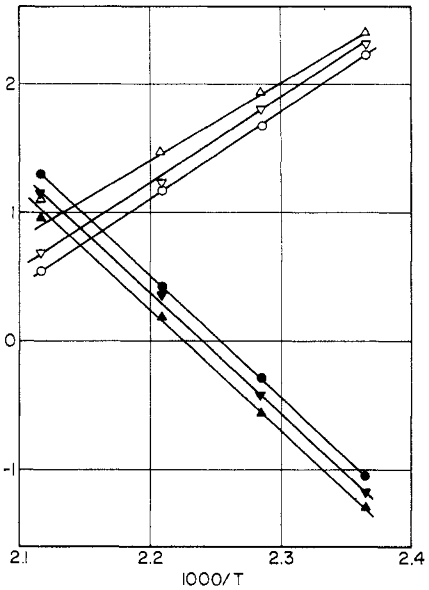

Figure 2.—Values of equilibrium constants as a function of temperature; full symbols indicate K_s(A–B) and empty symbols indicate K_{AB} for the mixed halide systems: chloride–bromide, O; chloride–iodide, ▽; bromide–iodide, △.

peratures are in progress), low stability in the salt phase was found for HgClI and HgBrI, but not for HgClBr. This low stability was attributed to steric effects, taking into account the two nitrate ions which are assumed to complex the neutral mercury halide in the (nitrate) melt phase.[5] In the case of the smaller Zn(II) ion, such a steric effect should be expected also in the case of ZnClBr, as was found in this work. However, the magnitude of this effect and its disappearance at higher temperatures still remains unexplained. Apparently, as was pointed out in the preceding paper,[1] pure zinc dihalides are so stable that the zinc–halogen bonds cannot be broken at lower temperatures even in order to exchange one halide for another. It may be pointed out that the $\Delta H°$ values involved in the replacement of a halide by a nitrate[1] are of the same order of magnitude as those involved in the formation of the mixed halide complex.

Acknowledgment.—Thanks are due to Mr. S. Shamash for technical assistance.

(5) M. Zangen and Y. Marcus, *Israel J. Chem.*, **2**, 49, 155 (1964).

CONTRIBUTION FROM THE CHEMISTRY DIVISION,
ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS 60439

Synthesis of Thallium Platinate at High Pressure[1]

BY HENRY R. HOEKSTRA AND STANLEY SIEGEL

Received July 19, 1967

The double oxide $Tl_2Pt_2O_7$ has been prepared by reaction of Tl_2O_3 with platinum metal or PtO_2 at 1000° and 40 kbars pressure. The brown solid is insoluble in aqua regia and is thermally stable to 750° at atmospheric pressure. The cell is face-centered cubic with $a = 10.132 \pm 0.004$ A and the structure is assumed to be of the cubic pyrochlore type based on space group Fd3m. The measured density is 11.12 g/cm^3 and the computed value is 11.63 g/cm^3, with $Z = 8$. Fifteen diffraction lines were observed and used in a least-squares refinement to determine the one unknown coordinate. The R factor is 3.6% based on observed maxima only. Each platinum is bonded octahedrally to six oxygens at 2.08 ± 0.04 A, each thallium to six oxygens at 2.32 ± 0.04 A and two oxygens at 2.19 ± 0.002 A. Some general aspects of the pyrochlore structure are discussed. The infrared spectrum of $Tl_2Pt_2O_7$ (to 200 cm^{-1}) has four sharp maxima at 684, 562, 449, and 363 cm^{-1}.

Introduction

Information concerning the preparation and properties of anhydrous platinum oxides is scanty and often contradictory. Three oxides (PtO, Pt_3O_4, and PtO_2) and two double oxide compositions ($M^IPt_3O_4$ and $M_2^IPtO_3$, where M is lithium or sodium) have been reported in relatively recent publications.

Moore and Pauling[2] treated $PtCl_2$ with KNO_3 and on the basis of very meager crystal data, concluded that the product was PtO, isostructural with the corresponding palladium oxide. The existence of PtO has been questioned by later workers.[3] Galloni and Roffo[4] determined the structure of several crystals of a cubic oxide which had been obtained from a platinum wire electrode. The assigned formula was Pt_3O_4, but confirmatory analysis was not possible on the small sample, and its true composition remains in doubt. Ariya, *et al.*,[5] reported that the oxidation of platinum sponge at oxygen pressures to 310 bars produced only one thermodynamically stable oxide, Pt_3O_4. Its structure, however, was not that of the Galloni compound. Platinum dioxide has been prepared by fusing H_2PtCl_6 with an alkali metal nitrate.[3,6]

Waser and McClanahan[7] report that cubic $NaPt_3O_4$

---

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission. Paper presented at 153rd National Meeting of American Chemical Society, Miami Beach, Fla., April 1967.

(2) W. J. Moore and L. Pauling, *J. Am. Chem. Soc.*, **63**, 1392 (1941).

(3) E. E. Galloni and R. H. Busch, *J. Chem. Phys.*, **20**, 198 (1952).

(4) E. E. Galloni and A. E. Roffo, *ibid.*, **9**, 875 (1941).

(5) S. M. Ariya, M. P. Morozova, G. S. Markevich, and A. A. Reikhardt, *Sb. Statei Obshchei Khim. Akad. Nauk SSSR*, **1**, 76 (1953); see *Chem. Abstr.*, **48**, 12533 (1954).

(6) R. Adams and R. L. Shriner, *J. Am. Chem. Soc.*, **45**, 2171 (1923).

(7) J. Waser and E. D. McClanahan, *J. Chem. Phys.*, **19**, 413 (1951); **20**, 199 (1951).

is the product obtained when chloroplatinic acid is fused with sodium carbonate at 850°, but Galloni and Busch[3] contend that sodium is not an essential constituent of the oxide and that its true composition is Pt_3O_4. This structure may consist of a solid solution having the formula $Na_xPt_3O_4$. Scheer, *et al.*,[8] report that the fusion of mixtures of platinum metal with lithium or sodium carbonates in a magnesia boat leads first to the formation of the double oxide composition $M_xPt_3O_4$ (as described above) and then to M_2PtO_3. The latter composition is obtained after the reactants have been heated gradually over a 20-hr period to 1000°.

The present paper describes the preparation and properties of a new platinum oxide, $Tl_2Pt_2O_7$. This oxide was first synthesized during an investigation into the effects of high pressure on the stability relationships between cubic type C and monoclinic type B rare earth sesquioxides.[9] When the isostructural (type C) Tl_2O_3 was studied at high pressure, a reaction occurred which led to the formation of the thallium–platinum double oxide.

Experimental Section

Materials.—The 2-ml platinum foil cups used to contain powder samples in the high-pressure syntheses analyzed 99.9+% Pt. In experiments requiring platinum in a powdered form the metal was prepared by thermal decomposition of K_2PtCl_6. Potassium chloride was removed from this product by washing it thoroughly with water. Thallium sesquioxide was prepared by the method of Rabe[10] in which an alkaline thallous solution is oxidized and precipitated as virtually anhydrous Tl_2O_3 by the addition of dilute hydrogen peroxide. The sesquioxide was separated by filtration and dried at 500°. Analysis of the product gave 89.4% thallium (89.49% theoretical).

Platinum dioxide was prepared by heating K_2PtCl_4 or K_2PtCl_6 in molten KNO_3 at 350° for 24 hr. Excess KNO_3 was dissolved in water and the insoluble product treated with aqua regia to dissolve any metallic platinum and leave a residue of PtO_2. Analysis gave 86.1% platinum (85.92% theoretical).

Methods.—The reactant powders for high-pressure experiments were tamped firmly to a depth of about 5 mm in platinum foil cups 6.3 mm in height and in diameter. The sample was covered with a platinum disk, the projecting portion of the cup wall crimped to close the container, and the resulting pellet compressed in a 3-ton hydraulic press to 0.5 kbar. Several of these platinum-encased samples were then loaded into the sample cavity of a pyrophyllite tetrahedron. Details of the high-pressure sample assembly have been described previously.[9] The tetrahedron was then exposed to the desired pressure in the high-pressure apparatus, heated to induce reaction, cooled rapidly to room temperature, and finally returned slowly to atmospheric pressure.

The reaction products were recovered from the tetrahedron and investigated by chemical analysis, X-ray diffraction, infrared, differential thermal, and thermogravimetric methods. A 114.59-mm diameter X-ray camera was used with nickel-filtered copper radiation. Calculations were based on λ 1.5417 A for Cu Kα. Infrared spectra were obtained with a Beckman IR-12 spectrophotometer on thallium bromide disks containing 1% of the oxide sample, or on Nujol mulls. Simultaneous dta–tga analyses were carried out on a Mettler recording thermoanalyzer.

Initial high-pressure experiments on pure Tl_2O_3 in platinum foil envelopes gave evidence of a phase transition in the sesquioxide after 1 hr at 40 kbars pressure at 550°. This phase has tentatively been indexed as a hexagonal cell isostructural with a recently reported phase of In_2O_3.[11] Additional information on this compound will be given in a subsequent publication. Experiments at 40 kbars and 1000° indicated that a further reaction had occurred at the higher temperature. The platinum foil envelope became brittle and partially disintegrated, while the outer surface of the sesquioxide disk was transformed from black to brown. A qualitative analysis of the brown powder revealed that it contained both thallium and platinum.

In subsequent runs powdered platinum was mixed with thallium sesquioxide to promote formation of the double oxide. The product in these experiments consisted of a brown oxide pellet mixed with unreacted excess platinum metal. Solubility tests indicated that the new oxide was insoluble in concentrated mineral acids including aqua regia. This observation permitted purification of the double oxide and suggested the presence of trivalent thallium and tetravalent platinum. Analysis confirmed this suggestion and indicated a 1:1 molar ratio for thallium and platinum. The equation for synthesis of the new oxide then becomes

$$3Tl_2O_3 + 2Pt \longrightarrow Tl_2Pt_2O_7 + 2Tl_2O$$

The thallous oxide is dissolved during the purification procedure.

The synthesis was then further simplified by mixing platinum dioxide and thallium sesquioxide in the required proportions

$$Tl_2O_3 + 2PtO_2 \longrightarrow Tl_2Pt_2O_7$$

The aqua regia purification step was retained in order to remove any traces of platinum metal from the product.

Analysis.—The double oxide has been analyzed in several ways. A sample which had been heated slowly in air to 1000° left a metallic residue comprising 42.84% of the original weight. X-Ray diffraction and spectrographic analysis identified the product as platinum. Other samples were analyzed chemically for thallium and platinum after solution in an $HCl–HClO_4$ mixture at 275° in sealed heavy-wall glass tubes. The dissolved thallium(III) and platinum(IV) were converted to the bromides with HBr and bromine water. Thallium was then extracted with ether, reduced to Tl(I) with SO_2, and precipitated as TlI. Platinum was precipitated from the ether-extracted aqueous solution with magnesium powder and weighed as the metal. In two samples the thallium content averaged 45.0% and platinum 42.4%. Another portion of the oxide was analyzed for oxygen by the $KBrF_4$ method;[12] 12.2% oxygen was found. Theoretical values for $Tl_2Pt_2O_7$ are 44.86% thallium, 42.85% platinum, and 12.29% oxygen.

Synthesis of $Tl_2Pt_2O_7$ at Atmospheric Pressure.—Several ambient pressure methods for the synthesis of $Tl_2Pt_2O_7$ were investigated. In one experiment the direct combination of the individual oxides, PtO_2 and Tl_2O_3, was attempted. The compacted mixed oxides gave no evidence of reaction after several days at 400° but after 4 days at 520° X-ray and infrared analyses indicated that a partial reaction had occurred. Attempts to further the reaction at somewhat higher temperatures resulted in decomposition of the PtO_2.

Another preparative procedure involved the oxidation of the alloy, TlPt,[13] which had been prepared by heating an equimolar mixture of the elements for 18 hr at 750° in an evacuated and sealed silica tube. Formation of the alloy was confirmed by its X-ray diffraction pattern. Oxidation experiments on powdered TlPt were run at constant temperature. After 30 days at 350° the empirical composition reached $TlPtO_2$, but powder X-ray diffraction data on the product showed the presence of Tl_2O_3 and a small amount of a second phase which may have been a

---

[8] J. J. Scheer, A. E. VanArkel, and R. D. Heyding, *Can. J. Chem.*, **33**, 683 (1955).

[9] H. R. Hoekstra, *Inorg. Chem.*, **5**, 754 (1966).

[10] O. Rabe, *Z. Anorg. Allgem. Chem.*, **48**, 427 (1906).

[11] A. N. Christensen, N. C. Broch, O. von Heidenstam, and A. Nilsson, *Acta Chem. Scand.*, **21**, 1046 (1967).

[12] I. Sheft, A. F. Martin, and J. J. Katz, *J. Am. Chem. Soc.*, **78**, 1557 (1956).

[13] E. Zintl and A. Harder, *Z. Elektrochem.*, **41**, 767 (1935).

platinum oxide. No $Tl_2Pt_2O_7$ was detectable. When the temperature was increased to 500°, the formation of the double oxide was discernible by both X-ray and infrared methods, but a pure product could not be prepared.

Results and Discussion

Thermal Stability.—Both of the constituent oxides of $Tl_2Pt_2O_7$ have limited thermal stability. A tga curve of PtO_2 run at 6°/min indicated that trace amounts of oxygen are lost at temperatures as low as 350° but that the main decomposition reaction occurs in the temperature interval between 600 and 680°. A similar curve for type-C Tl_2O_3 showed the onset of thermal decomposition at 625°. However, no appreciable weight change was noted in a sample of $Tl_2Pt_2O_7$ until the furnace temperature reached 750°. Rapid decomposition began at 800° and was complete at 925° Thus the double oxide structure is appreciably more stable than either of its constituent oxides.

Structure.—We have been unable to prepare single crystals of $Tl_2Pt_2O_7$; hence the structural work has been confined to powder methods. Our observed X-ray pattern is indexible in terms of a small face-centered-cubic cell measuring 5.066 A. In order to account for this pattern, one could describe the structure as derived from the fluorite cell and the composition as $MO_{1.75}$ (where M includes both metals distributed statistically throughout the cation lattice sites and one-eighth of the anion sites are left vacant). However, in view of the oxidation states and the radii of the metals involved, this possibility seems highly unlikely. The high-pressure synthesis also argues against a structure containing vacant anion sites. In addition, regardless of the reactant Tl:Pt ratio, each preparation gave a 1:1 metal ratio in the final product and an identical unit cell dimension. All of these facts indicate that the constituent atoms must be located on ordered lattice sites.

The composition of this oxide, $Tl_2Pt_2O_7$, is proper for a cubic pyrochlore-type structure based on the space group $Fd3m\text{-}O_h^7$. Known pyrochlore structures show cell dimensions on the order of 10 A. The observed X-ray intensities are in agreement with this structure and the bond distances derived are consistent with known distances for the atoms involved. We accordingly feel justified in doubling the apparent cell to give a true cell of 10.132 ± 0.004 A and a calculated density of 11.63 g/cm^3 with $Z = 8$. The pycnometrically measured density is 11.12 g/cm^3.

Equivalent positions in the pyrochlore-type cell, as given in the "International Tables of Crystallography,"[14] are $(0, 0, 0;\ 0, {}^1/_2, {}^1/_2;\ {}^1/_2, 0, {}^1/_2;\ {}^1/_2, {}^1/_2, 0) +$ 16 Tl in (c) ${}^1/_8, {}^1/_8, {}^1/_8;\ {}^1/_8, {}^3/_8, {}^3/_8;\ {}^3/_8, {}^1/_8, {}^3/_8;\ {}^3/_8, {}^3/_8, {}^1/_8$; 16 Pt in (d) ${}^5/_8, {}^5/_8, {}^5/_8;\ {}^5/_8, {}^7/_8, {}^7/_8;\ {}^7/_8, {}^5/_8, {}^7/_8;\ {}^7/_8, {}^7/_8, {}^5/_8$; 8 O_I in (a) $0, 0, 0;\ {}^1/_4, {}^1/_4, {}^1/_4$; 48 O_{II} in (f) $x, 0, 0;\ \bar{x}, 0, 0;\ {}^1/_4 + x, {}^1/_4, {}^1/_4;\ {}^1/_4 - x, {}^1/_4, {}^1/_4;\ 0, x, 0;\ 0, \bar{x}, 0;\ {}^1/_4, {}^1/_4 + x, {}^1/_4;\ {}^1/_4, {}^1/_4 - x, {}^1/_4;\ 0, 0, x;\ 0, 0, \bar{x};\ {}^1/_4, {}^1/_4, {}^1/_4 + x;\ {}^1/_4, {}^1/_4, {}^1/_4 - x$.

Films of varying exposure times were produced in order to allow measurements of line intensities within reasonable density ranges. Intensities were obtained from densitometer tracings of the films and the data were then reduced in the usual manner. However, it was necessary to include an absorption correction because of the very large μ value of 2245 cm^{-1} for this compound. For the particular capillary used, and with an estimate of the packing in the capillary based on a measurement of the grain sizes, a value of $\mu r = 13.5$ was obtained. This value served as the basis for the absorption correction. The oxygen contribution to the scattering is dominated by the heavy cation scattering, and this, with the high absorption, places a severe limitation on the accuracy of the coordinate determination for the oxygen atoms.

An approximate value of x was found by trial to satisfy intensity requirements. A least-squares refinement, based on "A Fortran Crystallographic Least Squares Program," by Busing, Martin, and Levy, led to a final value of $x = 0.270 \pm 0.006$ for the 48-fold O_{II} position. The structure factors were computed with atomic scattering factors for the metals given in Vol. III of the "International Tables for Crystallography" and the O^{2-} scattering curve reported by Tokonami.[15] The calculated structure factors were also corrected for anomalous dispersion using values given by Cromer.[16]

The R factor, omitting zeros, is 3.6% based on $R = \Sigma\{|F_o| - |F_c|\}/\Sigma|F_o|$. The low R factor does not measure the accuracy of the x-coordinate determination because of the dominance of the cation scattering. This is indicated by the high error in x.

The observed and computed intensities are presented in Table I. A reflection *hkl* indicated by an asterisk calculates zero intensity because of the point positions for this structure. A dashed line in the $\sin^2 \theta_0$ column indicates that the line was not observed on the film. Numerical values of I_o given in the table for these unobserved reflections are limiting intensities on the densitometer tracings corresponding roughly to the noise level of the tracing background. Clearly, one may observe lines visually on the film of intensities substantially lower than those detectable by the densitometer. We have indicated that for our case no additional lines were observed visually on the film after prolonged exposures. The final calculated intensities have been corrected for the effects of thermal motion using a value of 1.80 A^2 for B. Absolute values for I_o are obtained by multiplying the calculated quantities by 10^7.

In the proposed structure, each platinum atom is bonded to six oxygen atoms, with $Pt\text{-}6(O_{II}) = 2.08 \pm 0.04$ A. This value is in good agreement with the Pauling[17] and Ahrens[18] radii sum of 2.05 A (0.65 + 1.40 A for ionic bonding or 1.31 + 0.74 A for covalent bonding). Each thallium atom is bonded to eight

---

(14) "International Tables for X-Ray Crystallography," Vol. 1, The Kynoch Press, Birmingham, England, 1952.

(15) M. Tokonami, *Acta Cryst.*, **19**, 486 (1965).

(16) D. Cromer, *ibid.*, **18**, 17 (1965).

(17) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.

(18) L. H. Ahrens, *Geochim. Cosmochim. Acta*, **2**, 155 (1954).

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR $Tl_2Pt_2O_7$

hkl	$\sin^2\theta_o$	$\sin^2\theta_c$	I_o	I_c
111	--	0.01761	< 5.0	0.24
200*	--	.02375	< 4.0	0
220	--	.04691	< 2.0	0.11
311	--	.06446	< 2.0	< 0.01
222	0.07034	.07031	87.6	84.4
400	.09365	.09365	28.4	29.8
331	--	.1112	< 1.0	.50
420*	--	.1170	< 1.0	0
422	--	.1403	< 1.0	.05
511	--	.1577	< 2.0	.12
333	--	.1577		
440	.1862	.1867	31.9	32.6
531	--	.2041	< 0.7	.07
600*	--	.2099	< 1.1	0
442*	--	.2099		
620	--	.2330	< 0.6	< .01
533	--	.2504	< 0.6	< .01
622	.2563	.2562	21.8	28.2
444	.2796	.2793	7.1	6.5
711	--	.2964	< 1.0	.05
551	--	.2964		
640*	--	.3024	< 0.5	0
642	--	.3255	< 0.4	< .01
731	--	.3428	< 0.9	.02
553	--	.3428		
800	.3718	.3717	3.8	3.8
733	--	.3880	< 0.4	0.6
820*	--	.3947	< 0.7	0
644*	--	.3947		
822	--	.4179	< 0.7	< .01
660	--	.4179		
751	--	.4351	< 0.7	.01
555	--	.4351		
662	.4410	.4409	8.9	9.1
840	.4640	.4640	7.3	7.1
911	--	.4813	< 0.6	.04
753	--	.4813		
842*	--	.4870	< 0.3	0
664	--	.5101	< 0.3	< .01
931	--	.5274	< 0.3	.01
844	.5564	.5562	6.2	6.5
$933\alpha_1$	--	.5736	< 0.8	.03
$771\alpha_1$	--	.5736		
$755\alpha_1$	--	.5736		
10,0,0*	--	.5793	< 0.5	0
860*	--	.5793		
10,2,0	--	.6024	< 0.5	< .01
862	--	.6024		
$951\alpha_1$	--	.6192	< 0.5	.02
$773\alpha_1$	--	.6192		
$10,2,2\alpha_1$	.6254	.6255	6.9	6.9
$10,2,2\alpha_2$	.6287	.6287		
$666\alpha_1$	.6254	.6255		
$666\alpha_2$	.6287	.6287		
$953\alpha_1$	--	.6657	< 0.2	< .01
$10,4,0\overset{*}{\alpha}_1$	--	.6715	< 0.4	0
$864\overset{*}{\alpha}_1$	--	.6715		
$10,4,2\alpha_1$	--	.6946	< 0.2	< .01
$11,1,1\alpha_1$	--	.7119	< 0.2	< .01
$775\alpha_1$	--	.7119		
$880\alpha_1$	.7406	.7406	3.5	2.6
$880\alpha_2$	.7442	.7444		
$11,3,1\alpha_1$	--	.7579	< 0.5	.04
$971\alpha_1$	--	.7579		
$955\alpha_1$	--	.7579		
$10,4,4\overset{*}{\alpha}_1$	--	.7637	< 0.4	0
$882\alpha_1$	--	.7637		
$10,6,0\alpha_1$	--	.7868	< 0.3	< .01
$866\alpha_1$	--	.7868		
$11,3,3\alpha_1$	--	.8040	< 0.3	< .01
$973\alpha_1$	--	.8040		
$10,6,2\alpha_1$	.8099	.8098	12.4	9.4
$10,6,2\alpha_2$	.8145	.8139		
$12,0,0\alpha_1$	.8333	.8328	7.9	5.4
$12,0,0\alpha_2$	.8373	.8371		
$884\alpha_1$	.8333	.8328		
$884\alpha_2$	.8373	.8371		
$11,5,1\alpha_1$	--	.8500	< 0.3	.02
$777\alpha_1$	--	.8500		
$12,2,0\overset{*}{\alpha}_1$	--	.8558	< 0.2	0
$12,2,2\alpha_1$	--	.8789	< 0.3	.01
$10,6,4\alpha_1$	--	.8789		
$11,5,3\alpha_1$	--	.8961	< 0.3	.01
$975\alpha_1$	--	.8961		
$12,4,0\alpha_1$	.9251	.9250	7.1	7.2
$12,4,0\alpha_2$	.9296	.9296		
$991\alpha_1$	--	.9422	< 0.2	< .01
$12,4,2\overset{*}{\alpha}_1$	--	.9480	< 0.4	0
$10,8,0\overset{*}{\alpha}_1$	--	.9480		
$886\overset{*}{\alpha}_1$	--	.9480		
$10,8,2\alpha_1$	--	.9706	< 0.1	< .01
$13,1,1\alpha_1$	--	.9882	< 0.6	.06
$11,7,1\alpha_1$	--	.9882		
$11,5,5\alpha_1$	--	.9882		
$993\alpha_1$	--	.9882		
$10,6,6\alpha_1$	.9938	.9940	6.4	13.5

oxygens with Tl–2(O_I) = 2.19 ± 0.002 A and Tl–6-(O_{II}) = 2.32 ± 0.04 A. The weighted average bond length is 2.29 A for the eight bonds, as compared with the Pauling radii sum (0.95 + 1.40 A) of 2.35 A. Three oxygen–oxygen distances are found: O_I–O_{II} = 2.74 ± 0.06 A, O_{II}–O_{II} = 2.55 ± 0.01 A, and O_{II}–O_{II} = 3.30 ± 0.09 A.

Figure 1 illustrates a comparison of the $Tl_2Pt_2O_7$ cell dimension with other known pyrochlore-type compounds, including the rare earth titanates,[19–21] ruthenates,[22] stannates,[23] and zirconates,[19] together with $Cd_2Ta_2O_7$ and $Cd_2Nb_2O_7$.[24,25] The $Tl_2Pt_2O_7$ parameter is seen to fall very close to the line connecting the ruthenate(IV) pyrochlores. The agreement in cell dimension is excellent, since Ru(IV) has been assigned a radius of 0.63 A by Pauling[17] and 0.67 A by Ahrens.[18]

Pyrochlore Structure.—Figure 2 illustrates a portion of a pyrochlore-type unit cell—one of the eight units which constitute the true cell of this space group.

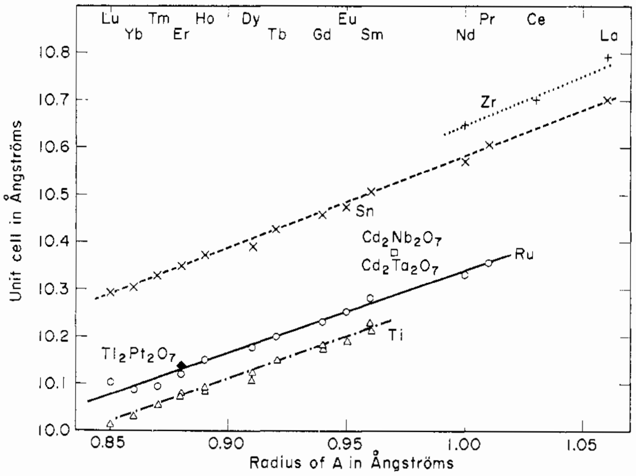

Figure 1.—Cell dimensions of $A_2B_2O_7$ compounds.

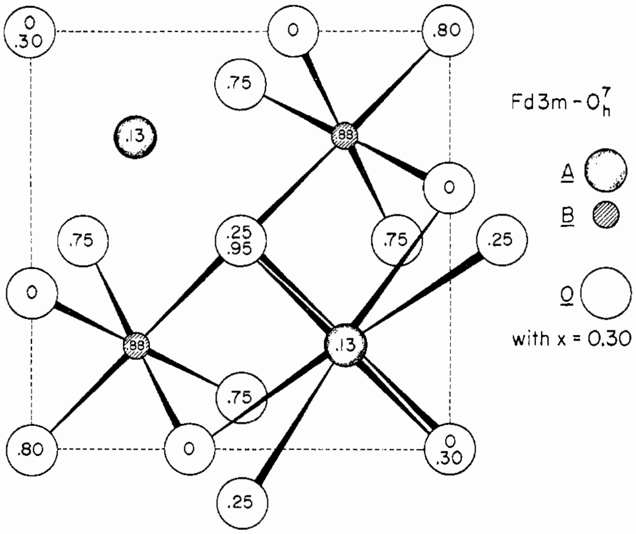

Figure 2.—Atomic positions in $A_2B_2O_7$.

The distorted octahedral arrangement of oxygen atoms about each B atom and the eightfold configuration about each A atom to form a distorted cube can be seen. Since each oxygen atom in the three-dimensional array of BO_6 octahedra is shared between two B metal atoms, the over-all composition becomes $(B_2O_6)_n$ for the octahedral lattice. The space group requires that all B–O distances are equivalent, but not that the octahedra are symmetrical. It also requires that six of the eight A–O bonds be equivalent; the other two can be, but usually are not, equal in length to the six.

Since the A, B, and O_I atom sites are invariant in the unit cell and the O_{II} sites contain only a single variable, one can plot metal–oxygen and oxygen–oxygen distances (in terms of fraction of the unit cell parameter) as a function of x. As shown by Figure 3, the A–2(O_I) distances are independent of x, but the A–6(O_{II}) distances do vary with x; the eight bonds become equal at x = 0.25. The A–8(O) line represents the weighted average bond length between these atoms. Distances between atoms in the octahedra are given by the B–6(O_{II}) line and the two O_{II}–O_{II} lines. The oxygen–oxygen distances are equivalent and the octahedra are

---

[19] R. S. Roth, *J. Res. Natl. Bur. Std.*, **56**, 17 (1956).

[20] L. H. Brixner, *Inorg. Chem.*, **3**, 1065 (1964).

[21] O. Knop, F. Brisse, L. Castelliz, and Sutarno, *Can. J. Chem.*, **43**, 2812 (1965).

[22] F. Bertaut, F. Forrat, and M. Montmory, *Compt. Rend.*, **249**, 829 (1959).

[23] C. G. Whinfrey, D. W. Eckart, and A. Tauber, *J. Am. Chem. Soc.*, **82**, 2695 (1960); **83**, 755 (1961).

[24] A. Byström, *Arkiv Kemi, Mineral. Geol.*, **18A**, No. 21 (1944).

[25] F. Jona, G. Shirane, and R. Pepinsky, *Phys. Rev.*, **98**, 903 (1955).

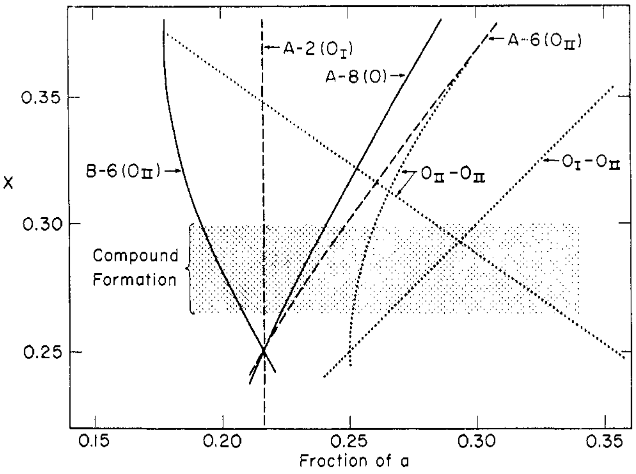

Figure 3.—Atomic distances in pyrochlore-type structures $Fd3m\text{-}O_h^7$.

regular at $x = 0.3125$. The O_I–O_{II} line represents the distance between an O_I atom and the nearest O_{II} atom in an adjacent octahedron.

The shaded area indicates the observed range of x in those pyrochlores whose oxygen positions have been located. The region of compound formation appears to lie approximately midway between $x = 0.3125$, where regular octahedra obtain, and $x = 0.2500$, where perfect cubes are formed.

The minimum cell size which has been reported among the pyrochlore-forming compounds, 9.801 A in $Sc_2Ti_2O_7$,[20] must represent a virtual lower limit for the structure because of the volume requirements imposed by the 56 oxygen atoms in each unit cell.

Infrared Data.—The infrared spectrum of $Tl_2Pt_2O_7$ is somewhat unusual when compared with other pyrochlore spectra. Figure 4 illustrates the spectra of two typical examples, $Yb_2Ru_2O_7$ and $Y_2Sn_2O_7$, which were prepared for comparison purposes. A representative titanate pyrochlore spectrum has been given by Knop, *et al.*[21] Figure 5 shows the absorption spectrum of $Tl_2Pt_2O_7$, characterized by four sharp absorption bands at 684, 562, 449, and 363 cm^{-1}. It is apparent that the general features of the spectra are similar, but that the absorption maxima in the platinum compound are much sharper. This effect may be due to increased covalent character of the bonding in $Tl_2Pt_2O_7$. Although the ruthenium electronegativity[17] is comparable with platinum (2.2), thallium (1.8) is appreciably more electronegative than the rare earths (1.1–1.2).

The strong broad absorption bands of the erbium titanate spectrum have tentatively been assigned[21] to Ti–O modes; the higher frequency maximum has been assigned to a Ti–O stretching vibration and the lower one, to a bending mode. It has also been suggested that the minor features (shoulders and subsidiary maxima) are associated with the oxygen environment of the erbium atoms. A similar interpretation for the $Tl_2Pt_2O_7$ spectrum would assign the 684-cm^{-1} band to a Pt–O stretching mode, the 449-cm^{-1} band to an O–Pt–O bending mode, and the two weaker bands at 562 and 363 cm^{-1} to Tl–O_I stretching and bending modes. Further work is required to establish the validity of these tentative assignments.

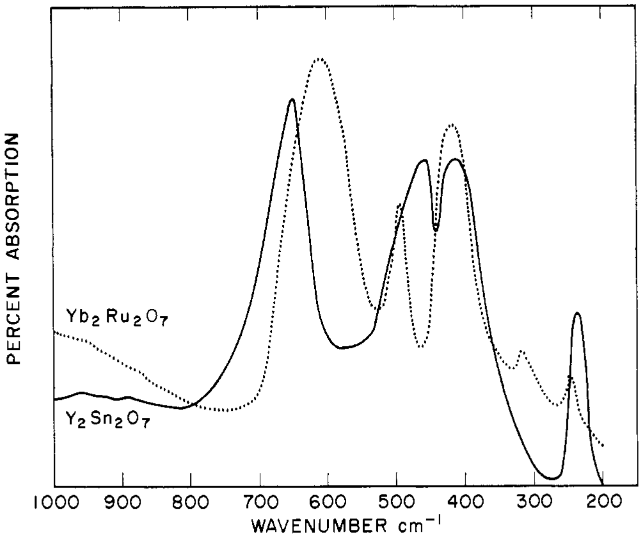

Figure 4.—Infrared spectra of pyrochlores.

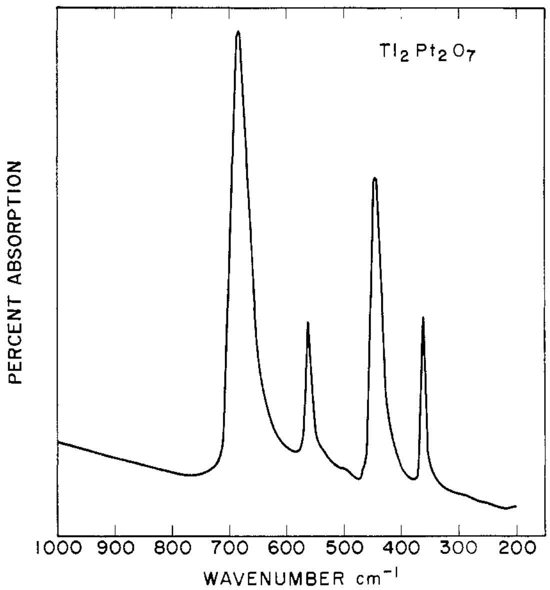

Figure 5.—Infrared spectrum of thallium platinate.

Acknowledgment.—We are indebted to the assistance provided by Frank Gallagher in carrying out the high-pressure experiments.