The observations are summarized in Table III. Systematic intercomparison of all possible pairs (66) showed that only in the following three groups does isomorphism definitely appear to exist

1. $\{[Mn((C_6H_5)_3AsO)_2Cl_2], [Mn((C_6H_5)_3PO)_2Cl_2], [Co((C_6H_5)_3AsO)_2Cl_2], [Co((C_6H_5)_3PO)_2Cl_2]\}$
2. $\{[Co((C_6H_5)_3AsO)_2Br_2], [Ni((C_6H_5)_3AsO)_2Br_2]\}$
3. $\{[Mn((C_6H_5)_3PO)_2Br_2], [Ni((C_6H_5)_3PO)_2Br_2]\}$

Included in these results are some previously mentioned.[11] Since the cobalt compounds can be assigned tetrahedral configurations with certainty, it follows that those isomorphous with them thus are proved to have tetrahedral configurations. This provides good independent support for such assignments previously made on the basis of spectral and magnetic data for $[Ni((C_6H_5)_3PO)_2X_2]$[9] and $[Ni((C_6H_5)_3AsO)_2X_2]$[16] compounds, and on the basis of spectral data for $[Mn((C_6H_5)_3PO)_2X_2]$[11] and $[Mn((C_6H_5)_3AsO)_2X_2]$[11] compounds.

Acknowledgment.—We express our appreciation to the U. S. Atomic Energy Commission for financial support under Contract AT(30-1)-1965.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CONNECTICUT, STORRS, CONNECTICUT

Compounds of Osmium and Rhenium with the Ordered Perovskite Structure

BY ARTHUR W. SLEIGHT, JOHN LONGO, AND ROLAND WARD

Received October 31, 1961

A description is given of the preparation and characterization of a number of compounds of the type $A_2BB^1O_6$ where A = Ca, Sr, Ba; B^1 = Re or Os; and B represents a variety of univalent, divalent, and trivalent cations. Evidence is obtained for the existence of heptavalent osmium in the compound Ba_2LiOsO_6. The structure of many of these compounds is of the ordered perovskite type, but the hexagonal barium titanate structure is adopted in the osmium compounds when A is barium and B is a transition metal cation having d electrons. This structure also is found with the compounds $Ba_3Cr_2ReO_9$ and $Ba_3Fe_2ReO_9$. Preliminary measurements of the magnetic properties of some of the compounds are reported.

The discovery of thermally stable compounds of hexavalent and heptavalent rhenium having the ordered perovskite structure[1,2] led us to inquire whether similar compounds of other elements with high oxidation states could be obtained. The obvious choice among the metallic elements was osmium. This paper describes a number of quaternary phases containing osmium in oxidation states extending up to heptavalent osmium. A comparison is made between these and systems containing rhenium.

The general formula for the type of compound sought in these experiments is $A_2BB^1O_6$ where A is a large divalent cation capable of 12-fold coördination with oxygen. The sum of the valences of B and B^1 must be eight and the size must be suitable for octahedral coördination with oxygen. The oxidation state of B^1, which represents osmium or rhenium in this instance, thus may be controlled by appropriate selection of the B cation.

For the preparation of crystalline compounds of this kind, the most usual procedure has been to heat stoichiometric mixtures of the oxides in a closed system. In many instances, suitable compounds of osmium were not available for the application of this method. It was found, however, that many of the compounds could be obtained by heating in air mixtures of osmium powder and the oxides or carbonates of the A and B metals. The temperatures at which these reactions were carried out lay in the range of 600 to 1000°. It is a testimony to the stability of these compounds that little or no osmium was lost from the samples. Apparently the reactions proceed by means of some gaseous species for many of the reactions were virtually complete in a few minutes.

The products were characterized by means of their X-ray powder diffraction patterns using a General Electric XRD-5 diffractometer. Chemical analyses, magnetic susceptibility measure-

---

(1) A. W. Sleight and R. Ward, *J. Am. Chem. Soc.*, **83**, 1088 (1961).

(2) J. Longo and R. Ward, *ibid.*, **83**, 2816 (1961).

ments, and saturation magnetization data were obtained in a few instances.

Experimental

Reagents.—The alkaline earth oxides, magnesium, manganese, iron, cobalt, nickel, cadmium compounds, and rhenium metal were similar to those previously described.[1] The osmium powder (325 mesh) was 99.8%. We are indebted to Dr. Cox of the Central Research Department, du Pont Company, for the sample of chromium dioxide which was prepared by the oxidation of hydrous chromium sesquioxide. The scandium sesquioxide was 99.0% Sc_2O_3.

Procedures for Preparations.—The reactions represented by the following equations were carried out by heating intimate mixtures of the solid reagents in zirconium silicate boats placed in electric muffle furnaces. The small samples (approximately 0.3 g.) were exposed to the air during the heating period. The products were examined microscopically and by X-rays.

$$8BaO_2 + 2B_2CO_3 + 4B^1 + 3O_2 \longrightarrow 4Ba_2BB^1O_6 + 2CO_2$$

$$8AO + 2B_2CO_3 + 4B^1 + 7O_2 \longrightarrow 4A_2BB^1O_6 + 2CO_2$$

A = Sr or Ca, B = Li or Na, B^1 = Re or Os.

The following compounds were made by heating for about 15 min. at the temperatures given in parentheses: Sr_2LiReO_6 (600°), Ca_2LiReO_6 (600°), Ba_2LiOsO_6 (800°), Sr_2LiOsO_6 (600°), Ca_2LiOsO_6 (600°), Sr_2NaReO_6 (800°), Ca_2NaReO_6 (600°), Ba_2NaOsO_6 (800°), Sr_2NaOsO_6 (800°), Ca_2NaOsO_6 (600°). The same procedure was used to prepare a series of phases $Ba_2\{Li(Re_{1-x}Os_x)\}O_6$ where x = 1/2, 1/4, and 1/8. These were made in sufficient quantity for magnetic susceptibility measurements.

A similar procedure was followed to make compounds containing divalent ions as the B cations.

$$2BaO_2 + BO + Os + {}^1/_2O_2 \longrightarrow Ba_2BOsO_6$$

B = Mg, Ca, Sr, Zn, Cd

$$3BaO_2 + Os \longrightarrow Ba_3OsO_6$$

$$2AO + BO + Os + {}^3/_2O_2 \longrightarrow A_2BOsO_6$$

A = Sr or Ca, B = Mg, Ca, Sr, Zn, Cd

In most instances the products appeared to be homogeneous and to have the ordered perovskite structure. Ba_2CaOsO_6 and Ba_2ZnOsO_6 were obtained free from impurities, however, only after the product was subjected to prolonged heating *in vacuo*. All of these preparations were carried out at 1000°. The compounds obtained in this way were Ba_2BOsO_6 (where B = Mg, Ca, Sr, Ba, Zn, Cd); Sr_2BOsO_6 (where B = Mg, Ca, Sr, Cd); and Ca_3OsO_6.

In several instances because of the oxidizable nature of the second B cation it was convenient to use stoichiometric mixtures of compounds which could be heated in a closed system. The following equation represents reactions with pelleted mixtures in evacuated silica capsules. The temperature used in all cases was 1000°.

$$ {}^2/_3A_3OsO_6 + CrO_2 + {}^1/_3Os \longrightarrow A_2CrOsO_6 \text{ (where A = Sr or Ca)}$$

Heterogeneous products were obtained with manganese dioxide in place of chromium dioxide. Attempts to carry out a similar reaction with barium led to the formation of a phase with the hexagonal barium titanate structure mixed with metallic osmium.

It was found that the reaction indicated by the equation

$$3BaO + Cr_2O_3 + ReO_3 \longrightarrow Ba_3Cr_2ReO_9$$

gave a product having the hexagonal barium titanate structure. (Traces of some impurities could be detected by X-ray diffraction.) A mixture containing equi-atomic proportions of chromium and rhenium on the other hand gave a heterogeneous product containing only a small proportion of the same hexagonal phase.

In contrast to this behavior with chromium, the reaction of barium and rhenium oxides with ferric oxide was found to be dependent upon the composition of the mixture. The proportions represented by reaction 1 gave the cubic or-

$$2BaO + {}^1/_2Fe_2O_3 + {}^5/_6ReO_3 + {}^1/_6Re \longrightarrow Ba_2FeReO_6 \quad (1)$$

$$3BaO + Fe_2O_3 + ReO_3 \longrightarrow Ba_3Fe_2ReO_9 \quad (2)$$

dered perovskite phase previously reported,[2] while the proportions represented by (2) gave a phase with the hexagonal barium titanate structure. These reactions were carried out under vacuum at 1000°.

Other preparations obtained in this way at 1000° *in vacuo* are represented by the equations

$$2BaO + {}^1/_2Sc_2O_3 + {}^5/_6ReO_3 + {}^1/_6Re \longrightarrow Ba_2ScReO_6$$

$$2AO + BO + ReO_3 \longrightarrow A_2BReO_6$$

where A = Ca, B = Mn, Co, Ni, Mg, Cd, Ca

where A = Sr, B = Mn, Co, Ni, Mg, Zn, Cd, Sr

All of these products were of the ordered perovskite type.

The reactions involving osmium with these transition metals were not accomplished in the same way. A mixture corresponding to $4BaO_2 + Sc_2O_3 + 2Os$ was heated in air at 1000° for 15 min. The heterogeneous product, which did not contain metallic osmium, then was heated *in vacuo* at 1000° for 20 hr. The product was found to be a cubic ordered perovskite presumably having the composition Ba_2ScOsO_6.

Upon heating barium peroxide and osmium metal with Fe_2O_3, CoO, or NiO in air at 1000°, products having the hexagonal barium titanate structure were obtained. Strontium oxide in place of barium peroxide, however, gave cubic phases with the probable compositions Sr_2FeOsO_6 and Sr_2CoOsO_6. No recognizable phase was obtained with nickel oxide. With calcium oxide an orthorhombic phase, presumably Ca_2CoOsO_6, was found.

Identification of Phases.—The characterization of most of the compounds described here rests on their X-ray powder diffraction patterns. In most instances the compounds gave patterns which could be completely indexed on the basis of the ordered perovskite structure or of the hexagonal barium titanate structure. The lattice constants of some of the compounds prepared and identified are given in Table I. Some of the rhenium compounds have been reported before[1,2] but are included here for comparison.

Compounds whose X-ray patterns were identified but not indexed are indicated in the table. The compounds Ba_2LiOsO_6 and Ba_2NaOsO_6 gave patterns of the cubic ordered perovskite structure. The relative intensities of

TABLE I

LATTICE CONSTANTS OF COMPOUNDS OF THE TYPE $A_2BB^1O_6$[a]

A	Ba		Sr		Ca	
B	B¹ Re	Os	Re	Os	Re	Os
Li	8.118	8.100	7.87	7.86	7.83[b]	7.83[b]
Na	8.296	8.281	8.13	8.13	X	X
Mg	8.082	8.08	T $a = 7.88$ $c = 7.94$	$a = 7.86$ T $c = 7.92$	O $a = 5.48$ $b = 7.77$ $c = 5.56$	X
Zn	8.106	8.095	T $a = 7.89$ $c = 8.01$	X	X	X
Cd	8.322	8.325	O $a = 5.73$ $b = 8.16$ $c = 5.81$	X	O $a = 5.64$ $b = 7.99$ $c = 5.77$	X
Ca	8.356	8.362	O $a = 5.76$ $b = 8.21$ $c = 5.85$	8.21[b]	O $a = 5.67$ $b = 8.05$ $c = 5.78$	O $a = 5.73$ $b = 7.87$ $c = 5.80$
Sr	T $a = 8.60$ $c = 8.29$	T $a = 8.43$ $c = 8.72$	T $a = 8.41$ $c = 8.13$	T $a = 8.32$ $c = 8.12$		
Ba	T $a = 8.65$ $c = 8.33$	T $a = 8.66$ $c = 8.34$				
Mn	8.18	H $a = 5.04$ $c = 14.2$	8.01[b]	X	O $a = 5.52$ $b = 7.82$ $c = 5.55$	X
Fe	8.05	H $a = 4.99$ $c = 14.1$	T $a = 7.86$ $c = 7.89$	7.85[b]	O $a = 5.41$ $b = 7.69$ $c = 5.53$	X
Co	8.086	H	T $a = 7.88$ $c = 7.98$	T $a = 7.86$ $c = 7.92$	O $a = 5.46$ $b = 7.71$ $c = 5.58$	O $a = 5.47$ $b = 7.70$ $c = 5.59$
Ni	8.04	H	T $a = 7.85$ $c = 7.92$	X	O $a = 5.45$ $b = 7.67$ $c = 5.55$	X
Sc	8.163	8.152	8.02[b]	8.02[b]	O $a = 5.49$ $b = 7.86$ $c = 5.63$	X
Cr	H	H	7.82	7.84	O $a = 5.38$ $b = 7.67$ $c = 5.47$	O $a = 5.38$ $b = 7.66$ $c = 5.47$
In	8.258	8.224	8.071	8.06	X	X
Ga	X	X	7.843	7.82	X	X

[a] H = hexagonal barium titanate structure, T = tetragonal, O = orthorhombic, X = unsuccessful attempt at synthesis. [b] Slightly distorted.

the reflections agreed exactly with those of the corresponding rhenium compounds for which calculated and observed intensities compare very satisfactorily.[1] Table II gives a comparison of the calculated and observed intensities in the diffraction patttern of Ba_2CaOsO_6. The compounds Ba_2ScOsO_6 and Ba_2ScReO_6 gave patterns which matched very closely with each other and with the calcium compound.

Among the hexagonal phases, it was found that the relative intensities in the patterns of $Ba_3ReCr_2O_9$, $Ba_3ReFe_2O_9$, and $Ba_3OsTi_2O_9$ corresponded closely to those reported for $Ba_3IrTi_2O_9$.[3] Attempts to vary the ratio of rhenium to chromium led to products containing impurities. Contrary to this, the hexagonal phases of osmium containing manganese, iron, cobalt, or nickel gave X-ray patterns which could be completely accounted for on the basis of the hexagonal barium titanate structure when the composition was made to correspond with the formula Ba_2BOsO_6.

Variation in the composition of a mixture did not always lead to an impure product. The phase of composition Sr_2CrReO_6 gave the cubic ordered perovskite structure, for which the calculated and observed relative intensities are given in Table III. When the composition was changed to correspond to $Sr_3Cr_2ReO_9$ no new phase appeared but the lattice expanded slightly and the relative intensities of the super-lattice lines showed a marked decrease.

Magnetic susceptibility measurements were made on the phases Ba_2LiOsO_6, $Ba_2LiOs_{1/2}Re_{1/2}O_6$, and Ba_2CaOsO_6. The Gouy balance used for these measurements has been described previously.[3] The measurements were made over the temperature range −20 to +80°. These results

---

(3) J. G. Dickinson, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **83**, 3026 (1961).

were obtained

	μ_{eff}	No. of unpaired electrons per Os atom
Ba_2LiOsO_6	1.44	0.75
$Ba_2LiOs_{1/2}Re_{1/2}O_6$	1.79	1.1
Ba_2CaOsO_6	2.20	1.4

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR Ba_2CaOsO_6

hkl	$\sin^2\theta$ obsd.	$\sin^2\theta$ calcd.	I obsd.	I calcd.
111	0.0252	0.0254	18.7	18.9
220	.0676	.0678	100.0	100.0
311	.0930	.0932	11.8	11.7
222	.1015	.1017	3.6	3.3
400	.1354	.1356	30.1	30.0
331	.1608	.1610	4.8	6.1
422	.2032	.2034	39.7	41.2
333 511	.2290	.2288	4.8	4.7
440	.2713	.2712	16.7	18.5
531	.2966	.2966	4.3	4.6
442	.3054	.3951	0.5	0.5
620	.3391	.3390	14.8	17.8
533	.3644	.3644	1.5	1.7
444	.4070	.4068	5.9	6.1
711 551	.4324	.4322	2.6	2.6
642	.4749	.4746	17.4	21.5
731 553	.5002	.5000	3.0	3.3
800	.5420	.5424	3.6	3.1
733	.5678	.5678	1.1	1.0
822 660	.6103	.6102	11.1	13.1
751 555	.6353	.6356	2.0	2.2
662	.6441	.6441	0.4	0.3
840	.6781	.6780	8.9	11.5
911 753	.7032	.7034	2.0	2.2
664	.7461	.7458	6.9	9.2
931	.7712	.7712	2.0	2.1
844	.8137	.8136	8.2	13.9
933 771 755	.8390	.8390	2.0	3.7
1020 862	.8815	.8814	18.4	39.8
773 951	.9068	.9068	2.5	4.8

Saturation magnetization values were obtained using a magnetometer of the moving coil type. The data are for liquid helium temperature and are listed in Table IV. The phases Sr_2CrReO_6 and Ca_2CrReO_6 were found to be magnetic at room temperatures.

Lattice constants (in Å.) were determined for the following compounds having the ordered perovskite structure. $Sr_3Cr_2ReO_9$ (8.01_5); $Sr_3Fe_2ReO_9$ (7.89_0); $Sr_3In_2ReO_9$ (8.297); Ba_2NdReO_6 (8.51); Ba_2LaReO_6 (8.58); Ba_2YReO_6 (8.372); Ba_2GdReO_6 (8.431); Ba_2ErReO_6 (8.354); Ba_2NaIO_6 (8.33). Two phases with the hexagonal barium titanate structure are: $Ba_3Fe_2ReO_9$ (a = 5.03, c = 14.10) and $Ba_3Cr_2ReO_9$ (a = 4.94, c = 13.8).

TABLE III

X-RAY POWDER DIFFRACTION DATA FOR Sr_2CrReO_6

hkl	$\sin^2\theta$ obsd.	$\sin^2\theta$ calcd.	I obsd.	I calcd.
111	0.0288	0.0291	16.5	23.0
200	.0384	.0388	7.7	6.2
220	.0773	.0776	100.0	100.0
311	.1064	.1067	5.2	14.4
222	.1163	.1164	1.1	3.4
400	.1552	.1552	32.4	29.0
331	.1840	.1843	3.9	6.8
420	.1942	.1940	3.1	2.4
422	.2328	.2328	35.3	35.3
333 511	.2615	.2619	1.8	5.2
440	.3105	.3105	17.1	16.4
531	.3397	.3396	3.1	5.4
620	.3488	.3393	2.1	1.0
533	.4175	.4172	0.6	2.0
622	.4263	.4269	0.5	0.1
444	.4660	.4657	4.3	5.6
711 551	.4948	.4948	1.2	0.3
642	.5430	.5430	15.5	19.9
731 553	.5722	.5723	1.8	4.4
800	.6210	.6208	2.2	3.2
733	.6506	.6499	0.8	1.4
660	.6986	.6984	9.6	13.9
751 555	.7276	.7275	1.9	3.5
840	.7760	.7760	8.8	14.2
911 753	.8045	.8051	1.3	5.2
664	.8536	.8536	7.3	12.1
931	.8830	.8827	1.4	4.4
844	.9313	.9312	12.7	25.1

TABLE IV

SATURATION MOMENTS FOR SOME ORDERED PEROVSKITE PHASES

Compound	μ found	μ predicted (spin only) Re^V	Re^{VI}
Ba_2FeReO_6	1.15	1.5	1.5
$BaSrFeReO_6$	0.62	1.5	1.5
Sr_2FeReO_6	1.26	1.5	1.5
Ca_2FeReO_6	1.01	1.5	1.5
Ba_2MnReO_6	0.58	1.0	2.0
Sr_2MnReO_6	.75	1.0	2.0
Ca_2MnReO_6	.23	1.0	2.0
Ba_2CoReO_6	.05	0 (low spin Co^{III}) 1.0 (high spin Co^{III})	1.0
Ba_2GdReO_6	1.39	2.5	
Ba_2ErReO_6	1.08	0.5	

Discussion

Perhaps the most interesting example of the adjustment of the oxidation state by valence compensation is the preparation of the compounds Ba_2LiOsO_6 and Ba_2NaOsO_6. If the compounds are stoichiometric, the valence of osmium would be 7, a value not hitherto reported for osmium so far as we are aware. The compounds are isotypic with the rhenium compounds and solid solutions $Ba_2LiOs_{1-x}Re_xO_6$ are obtained readily. The magnetic susceptibility of the phase Ba_2LiOsO_6 is in support of heptavalent osmium. The low value of 0.75 unpaired electron per osmium atom may be due to the rather high electrical conductivity of the compound or to some Os–Os interaction in the crystal. Replacement of half of the osmium with rhenium brings the number of unpaired electrons to 1.0 per osmium atom although the interpretation $Ba_2LiOs_{1/2}{}^{VIII}Re_{1/2}{}^{VI}O_6$ would agree equally well. Attempts were made to determine the oxidation state of osmium in these compounds by potentiometric titrations using ceric ion as the oxidizing agent. The OsO_4 liberated in the reaction, however, appears to be a catalyst for the reduction of ceric ion and the procedure was found to be quite unreliable. The osmium content of the product was estimated by fuming a sample with sulfuric and nitric acids. This removed all the osmium as OsO_4, leaving a residue of barium and alkali metal sulfate which was weighed. The percentage of osmium given by this procedure was 33.2 (32.6% calcd.). A complete analysis of these products is not very significant unless some purification can be brought about. The short heating times and relatively low temperatures used to prepare these samples would not be likely to cause any loss of barium or alkali metal from the mixture. Osmium is the only metal in the mixtures which might be removed by heating in air. This apparently did not occur. It seems reasonable to suppose that the osmium is present in Ba_2NaOsO_6 in the heptavalent state but these systems should be examined more closely. It is possible to prepare the oxygen-deficient compound $Ba_2LiReO_{5.5}$. The possibility of oxygen deficiency in the osmium compounds exists but does not seem likely because of the method of preparation. The corresponding compounds were made with strontium and calcium in the A position, osmium and rhenium in the B position, and lithium as the compensating ion. With sodium in place of lithium, however, comparable compounds of osmium and rhenium were obtained with strontium in the A position. The compound Ca_2NaOsO_6 was obtained but attempts to make the rhenium analog invariably led to the formation of sodium perrhenate.

The only other heptavalent ion with a tendency toward octahedral coördination is iodine. It is interesting that a compound with the ordered perovskite structure can be obtained by heating a mixture of barium oxide and sodium iodate in air at 400°. Some loss of iodine was observed. The same compound is precipitated from a solution of sodium periodate upon the addition of barium hydroxide. The compound is presumably Ba_2NaIO_6.

Hexavalent osmium is obtained readily by using a divalent cation for valence compensation. The compound Ba_2CaOsO_6 gave a very clean X-ray diffraction pattern. The observed intensities of reflections and those calculated on the basis of the ordered perovskite structure agree well, as is shown in Table II. Magnetic susceptibility measurements indicate 1.4 unpaired electrons per osmium atom, which perhaps is consistent with the value obtained for the lithium compound. The percentage of osmium found by analysis was 31.1 (31.6% theory). The cubic perovskite structure was obtained in each case when the divalent compensating ion is diamagnetic. In contrast to the behavior of rhenium, however, all of the divalent transition metals led to products having the hexagonal barium titanate structure when the A cation was barium. It is quite possible that the oxidation states of the transition metals in these compounds are to be represented as $Ba_2M^{III}Os^{V}O_6$.

With strontium as the A cation, phases with the ordered perovskite type of structure were obtained with hexavalent rhenium or osmium with all of the divalent diamagnetic cations listed in Table I except that no compound could be obtained in the Sr–Zn–Os system. It may be of some interest to note that in the tetragonal compounds Ba_2BaReO_6, Ba_2BaOsO_6, and Ba_2SrReO_6 c/a is less than unity whereas in Ba_2SrOsO_6 c/a is greater than unity.

Neither Sr_2FeOsO_6 nor Sr_2CoOsO_6 was magnetic at room temperatures. The saturation magnetizations of Sr_2FeReO_6 and Sr_2MnReO_6 agree best with the assumption that the manganese is trivalent and the rhenium pentavalent. If this also were to hold in the case of Sr_2CoReO_6, the absence of ferrimagnetism in this compound could be due to the diamagnetic character of Co^{III} in octahedral coördination. This explanation is perhaps more plausible than the suggestion that the compound was antiferromagnetic.[2] The latter would lead one to predict that Sr_2CoOsO_6 would be ferrimagnetic. The magnetic properties of this compound have not been studied but it is not ferromagnetic at room temperatures.

The compound Sr_2CrReO_6 is ferromagnetic at room temperatures. The structural data given in Table III show clearly that this substance is of the ordered perovskite type but suggest that the ordering is not complete. The intensities of all of the super-lattice lines lie far below the calculated values. Qualitative observation of the pattern of $Sr_3Cr_2ReO_4$ shows that all of the ordering lines are relatively less intense. A quantitative correlation of the variation in ordering with the magnetic properties is planned.

The corresponding osmium compound Sr_2CrOsO_6 is not ferromagnetic at room temperatures. It seems reasonable to suppose that it is antiferrimagnetic. Hexavalent compounds of rhenium and osmium are not formed readily with calcium in the A position. Mixtures of calcium and magnesium oxides with metallic osmium heated in air gave a product with the same lattice constants as those obtained from calcium oxide and osmium metal. Manganese, iron, cobalt, and nickel all yield ordered perovskite phases when their monoxides or the equivalent are heated *in vacuo* with ReO_3 and calcium oxide, but only cobalt gave a corresponding phase with osmium. These differences probably are to be attributed to the difference in methods of preparation. The readiness with which the cobalt compound is obtained indicates some additional stabilization energy which may be due to the formation of trivalent cobalt in octahedral association with oxygen. It should be noted that chromium also yields stable phases with rhenium and osmium in combination with all of the A cations. In this case, however, the osmium compounds were able to be prepared under controlled conditions.

The incidence of the hexagonal barium titanate structure among these compounds is of considerable interest. In general the explanation put forward by Dickinson[3] seems to be upheld. The additional electron introduced by the substitution of osmium for rhenium could provide the extra lattice energy in the formation of a metal–metal bond between the transition metals. The only rhenium compounds which were obtained with the hexagonal structure appear to contain hexavalent rhenium and correspond to the formulas $Ba_3Re^{VI}Cr_2^{III}O_9$ and $Ba_3Re^{VI}Fe_2^{III}O_9$. The relative intensities of the reflections in the X-ray patterns of these compounds agree closely with those obtained by Dickinson for $Ba_3IrTi_2O_9$. Hence one would conclude that the rhenium adopts the fourfold position in the lattice. The osmium compounds, however, do not appear to conform to this formula. The pattern obtained from mixtures designed to give Ba_2FeOsO_6 corresponds well with that given by Ba_2FeIrO_6, which appears to have an ordered hexagonal barium titanate structure.[4] The suggestion of Dickinson that to get the hexagonal barium titanate structure both B cations must be transition metals and that one of them must have d electrons appears to hold with the rhenium and osmium compounds. The compounds Ba_2ScReO_6, Ba_2ScOsO_6, and $BaInReO_6$ are of the cubic ordered perovskite type. We have found, however, that the compounds Ba_2IrScO_6 and Ba_2IrInO_6 have the hexagonal barium titanate structure. The latter would appear to be an exception to the generalization. No hexagonal phases have been found with A cations other than barium. The size of the B cation is also a factor in the preparation of these compounds. While many trivalent cations are readily incorporated into this lattice, it is noteworthy that gallium does not give a perovskite phase with barium as the A cation but does so readily with strontium.[5] A few compounds of rhenium with rare earth elements as B cations have been made. They have the ordered perovskite structure and it is of some interest to note that the compounds Ba_2GdReO_6 and Ba_2ErReO_6 are magnetic at liquid helium temperatures. A systematic study of these compounds is being initiated.

Many of the rhenium compounds which had been prepared *in vacuo* were found to be unstable when heated in air at 1000° for a few minutes. The products obtained in many instances have a structure of the $Ba_5Ta_4O_{15}$ type.[6] This metamorphosis will be investigated further.

We are grateful to Dr. Aaron Wold of the Lincoln Laboratory for arranging for the measurement of magnetic moments of some of our preparations. This research was carried out under a grant from the National Science Foundation.

---

[4] Master's Thesis of A. Paton, University of Connecticut, 1962.

[5] R. Roy, *J. Am. Ceram. Soc.*, **37**, 581 (1954).

[6] F. Galasso and L. Katz, *Acta Cryst.*, **14**, 647 (1961).