe, 0.002; Mg, 0.015; Cu, < 0.001; Na, < 0.05; Ti, <0.006; Ni, 0.001; Cr, 0.002; Ca, <0.06; V, 0.002; graphite, trace.

On the basis of aluminum and fluorine analysis together with trace analysis, the purity appears to be better than 99%. Purity can be increased by resublimation.

PERMANENTE, CALIFORNIA

[CONTRIBUTION FROM THE CANCER RESEARCH INSTITUTE OF THE NEW ENGLAND DEACONESS HOSPITAL]

Strontium–Calcium Hydroxyapatite Solid Solutions: Preparation and Lattice Constant Measurements[1]

BY ROBERT L. COLLIN

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Homogeneous solid solutions of strontium and calcium hydroxyapatite have been prepared over the entire composition range by heating to 950° precipitates formed by the addition of ammonium phosphate to solutions of calcium and strontium nitrate made strongly basic with ethylenediamine. The lattice constants of the solid solutions have been measured and found to vary linearly with composition between those of the pure end members. The solid samples have a much smaller ratio of strontium to calcium than the solutions from which they are precipitated.

Introduction

The ultimate site and mechanism of strontium incorporation into the bone structure of the body have been of great interest ever since the release of radioactive strontium into the atmosphere from nuclear bomb tests. As part of a more general program of research in this field the feasibility of preparing synthetic solid solutions of strontium in calcium hydroxyapatite has been investigated.

Calcium hydroxyapatite (CaHA), which exists in nature as the mineral hydroxyapatite, and is similar if not identical to bone mineral, can be prepared from aqueous solution.[2,3] Strontium hydroxyapatite (SrHA), although not found naturally, has also been prepared from aqueous solution by a number of workers.[4–6] X-Ray measurements of unit cell dimensions[4,6] indicate that these two hydroxyapatites are probably isomorphous and hence a possibility exists that solid solutions can be formed between the two compounds.

An attempt has been made by Lagergren and Carlström[6] to prepare solid solutions of SrHA and CaHA by precipitation from aqueous solution with subsequent heating above 600° to improve crystallinity. They were not successful and abandoned this procedure in favor of a solid state reaction at

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[1] This work was done under U. S. Atomic Energy Commission Contract AT(30-1)-901 with the New England Deaconess Hospital.

[2] R. Wallaeys and G. Chaudron, *Compt. rend.*, **231**, 355 (1950).

[3] E. Hayek and W. Stadlmann, *Angew. Chem.*, **67**, 327 (1955).

[4] R. Klement, *Z. anorg. allgem. Chem.*, **242**, 215 (1939).

[5] W. Rathje, *Ber.*, **74**, 342 (1941).

[6] C. Lagergren and D. Carlström, *Acta Chem. Scand.*, **11**, 545 (1957).