TABLE III
THERMODYNAMIC CONSTANTS FOR THE ACID DISSOCIATION OF COBALT(III)–AMINE COMPLEX IONS

Complex ion	Ref	Temp, °C	$pK_1{}^{*a}$
$Co(NH_3)_5H_2O^{3+}$	7	25°C	6.55
$Co(dien)(en)H_2O^{3+}$	This work	24	5.14
$Co(NH_3)_4(H_2O)^{3+}$	8	25	5.32
cis-$Co(NH_3)_4(H_2O)_2{}^{3+}$	7	25	5.95
cis-$Co(en)_2(H_2O)_2{}^{3+}$	9	25	6.06
trans-$Co(en)_2(H_2O)_2{}^{3+}$	9	25	4.45
$Co(NH_3)_3(H_2O)_3{}^{3+}$	10	15	4.73
$Co(NH_3)_2(H_2O)_4{}^{3+}$	10	15	3.40

[a] $pK_1{}^*$ is for the first acid dissociation of each ion.

possible combinations of the above ligands. This is in agreement with the acidity of *cis*-$Co(NH_3)_4(H_2O)_2{}^{3+}$ compared with those of *cis*-$Co(en)_2(H_2O)_2{}^{3+}$, of $Co(NH_3)_5H_2O^{3+}$, and of presumably mixed *cis*- and *trans*-$Co(NH_3)_4(H_2O)_2{}^{3+}$. Also in agreement is the acidity of *trans*-$Co(en)_2(H_2O)_2{}^{3+}$ relative to those of $Co(NH_3)_5H_2O^{3+}$, of *cis*-$Co(en)_2(H_2O)_2{}^{3+}$, and of $Co(dien)(en)H_2O^{3+}$; $Co(NH_3)_3(H_2O)_3{}^{3+}$ and $Co(NH_3)_2(H_2O)_4{}^{3+}$ appear to obey the predicted trend. In addition, Grinberg and Ryabchikov[11] observed a *trans*-effect influence on the acidities of square-planar *cis*- and *trans*-$Pt(NH_3)_2(H_2O)_2{}^{2+}$; the *trans* isomer was more acidic than the *cis* by a factor of 40.

There is a significant number of comparable pK^* values in Table III which leads one to conclude that the acidities do not obey a simple *trans* effect. These anomalous comparisons are of $Co(NH_3)_5H_2O^{3+}$ with *cis*-$Co(en)_2(H_2O)_2{}^{3+}$ and of $Co(dien)(en)H_2O^{3+}$ with $Co(NH_3)_5H_2O^{3+}$, with *cis*-$Co(en)_2(H_2O)_2{}^{3+}$, and with *cis*-$Co(NH_3)_4(H_2O)_2{}^{3+}$. Although the steric configuration of $Co(dien)(en)H_2O^{3+}$ as prepared is not known, the ligand *trans* to the water molecule must be a primary or secondary amine. That it may be a primary amine might be inferred from the inability of Crayton and Mattern[12] to isolate the *cis* isomers of several $Co(dien)X_3$ compounds. Analogy with compounds containing triethylenetetramine (trien) is difficult because Sargeson and Searle[13] observed that the *cis*-α isomer was predominant while Goto, *et al.*,[14] observed that C-substituted trien–cobalt complexes preferentially formed in the *cis*-β configuration.

While there are insufficient data to make definite explanations for the variances from expected relative acidities due to *trans* effects, possibilities may be suggested. It is logical to assume that the *trans* effect of the σ-bonding ligands does influence the acidity of the water molecule *trans* to them. If this be true, then the acidities should vary inversely with the *trans*-effect strengths of the ligands. However, the latter is shown to be not true for a significant number of cases if only *trans* effects are considered; therefore, if the *trans* effect is present, there must be additional influence on the acidities of these complex ions.

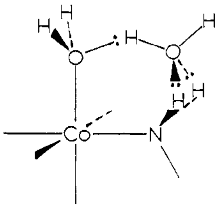

Figure 3.—Possible *cis* effect of coordinated amines through a water molecule in the outer coordination sphere (scale approximate).

One possible influence could be the nature of the ligands lying *cis* to the water molecule. Increased steric repulsion could cause an increase in acidity. Another *cis* effect might be due to the acidic character of the ligands *cis* to the water molecule. The various acidities of protons in water, ammonia, and primary and secondary amines could be transmitted to a *cis* water molecule *via* a water molecule in the outer coordination sphere which is hydrogen bonded to both ligands (see Figure 3). The magnitude or existence of such effects only can be revealed by careful study of a significant number of complex ions of known steric configuration.

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Rare Earth Plumbates with the Pyrochlore Structure

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Compounds with the pyrochlore structure and the formula $A^{III}{}_2B^{IV}{}_2O_7$, where A is a rare earth cation, have been reported[1-13] where B is Ti, Zr, Hf, Tc, Ru, Ir, Pd, Pt, Ge, or Sn. Brisse[13] has attempted to prepare rare earth pyrochlores of the type $A_2Pb^{IV}{}_2O_7$ but with only partial success. Concurrent work here revealed that pyrochlores of this type are readily prepared if the oxygen pressure is sufficiently high to prevent the re-

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duction of tetravalent lead. The preparation and characterization of $A_2Pb^{IV}_2O_7$ phases with the pyrochlore structure are reported herein.

Experimental Section

The starting materials were 99.9% pure rare earth oxides obtained from the American Potash and Chemical Corp. and reagent grade PbO_2. The reactants (A_2O_3–$2PbO_2$) were thoroughly mixed by grinding and then sealed in pressure-collapsible gold ampoules. These ampoules were heated at 700° for about 8 hr under 3 kbars of supporting pressure.

X-Ray powder patterns were obtained using a Debye–Scherrer camera of 114.6-mm diameter and Cu Kα radiation [λ(CuKα_1) 1.54051 Å and λ(CuKα_2) 1.54433 Å]. The cell dimensions were refined by least squares, and the indexed powder patterns have been sent to ASTM.

Results

Compounds of the type $A_2Pb^{IV}_2O_7$, where A is La, Pr, Nd, Sm, Eu, or Gd, were found to have the pyrochlore structure; however, when A is Tb, Dy, Ho, Er, or Y, a disordered fluoride structure is observed. The cell dimensions are given in Table I. For A = La–Gd the systematic absences of the powder patterns were found to be those expected for the pyrochlore structure,[14] and the relative intensities were also qualitatively in agreement with those expected for the pyrochlore structure. "Ordering lines," *i.e.*, lines with *h*, *k*, and *l* all odd, were present for A = La–Gd but not for the remaining compounds. The lack of ordering or superstructure lines means that the X-ray powder patterns can be indexed on the basis of a primitive cubic cell of the fluorite type where the cell edge is half that of the pyrochlore cell edge. In the fluorite structure there is only one cation site and only one anion site. Consequently, for the compounds where A is Tb, Dy, Ho, Er, or Y the cell dimensions are actually about half that of the others, and it must be concluded that the A cation and Pb^{4+} are disordered over the cation sites and that the oxygen vacancy is disordered over the anion sites of the fluorite structure.

TABLE I

CELL DIMENSIONS OF $A_2Pb_2O_7$

Compound	Cell edge, Å[a]	Compound	Cell edge, Å[a]
$La_2Pb_2O_7$	10.969	$Tb_2Pb_2O_7$	10.685/2
$Pr_2Pb_2O_7$	10.869	$Dy_2Pb_2O_7$	10.666/2
$Nd_2Pb_2O_7$	10.838	$Y_2Pb_2O_7$	10.634/2
$Sm_2Pb_2O_7$	10.769	$Ho_2Pb_2O_7$	10.630/2
$Eu_2Pb_2O_7$	10.642	$Er_2Pb_2O_7$	10.613/2
$Gd_2Pb_2O_7$	10.716		

[a] ±0.002 Å.

Chemical analyses were carried out on four products. *Anal.* Calcd for $La_2Pb_2O_7$: La, 34.55; Pb, 51.53; O, 13.92. Found: La, 34.95; Pb, 51.22; O, 13.98. Calcd for $Gd_2Pb_2O_7$: Gd, 37.40; Pb, 49.28; O, 13.32. Found: Gd, 36.85; Pb, 49.24; O, 13.56. Calcd for $Er_2Pb_2O_7$: Er, 38.86; Pb, 48.13; O, 13.01. Found: Er, 38.55; Pb, 48.45; O, 13.22. Calcd for $Y_2Pb_2O_7$: Y, 25.25; Pb, 58.84; O, 15.90. Found: Y, 24.96; Pb, 58.90; O, 16.10.

Pyrochlores of the type $A_2Pb^{IV}_2O_7$ are thermally no more stable than PbO_2. Thermogravimetric analysis shows that on heating these pyrochlores in air, oxygen begins to be lost at about 300°.

Discussion

Tetravalent lead is the largest cation which has been found on the octahedral sites of the pyrochlore structure. Therefore, compounds of the type $A_2Pb^{IV}_2O_7$ are of great importance in defining the stability field for the pyrochlore structure.[11,13] Tetravalent zirconium is only slightly smaller than Pb^{4+}, and for both $A_2Pb^{IV}_2O_7$ and $A_2Zr^{IV}_2O_7$ compounds the dividing line between the pyrochlore structure and the disordered fluorite structure is at Gd–Tb. The pyrochlore structure is found when A is Gd or a larger rare earth, and the disordered fluorite structure is found for smaller A cations.

For $A_2B_2O_7$ compounds where both A and B are too large for tetrahedral coordination either the pyrochlore structure or a disordered fluorite structure is frequently found. Which of these two types occurs apparently depends primarily on the A:B size ratio.[13] When the sizes of the A and B cations become too similar, ordering of these cations does not take place and the disordered fluorite structure is found.

The disordered fluorite structure for $A^{III}_2B^{IV}_2O_7$ compounds has been observed only when the corresponding BO_2 compound has a fluorite-type or fluorite-related structure. It is thus significant that Syono and Akimoto[15] have recently shown that PbO_2 can have the fluorite structure.

Brisse[13] attempted to prepare $A^{III}_2Pb^{IV}_2O_7$ compounds but succeeded only in preparing $La_2Pb_2O_7$. For this compound he gave a cell dimension of 10.971 Å in good agreement with the value found in this work (Table I). His failure to prepare other $A^{III}_2Pb^{IV}_2O_7$ compounds may be attributed to the difficulty in stabilizing tetravalent lead at high temperature.

High pressure has been successful in preparing new pyrochlore-type compounds for two different reasons: one, the stabilization of a high oxidation state; two, the stabilization of a high coordination number. High pressure was required to prepare pyrochlore-type $A_2Pt^{IV}_2O_7$ and $A_2Pd^{IV}_2O_7$ compounds recently reported by the author[12] and is also required to prepare $A_2Pb^{IV}_2O_7$ compounds. In these cases the high pressure is necessary to prevent the cation from being reduced. High pressure is also required to prepare $A^{III}_2Ge^{IV}_2O_7$ pyrochlores.[11] However, in this case it is a high coordination number, not an oxidation state, which is stabilized at high pressure.

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