bital containing the unpaired electron (b_{1g}). However, on lowering the symmetry about the metal ion, as when going from the nickel to the zinc host lattice, increased mixing of the s and d orbitals may occur. This increased mixing would lead to a more positive value for A_{iso}, consistent with the present results. It may be noted that displacement toward a distorted tetrahedral configuration leads to a mixing in of the 4p orbitals.[32] It is suggested[32] that this could lead to a shift in the isotropic interaction but would also give appreciable reduction in the anisotropic interaction, in contrast to the present results. Thus, mixing of the 4p orbitals is not anticipated to be a significant factor.

An entirely parallel reduction in A_{iso} is seen on base adduct formation. Thus, for $Cu(dtc)_2$ in a frozen glass of 40:60 $CHCl_3$–toluene, $A_{iso} = 78 \times 10^{-4}$ cm^{-1},[14] while in 40:60 $CHCl_3$–pyridine glass, $A_{iso} = 60 \times 10^{-4}$ cm^{-1}.[14]

Acknowledgment.—The support of the National Science Foundation, under Grant GP-7889, is acknowledged. Thanks also are extended to the Ferro Corp. which has made possible certain aspects of this study through a grant to the CWRU Center for the Study of Materials.

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Synthesis of Some Pyrochlore-Type Oxides of Platinum(IV) at High Pressure[1]

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The synthesis of 15 cubic pyrochlore-type double oxides, $A_2Pt_2O_7$, is described. The trivalent A atoms may be scandium, indium, yttrium, or any rare earth from praseodymium through lutetium. Cell parameters are reported and compared with other pyrochlore series. Thermal analysis shows that most platinum pyrochlores are stable to at least 1000°. Infrared spectra to 95 cm^{-1} are presented and interpreted.

We reported recently on the high-pressure synthesis of a new oxide of platinum, $Tl_2Pt_2O_7$.[2] Although pressure is frequently used to force an ion into an unusually high coordination configuration, it was employed in this instance to prevent decomposition of two reactants at the temperature required to achieve complete reaction and good product crystallinity. The crystal structure of $Tl_2Pt_2O_7$ could not be unambiguously determined from X-ray powder data, but the composition, the radii of its cations, and the properties of the double oxide all strongly suggest that the structure is that of pyrochlore, space group Fd3m.

In the general pyrochlore formula, $A_2B_2O_7$, the A atoms may be divalent with pentavalent B or trivalent with tetravalent B. The approximate radius range reported for A ions is 0.75–1.05 Å (based on Templeton and Dauben radii[3]) and for B ions is 0.6–0.8 Å. Details of the structure have been given by several workers.[4,5] Very briefly, the A and B atoms together with one of the oxygen atoms (O_I) occupy special positions in the unit cell. The remaining six oxygen (O_{II}) atom sites contain a single variable parameter, $x(O_{II})$. Each B atom is bonded to six O_{II} atoms in a trigonal antiprism, and each A atom forms two short collinear bonds to O_I atoms and six longer bonds to O_{II} atoms lying near a plane normal to the A–O_I axis.

Pyrochlore series in which trivalent rare earths constitute the A atoms and in which titanium, ruthenium, iridium, and tin constitute the B atoms have been reported.[6-12] In addition, partial series have been prepared with tetravalent technetium,[13] zirconium,[14] and hafnium.[15] Since high pressure proved to be an effective technique in the synthesis of the thallium–platinum pyrochlore, the same procedure has now been used to study the reaction of platinum dioxide with a series of metal sesquioxides.

Experimental Section

Platinum dioxide was prepared by the reaction of K_2PtCl_6 with molten KNO_3 at 400°. Reaction appeared to be complete within minutes, but heating was continued for at least 24 hr to

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission. Paper presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

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give a more crystalline product. The melt was then cooled and the KNO_3 dissolved in water. The PtO_2 was dried and then treated for several hours with warm aqua regia to remove any soluble impurities. The platinum dioxide was again washed with water and dried at 100°. A typical analysis gave 86.1% platinum (85.92% theoretical) and less than 0.1% potassium.

The sesquioxides used in the high-pressure experiments were of 99.9+% purity. Terbium and praseodymium sesquioxides were prepared by the reduction of Tb_4O_7 and Pr_6O_{11} with hydrogen at 900°. The remaining rare earth oxides, including the scandium, indium, and yttrium oxides, were heated 24 hr at 1000° to remove volatile impurities.

The high-pressure sample assembly, the tetrahedral anvil apparatus, and the experimental procedures used in the present work have been described previously.[16] In a typical experiment, three samples of the mixed oxides, each weighing approximately 0.5 g, were heated to 1200° for 30 min while being exposed to a 40-kbar pressure. No attempt has been made to determine the range of pressure and temperature under which pyrochlore synthesis could be accomplished. However, formation of the double oxide has been established over the pressure interval from 20 to 60 kbars and from 800 to 1600°. Trace amounts of platinum metal which were detected in most high-pressure reaction products were removed by solution in warm aqua regia. The double oxides are not appreciably soluble under these conditions. In addition to the 1:1 ratio of tri- and tetravalent metals required by the pyrochlore formula, a number of mixtures containing 2:1 and 1:2 ratios of the metal ions were investigated.

Products obtained in all high-pressure experiments were investigated by X-ray diffraction methods, by thermal analysis, and by infrared spectroscopy. X-Ray data were obtained with a Philips 114.59-mm powder camera using nickel-filtered copper radiation. Cell parameter calculations are based on Cu K$\bar{\alpha}$ 1.5418 A. The dta–tga results were obtained on a Mettler recording thermoanalyzer over the temperature interval 25–1400° with a heating rate of 6°/min and a sensitivity of 100 μV. Sample sizes varied from 40 to 120 mg. Infrared spectra were obtained on Beckman IR-12 and IR-11 spectrophotometers; the IR-12 was used from 1000 to 200 cm^{-1} (no maxima are observed in these samples at higher frequencies), and the IR-11, from 500 to 33 cm^{-1}. Nujol mulls were studied over the entire spectral range. The mulls were spread on polyethylene disks for the low-frequency portion of the spectrum and on KBr plates for the higher frequency region. Spectra given by KBr and TlBr disks (200 mg containing ~0.5% of the sample) were investigated to the lower limit of their usable frequency range.

Results and Discussion

Structure.—X-Ray diffraction data on the various products indicate that nearly all of the sesquioxides studied react with PtO_2 to form a face-centered-cubic phase of the $A_2Pt_2O_7$ composition. The double oxides $La_2Pt_2O_7$ and $Bi_2Pt_2O_7$ do not crystallize in the cubic system. The praseodymium–platinum double oxide is cubic when prepared at 1000° and 40 kbar but is obtained as a lower symmetry phase resembling $La_2Pt_2O_7$ when synthesized at 1200°. Evidently, Pr(III) is the largest ion which can be accommodated with Pt(IV) in the cubic structure under these experimental conditions. The 2:1 (A_2PtO_5) and 1:2 ($A_2Pt_4O_{11}$) mixtures do not give any additional phases; unreacted excess A_2O_3 or PtO_2 is observed with the cubic $A_2Pt_2O_7$ phase in each of the products.

If only the stronger X-ray diffraction lines are considered, the cubic phase is indexible in terms of a small face-centered-cubic cell measuring approximately 5 Å, as was reported previously for $Tl_2Pt_2O_7$. With the present series of compounds, however, weak additional lines indicative of the larger unit cell are visible in the diffraction patterns. The crystal data on two of these, $Sc_2Pt_2O_7$ and $Y_2Pt_2O_7$, are presented in Table I. Since these compounds show the maximum mass differential between the A(III) and Pt atoms, they are the most favorable compounds from which to establish the larger cell and the pyrochlore structure.

TABLE I

CRYSTAL DATA FOR $Sc_2Pt_2O_7$ AND $Y_2Pt_2O_7$

$Sc_2Pt_2O_7$, a = 9.8505 ± 10				Y_2PtO_7, a = 10.164 ± 10		
I	*d*(obsd)	*d*(calcd)	*hkl*	*I*	*d*(obsd)	*d*(calcd)
3	5.642	5.650	111	3	5.751	5.810
4	2.960	2.956	311	4	3.043	3.043
9	2.825	2.831	222	9	2.913	2.914
4	2.451	2.453	400	6	2.526	2.526
3	2.256	2.252	331	1	2.319	2.319
3	1.893	1.891	511, 333	4	1.948	1.947
7	1.737	1.738	440	8	1.790	1.790
3	1.663	1.662	531	3	1.712	1.712
2	1.499	1.500	533	...	...	...
7	1.482	1.483	442	8	1.528	1.528
4	1.421	1.421	444	5	1.464	1.463
2	1.379	1.378	711, 551	...	...	...
3	1.281	1.281	731, 553	4	1.322	1.321
3	1.230	1.230	800	5	1.268	1.268
1	1.203	1.203	733	...	...	...
2	1.136	1.137	751, 555	1	1.172	1.172
5	1.129	1.129	662	6	1.165	1.165
4	1.101	1.101	840	6	1.135	1.135
2	1.081	1.081	911, 753	2	1.115	1.115
1	1.032	1.032	931	1	1.064	1.065
5	1.005	1.005	844	6	1.036	1.037
2	0.9898	0.9898	931, 771, 755	1	1.021	1.021
2	0.9520	0.9520	951, 773	...	...	...
5	0.9478	0.9478	10, 2, 2, 666	6	0.9775	0.9775
1	0.9183	0.9181	953	1	0.9470	0.9473
2	0.8881	0.8882	11, 1, 1, 775	1	0.9169	0.9161
4	0.8706	0.8709	880	4	0.8982	0.8981
3	0.8606	0.8607	11, 3, 1, 971, 955	3	0.8871	0.8876
3	0.8354	0.8353	11, 3, 3, 973	2	0.8624	0.8619
7	0.8325	0.8325	10, 6, 2	8	0.8587	0.8588
5	0.8209	0.8208	12, 0, 0, 884	7	0.8466	0.8468
2	0.8125	0.8126	11, 5, 1, 777	2	0.8379	0.8380
3	0.7913	0.7912	11, 5, 3, 975	3	0.8163	0.8163
7	0.7788	0.7788	12, 4, 0	7	0.8034	0.8035
			13, 1, 1, 11, 7, 1, 11, 5, 5, 993	4	0.7772	0.7772
			10, 6, 6	7	0.7751	0.7749

The unit cell dimension calculated for each of the 16 members of the series is given in Table II. The series is arranged in order of decreasing cell parameter and A(III) atom radius (as given by Templeton and Dauben[3] or as calculated from the sesquioxide cell parameter). It is interesting to note that, with a single exception ($Tl_2Pt_2O_7$) pyrochlores with unit cell smaller than that of $Gd_2Pt_2O_7$ are green, while the remaining pyrochlores are tan to brown. Figure 1 illustrates the straight-line relationship observed between the cell parameter and the A atom radius. A comparison is also provided with titanium, ruthenium, and tin pyrochlores. The slope of the line connecting members of the platinum series appears to be slightly greater than the others.

X-Ray and neutron diffraction studies have recently been reported on $Er_2Ti_2O_7$[8] and several rare earth–tin pyrochlores including $Y_2Sn_2O_7$ and $Sm_2Sn_2O_7$.[12] On the assumption that the weighted average bond length for each trivalent A atom does not change appreciably from one series to another, it becomes possible to

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

TABLE II

UNIT CELL AND THERMAL ANALYSIS OF PYROCHLORES

	A atom radius, Å	a, Å	Endotherm max, °C	Dta peak, °C
$Pr_2Pt_2O_7$	1.013	10.419	1075	1030–1110
$Nd_2Pt_2O_7$	0.995	10.378	1135	1020–1200
$Sm_2Pt_2O_7$	0.964	10.313	1165	1070–1190
$Eu_2Pt_2O_7$	0.950	10.286	1190	1050–1215
$Gd_2Pt_2O_7$	0.938	10.261	1210	1100–1260
$Tb_2Pt_2O_7$	0.923	10.222	1235	1100–1300
$Dy_2Pt_2O_7$	0.908	10.202	1220	1100–1300
$Ho_2Pt_2O_7$	0.894	10.170	1130	1030–1225
$Y_2Pt_2O_7$	0.894	10.164	1180	1050–1275
$Er_2Pt_2O_7$	0.881	10.144	1270	1210–1330
$Tl_2Pt_2O_7$	0.881	10.132	860	800–920
$Tm_2Pt_2O_7$	0.869	10.118	1160	1030–1225
$Yb_2Pt_2O_7$	0.858	10.095	1200	1000–1260
$Lu_2Pt_2O_7$	0.848	10.076	1285	1220–1370
$In_2Pt_2O_7$	0.789[a]	9.962	1025	900–1160
$Sc_2Pt_2O_7$	0.731[a]	9.851	1155	1050–1220

[a] Calculated from sesquioxide parameter as suggested by Templeton and Dauben.[3]

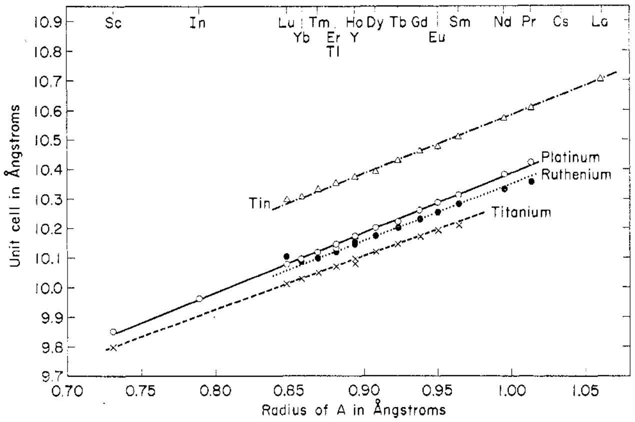

Figure 1.—Cell dimensions of $A_2B_2O_7$ compounds.

calculate $x(O_{II})$ and the platinum–oxygen bond length in the corresponding platinum pyrochlores.[2] Table III illustrates the excellent agreement obtained for the Pt–O bond lengths in these three compounds. Using the Templeton and Dauben radius for oxygen, we arrive at a Pt(IV) radius of 0.60 Å. Shannon[17] has reported an effective radius of 0.63 Å for Pt(IV) in orthorhombic PtO_2. It should be noted that the average Pt–O bond reported in the present study is approximately 0.1 Å shorter than that given for platinum(IV) in $Tl_2Pt_2O_7$. We are now engaged in a detailed study of the $Y_2Pt_2O_7$ and $ScPt_2O_7$ structures and will be able to report on the experimentally determined values for $x(O_{II})$ and the Pt–O bond length in the near future.

Thermal Stability.—As is shown by Table III, the rare earth–platinum pyrochlores are surprisingly stable toward thermal decomposition. Although PtO_2 decomposes between 600 and 700°,[2] the pyrochlores with two exceptions, $In_2Pt_2O_7$ and $Tl_2Pt_2O_7$, are stable to at least 1000°. The thermal stability of the platinates is affected to some extent by their sample crystallinity. Thus, compounds prepared at 1200° are somewhat more resistant to initial oxygen loss than the lower temperature products. A typical dta–tga run is illustrated in Figure 2. The observed weight loss is 8.45 mg compared with a 8.53-mg loss calculated for the decomposition of the double oxide to Er_2O_3 and Pt.

TABLE III

CALCULATED Pt–O BOND LENGTHS

Compound	a, Å	A-8(O), Å	$x(O_{II})$	B-6(O_{II}), Å	Ref
		(a) Experimental			
$Er_2Ti_2O_7$	10.076	2.399	0.295	1.955	8
$Y_2Sn_2O_7$	10.373	2.425	0.287	2.048	12
$Sm_2Sn_2O_7$	10.510	2.484	0.292	2.054	12
		(b) Calculated			
$Er_2Pt_2O_7$	10.144	2.399	0.291	1.98	
$Y_2Pt_2O_7$	10.164	2.425	0.296	1.97	
$Sn_2Pt_2O_7$	10.313	2.484	0.300	1.98	

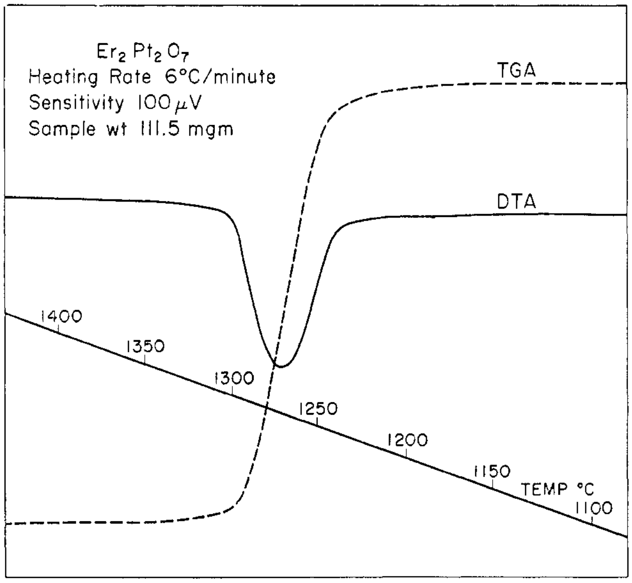

Figure 2.—Dta–tga data on $Er_2Pt_2O_7$.

Infrared Data.—The infrared spectrum of $Tl_2Pt_2O_7$ has been shown to contain four sharp absorption peaks in the wavelength region between 1000 and 250 cm^{-1}.[2] We found that the $Tl_2Pt_2O_7$ spectrum is typical of the entire platinum pyrochlore series and that sharp maxima are obtained at lower frequencies as well. Seven of the compounds were investigated to 95 cm^{-1}, and one, $Y_2Pt_2O_7$, to 33 cm^{-1}. Table IV summarizes the data obtained from the 16 compounds. No peaks were observed in the $Y_2Pt_2O_7$ spectrum between 95 and 33 cm^{-1}. For convenience in the following discussion the maxima have been numbered in order of decreasing vibrational frequency.

Figure 3 illustrates the spectrum to 250 cm^{-1} of two members of the series. Praseodymium is the largest trivalent ion to form a platinum pyrochlore, while indium is virtually the smallest ion to participate in the pyrochlore formation. The low-frequency portions of the $Tl_2Pt_2O_7$, $Pr_2Pt_2O_7$, and $Sc_2Pt_2O_7$ spectra are presented in Figure 4.

An interesting property is noted with regard to ν_1 and ν_3 in most spectra. These peaks appear as closely spaced doublets (at the frequencies listed in Table IV) when spectra are obtained from mulls but show only a single peak at approximately the higher of the doublet

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[17] R. D. Shannon, *Solid State Commun.*, **6**, 139 (1968).

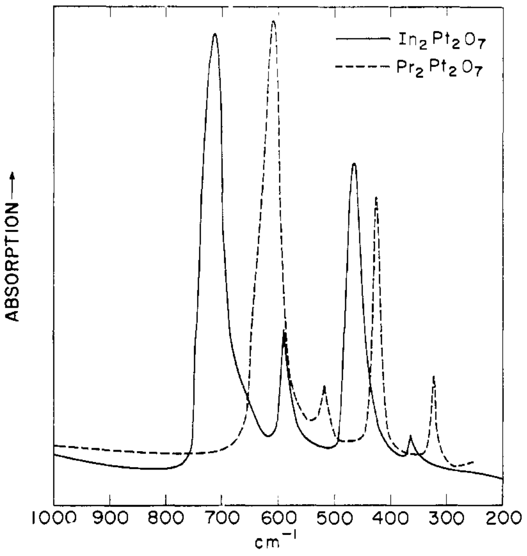

Figure 3.—Infrared spectra of $In_2Pt_2O_7$ and $Pr_2Pt_2O_7$.

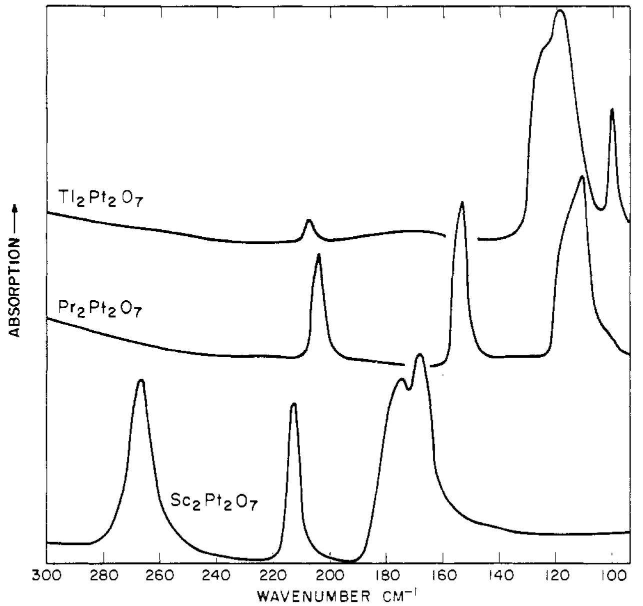

Figure 4.—Low-frequency spectra of $Tl_2Pt_2O_7$, $Pr_2Pt_2O_7$, and $Sc_2Pt_2O_7$.

Table IV

Infrared Absorption Maxima of Platinum Pyrochlores (cm^{-1})

Pyrochlore	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7
Scandium	718–702	580	426–407		268	212	174–168
Indium	713	587	463	362	219	161	137–131
Lutetium	686–667	564	444–434	349	210		
Ytterbium	682–664	563	445–435	348	210	143	123–117
Thulium	673–659	561	443–433	348	210		
Thalium	684	562	449	363	207	100	124–118
Erbium	670–650	557	442–432	347	210		
Yttrium	671–649	555	458–447	347	232	186	146–139
Holmium	669–648	553	440–431	346	209		
Dysprosium	665–645	550	442–435	341	208		
Terbium	657–630	545	440–432	340	207		
Gadolinium	652–627	542	441–429	339	207		
Europium	641–621	538	437–428	337	206		
Samarium	635–616	533	432–424	332	205	154	119–113
Neodymium	620–603	525	428–422	329	205		
Praseodymium	612–593	520	430–420	325	205	154	117–114

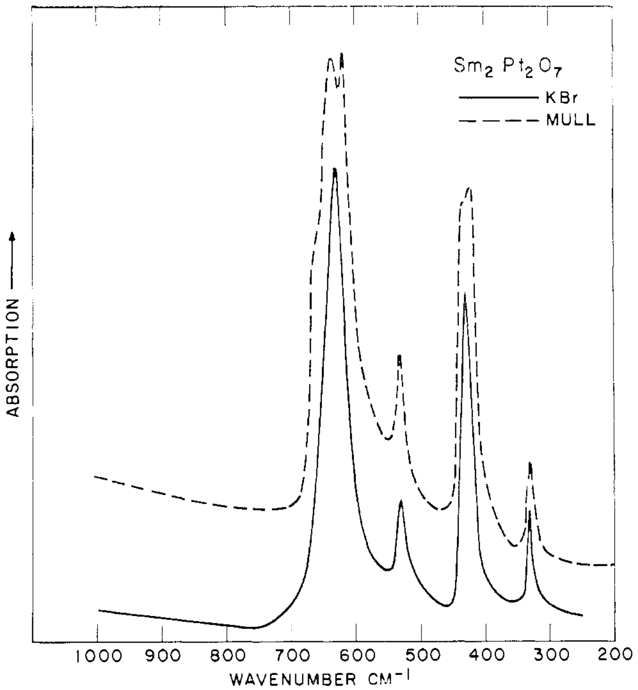

Figure 5.—Mull and KBr spectra of $Sm_2Pt_2O_7$.

frequencies in a KBr disk. The group IIIa pyrochlores show much less tendency to split ν_1 and ν_3; they appear as single maxima in both mull and disk. Figure 5 illustrates the splitting effect as it is observed in $Sm_2Pt_2O_7$. In some spectra two closely spaced maxima are observed; in other instances one obtains a single peak with a shoulder. It is apparent that ν_2 and ν_4 are not comparably affected by the preparative technique used. Reference to Figure 4 and to Table IV shows that ν_7 also occurs as a double peak. Since this frequency is outside the range accessible to the KBr disk, we could not investigate the effect of this technique on the low-frequency portion of the spectrum. We have assumed that the split maxima of ν_1, ν_3, and ν_7 are indicative of doubly degenerate vibrations and that the two maxima become separated by some process involved in the spectral sample preparation.

The spectral data on the seven compounds studied to 95 cm^{-1} are given in Figure 6; the relative shift in position and intensity of the seven maxima can be traced. No attempt has been made to assign quantitative intensity values to the maxima, since reproducibility in mull and disk samples is insufficient for this purpose. It is possible, however, to follow intensity changes through the series and compare peak intensi-

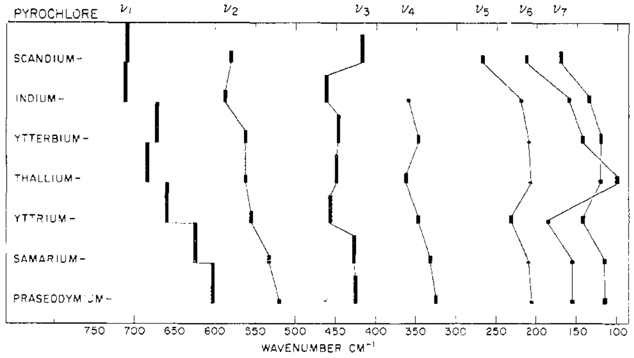

Figure 6.—Infrared data on some platinum pyrochlores.

ties within individual spectra. We find that ν_1 absorbs most strongly, with ν_3 at approximately 70% of the ν_1 intensity over the entire pyrochlore series. None of the remaining five peaks exceeds 30% of the ν_1 intensity. A comparison between ν_2 and ν_4 intensities indicates that ν_4 is the stronger when the A atom radius is large (see Figure 3) but becomes progressively weaker as A becomes smaller until it is no longer detectable in $Sc_2Pt_2O_7$. A similar observation was reported by Brisse and Knop[12] in the stannate pyrochlores.

In summary, it is apparent that three factors influence the location of absorption maxima in the platinate spectra: (1) the radius of the trivalent A atom, (2) the mass of the trivalent atom, and (3) the occurrence of the A element in group IIIa or IIIb. A plot of peak frequency *vs.* A atom radius gives straight-line relationships for the 12 A atoms between praseodymium and lutetium. Deviations from "expected" frequencies occur among the remaining four members of the series. The A atom radius exerts its strongest influence on peak location among the high-frequency maxima, where stretching vibrations are found. The group IIIa effect causes a minor increase in frequencies in $In_2Pt_2O_7$ and $Tl_2Pt_2O_7$. The mass effect of A is noted primarily at the lower frequencies where the bending and lattice modes are expected. The influence is most pronounced in ν_6, while ν_5 and ν_7 virtually parallel each other throughout the series.

On the basis of their formula and relatively large unit cell (2 molecules of 11 atoms each per Bravais cell), the pyrochlores might be expected to show considerable complexity in their infrared spectra. The relative simplicity of the observed spectra can be attributed in great part to the high symmetry of the A and B atom coordination polyhedra. Thus, the platinum pyrochlores consist of two interpenetrating three-dimensional networks of six-coordinated Pt atoms and eight-coordinated A(III) atoms. The six Pt–O bonds of the trigonal antiprism are of equal length, and the distorted cube about each A atom is formed from only two bond types. Coupling between modes is expected in the three-dimensional crystal network of the pyrochlores, but we believe that each peak arises predominantly from a single vibrational mode and that assignments consistent with structural and theoretical considerations can be made.

Three of the seven absorption peaks in the spectra are attributed to asymmetric stretching vibrations of the three different metal–oxygen bonds, and three of the remaining peaks are due to bending modes of these bonds. The seventh peak is assigned to a lattice vibration between A(III) and the platinum–oxygen antiprism. We assign ν_1 to the $Pt-O_{II}$ stretching vibration for three reasons: (1) the observed peak degeneracy, (2) the strongest bonds in the molecule reside in the platinum–oxygen antiprism, and (3) the observed frequency is close to the stretching maxima we find in orthorhombic PtO_2 at 750 and 720 cm^{-1}. The weaker maximum of ν_2 is assigned to the stretching vibration of the collinear $A-2(O_I)$ group, and ν_3 is assigned to the stretching vibration of the $A-6(O_{II})$ group. The observed peak degeneracy in ν_3 and the relative bond lengths (bond strengths) are in accord with these assignments. The ν_2 frequency is also comparable with the highest frequency stretching vibration observed in the corresponding cubic rare earth sesquioxides.[18] The $O_{II}-Pt-O_{II}$ bending mode is assigned to ν_4 and the $O_{II}-A-O_{II}$ bending to ν_5. As shown by Figure 6, the ν_4 frequencies are relatively insensitive to the identity of A, while ν_5 and ν_7 are more dependent upon the A atom mass. The degeneracy attributed to ν_7 is to be expected for a collinear O_I-A-O_I bending mode. The one peak which remains unassigned, ν_6, is believed to represent a lattice stretching mode between the A atom and the platinum–oxygen polyhedron. This vibration is strictly dependent upon the A atom mass is these compounds, and results in a reversal in the relative position of ν_6 and ν_7 in the $Tl_2Pt_2O_7$ spectrum. This assignment is required by the appearance of a single maximum (ν_6) at 100 cm^{-1} and a doublet (ν_7) at 120 cm^{-1}.

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(18) N. T. McDevitt and W. L. Baun, *Spectrochim. Acta*, **20**, 799 (1964).