Assuming that this assignment is valid, it follows from the above considerations that the stable tris-chelate of *d*-2,3-butylenediamine with cobalt(III) will be dextrorotatory at the D-line of sodium.

It is hoped that the method for correlation of absolute configurations which has been illustrated above will prove reliable and useful.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE UNIVERSITY OF CONNECTICUT]

The Preparation of Some Ternary Oxides of the Platinum Metals[1,2]

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Ternary oxides of the alkaline earth ions with ruthenium, rhodium, iridium and platinum have been prepared. $CaRuO_3$ and $SrRuO_3$ and $SrIr_{0.5}Ru_{0.5}O_3$ are orthorhombic substances of the perovskite type. $BaRuO_3$ has a hexagonal structure. Sr_2RuO_4, Sr_2RhO_4 are isotypic with Sr_2IrO_4 which has the K_2NiF_4 structure. Sr_4IrO_6, Sr_4PtO_6 and an oxygen-deficient Sr_4RhO_{6-y} were found to have the K_4CdCl_6 structure. Preliminary data suggest that $Sr_3Pt_2O_7$ is structurally related to $Ba_3Pt_2O_7$ and that ruthenium and iridium form ternary oxides with lead which have the pyrochlorite structure.

While there are many ternary oxides of transition metals, relatively few of these contain a platinum metal. Waser and McClanahan[3] have prepared a phase, at first formulated as $NaPt_3O_4$ and later as $Na_xPt_3O_4$. The presence of square PtO_4 groups in this preparation was ascertained by a structure determination. The existence of this phase later was confirmed by Scheer, Van Arkel and Heyding,[4] who have prepared the analogous palladium compound. These authors also have prepared the compounds $LiRhO_2$, Li_2RhO_3, $NaRhO_2$, Na_2IrO_3, Na_2PtO_3, Li_2PtO_3 and Li_2PtO_3 in which the platinum metal is in sixfold coördination with oxygen.

Ternary oxides of alkaline earth cations and platinum metals which have been reported are $Ba_3Pt_2O_7$[5,6] and Sr_2IrO_4.[7]

The quaternary oxides $BaTi_{0.75}Pt_{0.25}O_3$ and $Ba_4Ti_2PtO_{10}$ also have been described.[8] The former is isotypic with hexagonal barium titanate.

An example of a ternary oxide of a lanthanide element and a platinum metal has been found in $LaRhO_3$[9] which has the orthorhombic modification of the perovskite structure typified by $GdFeO_3$.[10]

This paper describes the preparation and characterization of a number of ternary oxides of the types ABO_3, A_2BO_4 and A_4BO_6, where A represents Ca, Sr or Ba and B represents Ru, Rh, Ir or Pt.

Experimental

General Method of Preparation.—For products prepared in air, the reactants were usually the alkaline earth carbonate and the platinum metal powder (~200 mesh). Reactants were ground thoroughly in an agate mortar and the mixture was fired in powder form, in air, at 1000 to 1500°. With the exception of the rhodium preparation, the reactions took place rapidly, and a pure product could be obtained in several hours with two intermediate grindings of the reaction mixture.

For the preparations made *in vacuo*, the reaction mixture, in pellet form, was sealed in an evacuated silica capsule.

The ruthenium products were blue-black in color, the rhodium and iridium preparations were black, while the platinum compounds were tan or brown.

ABO_3 Type Compounds.—The reaction of ruthenium metal with alkaline earth carbonates at 1200° for periods of 12 to 24 hr. gave homogeneous dark blue products. The X-ray powder pattern of the calcium and strontium compounds were interpreted by analogy with patterns of other known compounds. Thus the calcium ruthenium oxide was found to resemble closely $CaMoO_3$[11] which probably has the orthorhombic structure of the $GdFeO_3$ type.[10] The strontium ruthenium oxide on the other hand showed a strong resemblance to $LaVO_3$,[12] which has been indexed with a tetragonal cell. A number of "split" lines, however, are observed in the pattern of the strontium ruthenium oxide. On the assumption that the two lines of the first "split" (corresponding to the 404 reflection for the tetragonal cell) were the 404 and 044 reflections of an orthorhombic unit cell the entire pattern could be indexed. The lattice constants for calcium ruthenium oxide were a = 5.53 Å., b = 5.36 Å., c = 7.67 Å. and for the strontium compound a = 5.57 Å., b = 5.53 Å., c = 7.85 Å. The barium compound appeared to be quite different. The X-ray powder pattern was indexed on the basis of a hexagonal unit cell a = 9.95 Å., c = 21.54 Å.[13]

In view of the fact that a perovskite-type compound was not obtained in the strontium–iridium–oxygen system,[7] an attempt was made to substitute iridium for ruthenium in the strontium ruthenium oxide. Homogeneous products were obtained in the system $SrIr_xRu_{(1-x)}O_3$ between the limits $0 < x < 0.5$. In the region $0.5 < x < 1.0$, mixtures of $SrIr_{0.5}Ru_{0.5}O_3$, Sr_2IrO_4 and metallic iridium were formed. All the phases between $0 < x < 0.5$ were orthorhombic and the lattice constants at $x = 0.5$ were a = 5.58 A., b = 5.55 Å., c = 7.84 Å. It was not found possible to substitute any platinum for the ruthenium in this phase.

The composition of these phases is not precisely known. The A/B cation ratio is probably near unity. Attempts to prepare phases in the systems $SrRu_x^{III}Ru_{1-x}^{IV}O_{3-x/2}$ and $Sr_{1-x}Ru_x^{VI}Ru_{1-x}^{IV}O_3$ were fruitless. Heterogeneous products were always obtained and the lattice dimensions for the orthorhombic phase remained unchanged. Approximate measurements of conductivities of the alkaline earth ruthenium oxide phases using pressed pellets sintered at 1200° gave values of about one reciprocal ohm cm. Direct oxygen

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(2) This research was supported in part by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(3) J. Waser and E. McClanahan, *J. Chem. Phys.*, **19**, 40, 413 (1951).

(4) J. Scheer, A. Van Arkel and R. Heyding, *Can. J. Chem.*, **33**, 683 (1955).

(5) M. G. Rousseau, *Compt. rend.*, **109**, 144 (1889).

(6) W. O. Statton, *J. Chem. Phys.*, **19**, 40 (1951).

(7) J. J. Randall, Jr., L. Katz and R. Ward, THIS JOURNAL, **79**, 266 (1957).

(8) H. Blattner, H. Gränicher, W. Känzig and W. Merz, *Helv. Phys. Acta*, **21**, 341 (1948).

(9) A. Wold, B. Post and E. Banks, THIS JOURNAL, **79**, 6365 (1957).

(10) S. Geller and E. A. Wood, *Acta Cryst.*, **9**, 563 (1956).

(11) W. H. McCarroll, L. Katz and R. Ward, THIS JOURNAL, **79**, 5410 (1957).

(12) M. Kestigian, J. G. Dickinson and R. Ward, *ibid.*, **79**, 5598 (1957).

(13) The indexing of this pattern has been filed with the microfilm service.

analyses using the $KBrF_4$ method indicated that the strontium ruthenium oxide is somewhat oxygen-deficient ($SrRuO_{2.89 \pm 0.04}$).

A_2BO_4 Type Compounds.—Sr_2RuO_4 was prepared by heating strontium carbonate and ruthenium metal in a molar ratio of Sr/Ru = 2.00, in air at 1200° for 12 hr. The X-ray powder pattern of this preparation is very similar to that of Sr_2IrO_4 which has the K_2NiF_4 structure. The pattern can be indexed on the basis of a body centered tetragonal unit cell with a = 3.870 Å. and b = 12.74 Å. Calculated intensities, using parameters ($Z_O = 0.152, Z_{Sr} = 0.356$) analogous to those used for Sr_2IrO_4 are in good agreement with observed intensities estimated visually indicating this compound probably has the K_2NiF_4 structure.

Although it was not found possible to prepare Sr_2RhO_4 in a pure state, a phase which is evidently of the K_2NiF_4 type can be seen to be present in all strontium–rhodium–oxygen preparations where Sr/Rh was between 1.5 and 4.5 at temperatures from 1200 to 1300°. Lines belonging to this phase were picked out from one of these photographs and were indexed on the basis of a K_2NiF_4-like body centered tetragonal cell (a = 3.85 Å. and c = 12.90 Å.).

Compounds of the Type A_4BO_6.—Homogeneous products were obtained by the reaction of either strontium oxide or carbonate with elementary rhodium or rhodium sesquioxide, with $PtO_2 \cdot H_2O$ and with elementary iridium. The molar ratio of strontium to platinum metal was 4 except in the case of rhodium where 4.75 was found necessary to give a pure phase. The temperatures required to carry out the reactions were different in each case being 800, 1250 and 1500° for the platinum, rhodium and iridium compounds, respectively. The X-ray powder patterns of the platinum and iridium compounds can be indexed fairly well on the basis of a primitive cubic unit cell of size a = 6.88 Å., but the powder pattern of the rhodium preparation was not indexed nearly as well on this basis. Single crystal X-ray studies reported elsewhere,[14] showed the structure of these compounds to be actually rhombohedral (space group $R\bar{3}c$). The hexagonal cell dimensions are a = 9.74 Å., c = 11.90 Å.

All of these preparations are unusual in the respect that they hydrolyze instantly on contact with water, the platinum compound hissing noticeably. Complete solution could be effected by the addition of a small amount of hydrochloric acid. For the platinum compound, the solution first obtained on addition of acid was green, but turned to the color of the $PtCl_6^{--}$ ion on heating. This may be due to the initial formation of a hydroxy species. For the rhodium preparation, the original solution was a deep bluish-purple. On heating this solution or allowing it to stand in air for a week or two, the purple color changed to rose, due to reduction of Rh^{+4} to $RhCl_6^{---}$.

Analysis of Sr_4BO_6 Compounds.—Platinum in Sr_4PtO_6 was determined by precipitation as the metal with hydrazine, while strontium was precipitated from 50% alcohol solu-

TABLE I

X-Ray powder diffraction data for the product obtained by the reaction of strontium oxide and ruthenium metal in air at 1200°. (Sr/Ru = 1.5) (10 hr. exposure, 38KV. 17MA. $\lambda_{\alpha 1 \alpha 2}$ = 1.5418 Å. Camera radius 57.3 cm.

I	d/n	I	d/n
M−	10.5	S−	1.605
M	5.21	W−−	1.501
W	3.97	W−−	1.463
S	2.84	M	1.418
S−(B)[a]	2.77	M−	1.388
W+	2.35	W+	1.376
W	2.15	W−−	1.302
M	2.08	W−−−	1.291
W+	1.966	W(B)[a]	1.241
M+	1.948	W−	1.230
W−−	1.821	W−−−	1.161
W−−−	1.731	W+	1.146
M	1.656		

[a] B = broad line.

INDEXING OF $BaRuO_4$[a]

$CuK\alpha_1\alpha_2$ Radiation; $\lambda\alpha_1\alpha_2$ = 1.5418 Å., 38KV, 17MA, Exposure time, 10 hr.; camera radius, 57.3 mm. (Straumanis Method)

I	hkl	$d_{obsd.}$	$d_{calcd.}$
M−	111	4.86	4.85
W−	112	4.49	4.50
M−	114	3.66	3.65
S−	210	3.26	3.26
	115		3.26
S+	300	2.88	2.87
M−	117	2.62	2.62
W−−	009	2.392	2.393
	310		2.390
	305		2.390
M−	311	2.371	2.376
	118		2.368
M−	224	2.259	2.259
M+	119	2.155	2.156
	400		2.155
	225		2.155
	0,0,10		2.154
M−	320	1.980	1.977
	1,1.10		1.977
W+	227	1.935	1.935
M−	228	1.829	1.829
W	414	1.774	1.775
M−	229	1.723	1.725
	500		1.723
	415		1.723
	3.0,10		1.723
M	330	1.658	1.659
	2,0,12		1.657
	0,0,13		1.657
W+	420	1.631	1.629
	2,2,10		1.628
W+	417	1.606	1.605
W−	2,1,12	1.574	1.572
	1,1,13		1.572
M−	418	1.542	1.542
W−		1.474	
M	600	1.437	1.436
	0,0,15		1.436
W+	430	1.417	1.417
	4,1,10		1.417
W	520	1.381	1.380
	1,1,15		1.380
W−−	524	1.337	1.337
W	610	1.314	1.314
	525		1.314
	3,3,10		1.314
	2,1,15		1.314
	4,0,13		1.314
W−	527	1.260	1.259
W−	2,1,16	1.245	1.244
	440		1.244
	2,2,15		1.244
W−	701	1.230	1.229
W−	0,0,18	1.196	1.197
	529		1.196
W−	1,1,18	1.163	1.163
	5,2,10		1.162
	3,2,15		1.162
W−−	...	1.156	...

[a] Indexed on the basis of a hexagonal unit cell: a = 9.95 Å.; c = 21.45 Å.

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[14] Submitted to *Acta Cryst.*

tion as the sulfate. Calcd. for Sr_4PtO_6: Sr, 54.6; Pt, 30.4. Found: Sr, 54.8; Pt, 30.4.

The amount of Rh^{+4} in the rhodium preparation was determined by reduction to Rh^{+3} with excess iodide and titration of the iodine liberated with thiosulfate. Calcd. for Sr_4RhO_6: Rh^{+4}, 18.73. Found: Rh^{+4}, 14.40. The results of this analysis indicated that the compound probably also contained rhodium in a lower oxidation state than +4.

Analysis for total rhodium was accomplished using the method of Ayres, Tuffly and Forrester.[15] The purple solution obtained by dissolving the compound in hydrochloric acid was boiled until the purple color had disappeared, indicating complete reduction to Rh^{+3}. The per cent. of rhodium was then found by spectrophotometric analysis of a Rh^{+3}–$SnCl_2$ complex. This analysis gave 18.9% Rh.

It was found necessary to remove rhodium from the solution in order to analyze for strontium as $SrSO_4$. The removal was effected by precipitation as the sulfide.[16] Calcd. for $Sr_4Rh_{0.240}{}^{+3}Rh_{0.760}{}^{+4}O_{5.88}$: Sr, 64.0. Found: Sr, 64.0.

$A_3B_2O_7$-Type Compounds.—The interaction of strontium oxide and hydrous platinum dioxide with mixtures having a strontium to platinum ratio of $^3/_2$ gave a uniform product at 800°. The structure is hexagonal (a = 9.69 Å., c = 18.43 Å) and is probably related to the structure of $Ba_3Pt_2O_7$. The a-axis is comparable to that of the barium compound but the c axis is approximately twice as long.

The products formed by reaction of strontium oxide and ruthenium at 1200° when the composition of the mixtures was between Sr/Ru = 1.5 and Sr/Ru = 2.0 seem related to Sr_2RuO_4. However, a number of weak lines are present on the powder patterns of all phases and a few intensity discrepancies show that none of these preparations can contain more than a very small amount of Sr_2RuO_4. The d/n values and the relative intensities of the X-ray powder diffraction pattern for the product obtained with Sr/Ru = 1.5 are listed in Table I. With mixtures in which 1 < Sr/Ru <1.5, the products always contained $SrRuO_3$ and Sr_2RuO_4.

Some Miscellaneous Preparations.—Attempts to prepare suitable single crystals of some of the products led to the isolation of different phases for which some data were obtained but which were not properly characterized. The limited information, however, is presented here since it may be useful for future identification.

A sample of $Sr_4Pt_{0.25}Ir_{0.75}O_6$ heated at 1260° for one month provided small single crystals of various shapes. Weissenberg photographs showed these to be face-centered cubic (a = 16.2 Å.). The Laue group is m3m and the space group Fd3m. It was not found possible to prepare this substance in quantity and neither the density nor the composition is known.

In attempting to prepare single crystals of Sr_4RhO_6 by heating the reactants with a lead oxide flux in a platinum crucible according to the method Remeika,[17] well formed six-sided black needles were obtained. Weissenberg photographs showed the cell size to be a = 9.53 Å. and c = 8.44 Å. The space group is probably one of the following: P31c, $P\bar{3}1c$, $P6_3mc$, $P\bar{6}2c$ or $P6_3/mmc$. Since the preparation was carried out in a platinum crucible and the product was not the same as that obtained in powder form, it seems likely that lead is present in this product. Platinum may be substituted for rhodium without causing a change in structure.

When a morganite (fused Al_2O_3) crucible was used in place of platinum, platy, black, hexagonal shaped crystals were formed. These crystals are hexagonal with a = 10.27 Å. and c = 13.20 Å. The space group possibilities are $P6_3cm$., $P\bar{6}c2$ and $P6_3/mcm$. Again, the product is not the same as that obtained in powder form. This would seem to indicate that Pb^{+2} can replace Sr^{+2} in $Sr_4RhO_{(6-y)}$, thereby changing the structure.

Some evidence has been obtained for the existence of ternary oxides of ruthenium and iridium with lead.

By heating mixtures of PbO and Ru or Ir metals in a molar ratio of Pb/Ir or Pb/Ru = 2.00 at 800–850° in air, homogeneous black products were obtained. When Pb/Ru = 2.00 at 800°, PbO lines could be seen on the powder photographs. The powder patterns of these preparations can be indexed, with the exception of a few very weak lines, on the basis of face centered cubic unit cells of size 5.14 Å. for the iridium compound and 5.13 Å. for the ruthenium compound. If these unit cells are doubled, to 10.27 and 10.25 Å., respectively, the weak lines are included in the face-centered cubic indexing. These features suggest that the compounds may be of the pyrochlorite type with formula $Pb_2M_2O_7$, but the composition of the pure phases was not determined.

Discussion

Most of the compounds prepared appear to be stoichiometric, with the platinum metal in a single oxidation state (+4). Exceptions to this are the $Sr_4RhO_{(6-y)}$ and $SrRuO_{(3-y)}$ products, both of which apparently contain the platinum metals in both the +3 and +4 oxidation states. Progression from ABO_3 to A_2BO_4 to A_4BO_6 type compounds involves a change from the perovskite type of structure with B–O–B bonds in three dimensions, to the K_2NiF_4 phases with B–O–B bonds in two dimensions and finally to A_4BO_6 with discrete BO_6 octahedra (no B–O–B bonds).

The phases obtained between Sr/Ru = 1.5 and Sr/Ru = 2.0 seem very similar to $Sr_3Ti_2O_7$,[18] which is related to both the perovskite and K_2NiF_4 structures, but some lines were observed which are incompatible with a body centered tetragonal unit cell. It seems, at least, that the a axes for these phases are comparable to that of $Sr_3Ti_2O_7$.

Tolerance factors for the Goldschmidt equation

$$\left[t = \frac{(R_A + R_O)}{\sqrt{2}(R_B + R_O)}\right]$$

for all of the platinum metals in combination with an alkaline earth ion in the perovskite structure are between 0.87 and 1.01. This is about the range in which cubic perovskites are usually found.

It is interesting that of all the theoretically possible perovskite type compounds in these systems, the only ones which were found to form were $CaRuO_3$, $SrRuO_3$ and the phases in the system $SrRu_{(1-x)}Ir_xO_3$.

The orthorhombic distortion is greater for the calcium perovskite than for the strontium compound as would be expected, but, since $SrRuO_3$ is so close to being cubic, it might have been expected that $BaRuO_3$ would have the cubic structure instead of the hexagonal structure.

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[15] G. Ayres, B. Tuffly and J. Forrester, *Anal. Chem.*, **27**, 1742 (1955).

[16] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., p. 381.

[17] J. P. Remeika, THIS JOURNAL, **78**, 4259 (1956).

[18] S. Ruddleson and P. Popper, *Acta Cryst.*, **11**, 54 (1958).