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# The Crystal Structure of Barium Ruthenium Oxide and Related Compounds

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Barium ruthenium oxide ($BaRuO_3$) provides another example of a complex oxide structure based on essentially close-packed stacking of close-packed $BaO_3$ layers. The crystal lattice type is rhombohedral. Repetition in the hexagonal $c$ direction occurs after nine layers. The ruthenium ions are in octahedral sites. These octahedra are in strings of three sharing faces, and the strings are linked by corner sharing. The face sharing of the octahedra leads to a Ru–Ru–Ru arrangement in which the interionic separation is 2.55 Å., thus suggesting intermetallic bonding. There is evidence that $BaIrO_3$ and $BaPtO_3$ form similar structures. In addition, the isomorphous substitution of manganese for ruthenium has been carried out.

## Introduction

Complex oxides containing large cations in the ratio of one large cation (A) to three oxygens often have structures which may be described on the basis of close-packed $AO_3$ layers.[1] These layers are then stacked in a variety of close-packed sequences. Examples for different numbers of layers ($n$) in the hexagonal unit cell are $n = 2$, $BaNiO_3$[2]; $n = 3$, simple perovskites; $n = 4$, the high-temperature form of $BaMnO_3$[3]; $n = 5$, $Ba_5Ta_4O_{15}$[4]; $n = 6$, hexagonal barium titanate.[5] Twelve-layer and pseudo-eight-layer complex oxides have also been prepared.[6]

The close-packed stacking of $AO_3$ layers leads to the formation of one octahedron of oxygens for each $AO_3$ unit. If all the octahedra are occupied by B cations, the formula of the compound is $ABO_3$. If some of the octahedra are occupied by B cations but others are empty, the formula is $A_mB_nO_{3m}$ where $n$ is less than $m$.

The X-ray powder pattern of a compound prepared by Randall[7] from the reaction of a 1:1 mixture of ruthenium powder with BaO in air at 1000° was re-indexed on the basis of a hexagonal unit cell of dimensions $a = 5.75$, $c = 21.60$ Å. The $a$ axis corresponds to the usual close-packed dimension in a $BaO_3$ layer. The $c$ axis is about nine times the thickness of a $BaO_3$ layer (roughly 2.25 to 2.45 Å.). The compound was, therefore, examined as a possible example of a nine-layer structure.

## Experimental

**Preparation.**—$BaRuO_3$ was prepared by reaction of a mixture of barium peroxide and ruthenium powders in air at 1000° which may be represented by the equation

$$BaO_2 + Ru + {}^1\!/_2O_2 \xrightarrow[1000^\circ]{} BaRuO_3$$

The use of the peroxide instead of the oxide or carbonate led to products having X-ray powder patterns free from lines of impurities. The compound was insoluble in most acids except concentrated HCl, so that purification of the phase was relatively easy.

Single crystals were grown by using $BaCl_2$ as a flux mixed with $BaRuO_3$ powder in a ratio of 8:1. The mixture was heated to 1000° and cooled slowly. Black hexagonal plates of BaRuO formed which were separated from the $BaCl_2$ and crystals of a red phase by leaching with dilute HCl.

**Analysis and Density.**—The crystalline product was analyzed gravimetrically for ruthenium and barium. Ruthenium was determined as the metal by reduction of the hydrous oxide obtained from a solution of the crystals in hydrochloric acid. The solution was evaporated to dryness. The residue upon addition of water yielded the hydrous oxide. Barium was determined from the filtrate by precipitation as the sulfate. *Anal.* Calcd. for $BaRuO_3$: Ba, 48.0; Ru, 35.3. Found: Ba, 47.6; Ru, 35.6.

The density, measured pycnometrically, was found to be 6.90 ± 0.05 g./cc. The calculated value for $BaRuO_3$ is 6.89 g./cc.

## Structure Determination

**Powder Data.**—With the X-ray powder pattern indexed on the basis of the hexagonal unit cell with $a = 5.75$, $c = 21.60$ Å., the indices were consistent with the rhombohedral absence rule, $-h + k + l = 3n$. Using h to stand for a "hexagonal" layer (the two neighboring layers the same) and c to stand for a "cubic" layer (the two neighboring layers different), the rhombohedral nine-layer close-packed stacking sequence is chh.[1] The oxygen octahedra in this structure are in strings of three, sharing faces (the middle octahedron of the three shares two faces). The strings are linked by corner sharing. Figures 1 and 2 show the stacking sequence and the arrangement of octahedra.

With all the octahedral sites occupied by ruthenium ions, the $R$ factor *based on intensities* was reasonable for a correct structural arrangement, 16.0%. Powder data are given in Table I. A calculation performed before the analysis and density were obtained, in which one-third of the octahedral sites were left empty according to a nine-layer model postulated in ref. 1, showed large discrepancies. The subsequent chemical analysis, of course, also established the empirical formula $BaRuO_3$, rather than $Ba_3Ru_2O_9$.

**Single Crystal Data.**—The unit cell dimensions were confirmed using a rotation photograph around $c$ and Weissenberg photographs. Intensity data were collected from precession photographs and corrected for Lorentz and polarization effects. The data were partly corrected for absorption effects by assuming the crystal to be a sphere of volume equal to that of the actual crystal.

The calculation of structure factors and the refinement of parameters were carried out using the Busing,

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(1) L. Katz and R. Ward, *Inorg. Chem.*, **3**, 205 (1964).
(2) J. J. Lander, *Acta Cryst.*, **4**, 148 (1951).
(3) A. Hardy, *ibid.*, **15**, 179 (1962).
(4) F. Galasso and L. Katz, *ibid.*, **14**, 647 (1961).
(5) R. D. Burbank and H. T. Evans, Jr., *ibid.*, **1**, 330 (1948).
(6) J. Longo, L. Katz, and R. Ward, submitted for publication.
(7) J. J. Randall and R. Ward, *J. Am. Chem. Soc.*, **81**, 2629 (1959).

TABLE I

X-RAY POWDER DATA FOR $BaRuO_3$

| H | K | L | DOBS | DCAL | IOBS | ICAL |
|---|---|---|---|---|---|---|
| 1 | 0 | 1 | 4.870 | 4.852 | 12.7 | 7.2 |
| 0 | 1 | 2 | 4.557 | 4.522 | .9 | .4 |
| 1 | 0 | 4 | 3.668 | 3.661 | 15.9 | 15.4 |
| 0 | 1 | 5 | 3.270 | 3.263 | 55.8 | 50.4 |
| 1 | 1 | 0 | 2.885 | 2.875 | 101.9 | 100.0 |
| 1 | 0 | 7 | 2.627 | 2.623 | 19.3 | 17.1 |
| 0 | 0 | 9 | 2.400 | 2.400 |  | 3.2 |
| 0 | 1 | 8 | 2.377 | 2.374 | 31.4 | 20.0 |
| 0 | 2 | 4 | 2.261 | 2.261 | 16.5 | 14.5 |
| 1 | 1 | 6 | 2.250 | 2.246 |  | 1.8 |
| 2 | 0 | 5 | 2.159 | 2.157 | 24.6 | 30.5 |
| 1 | 0 | 10 | 1.983 | 1.982 | 15.9 | 13.6 |
| 0 | 2 | 7 | 1.937 | 1.938 | 9.4 | 9.5 |
| 2 | 1 | 1 | 1.873 | 1.875 | .4 | .5 |
| 1 | 1 | 9 | 1.840 | 1.842 |  | .7 |
| 2 | 0 | 8 | 1.831 | 1.830 | 18.4 | 14.4 |
| 0 | 1 | 11 | 1.825 | 1.827 |  | .7 |
| 0 | 0 | 12 | 1.801 | 1.800 | .5 | .3 |
| 2 | 1 | 4 | 1.776 | 1.777 | 2.9 | 3.8 |
| 1 | 2 | 5 | 1.725 | 1.725 | 14.8 | 15.7 |
| 3 | 0 | 0 | 1.660 | 1.660 | 23.7 | 20.1 |
| 0 | 2 | 10 | 1.631 | 1.632 | 9.0 | 9.6 |
| 2 | 1 | 7 | 1.606 | 1.607 | 7.5 | 8.3 |
| 1 | 0 | 13 | 1.576 | 1.576 | 3.4 | 4.3 |
| 1 | 2 | 8 | 1.542 | 1.544 | 14.6 | 11.7 |
| 1 | 1 | 12 | 1.526 | 1.526 | .9 | .9 |
| 0 | 1 | 14 | 1.473 | 1.474 | 3.9 | 3.9 |
| 2 | 2 | 0 | 1.437 | 1.437 | 17.1 | 18.1 |
| 2 | 1 | 10 | 1.418 | 1.418 | 10.5 | 10.0 |
| 0 | 2 | 13 | 1.381 | 1.382 | 5.4 | 5.2 |
| 1 | 3 | 1 | 1.372 | 1.378 |  | .3 |
| 3 | 0 | 9 | 1.362 | 1.365 | .9 | .2 |
| 1 | 2 | 11 | 1.359 | 1.359 |  | .2 |
| 1 | 3 | 4 | 1.337 | 1.338 | .9 | 1.9 |
| 3 | 1 | 5 | 1.316 | 1.315 | 9.4 | 7.1 |
| 2 | 0 | 14 | 1.312 | 1.311 |  | 4.1 |
| 1 | 3 | 7 | 1.259 | 1.261 | 6.3 | 3.5 |
| 2 | 1 | 13 | 1.245 | 1.246 | 6.4 | 3.8 |
| 2 | 2 | 9 |  | 1.233 |  | 1.5 |
| 0 | 1 | 17 | 1.229 | 1.231 | 5.9 | 1.1 |
| 3 | 1 | 8 |  | 1.230 |  | 5.0 |
| 4 | 0 | 4 | 1.210 | 1.213 | 2.1 | 1.5 |
| 0 | 0 | 18 | 1.199 | 1.200 |  | 2.6 |
| 0 | 4 | 5 | 1.196 | 1.196 | 10.3 | 3.9 |
| 1 | 2 | 14 | 1.193 | 1.193 |  | 3.7 |
| 1 | 3 | 10 | 1.163 | 1.164 | 4.3 | 4.9 |
| 4 | 0 | 7 | 1.154 | 1.154 | .9 | 1.6 |
| 0 | 4 | 8 |  | 1.131 |  | 2.7 |
| 2 | 0 | 17 | 1.130 | 1.132 | 2.1 | .4 |
| 3 | 1 | 11 |  | 1.130 |  | .4 |
| 3 | 2 | 4 | 1.119 | 1.118 | 1.7 | 1.2 |
| 1 | 1 | 18 | 1.107 | 1.107 |  | 8.6 |
| 2 | 3 | 5 | 1.104 | 1.104 | 12.8 | 4.5 |
| 2 | 1 | 16 |  | 1.097 |  | .3 |
| 4 | 1 | 0 | 1.086 | 1.087 | 8.6 | 5.4 |
| 4 | 0 | 10 | 1.078 | 1.079 | .7 | 2.5 |
| 3 | 2 | 7 | 1.071 | 1.071 | .4 | 2.1 |
| 1 | 3 | 13 | 1.060 | 1.062 | 2.7 | 1.7 |
| 1 | 2 | 17 |  | 1.053 |  | 1.2 |
| 2 | 3 | 8 | 1.051 | 1.052 | 4.3 | 3.1 |
| 0 | 4 | 11 |  | 1.051 |  | .2 |
| 0 | 2 | 19 | 1.029 | 1.034 | .8 | .5 |
| 3 | 1 | 14 |  | 1.029 |  | 2.9 |
| 3 | 2 | 10 | 1.009 | 1.010 | 1.7 | 3.4 |
| 4 | 0 | 13 | .998 | .996 |  | 2.1 |
| 2 | 1 | 19 |  | .973 |  | .9 |
| 3 | 0 | 18 | .972 | .972 | 8.3 | 3.5 |
| 5 | 5 | 0 |  | .970 |  | 1.6 |
| 0 | 4 | 14 | .970 | .969 |  | 2.0 |
| 3 | 3 | 0 | .958 | .958 | 1.8 | 4.8 |
| 3 | 1 | 17 | .937 | .937 |  | 1.3 |
| 5 | 0 | 8 |  | .935 |  | 1.8 |
| 1 | 4 | 12 | .928 | .930 | 2.5 | .3 |
| 2 | 4 | 4 |  | .927 |  | 1.9 |
| 0 | 1 | 23 | .923 | .923 |  | 1.2 |
| 2 | 2 | 18 | .921 | .921 | 14.3 | 10.1 |
| 4 | 2 | 5 | .919 | .919 |  | 5.2 |

Levy, and Martin least-squares program adapted for use on the I.B.M. 7040 by the University of Connecticut computer staff. Isotropic temperature factors were used for the individual atoms. Some of these temperature factors tended to go negative; these were fixed at zero and the remaining parameters were refined. The final $R$ factor (216 independent reflections) was 11.8%. The final parameters are shown in Table II. The observed and calculated structure factors are listed in Table III.

## Discussion

The structure of $BaRuO_3$ may be described as a nine-layer stacking of $BaO_3$ layers in the sequence chh. This leads to strings of three face-sharing octahedra; the strings are held together by corner sharing. All of the octahedral sites are occupied (by ruthenium ions). This is different from the situations in $Ba_5Ta_4O_{15}$ (five-layer) and $Ba_4Re_2CoO_{12}$ (twelve-layer) in which the central octahedra of the strings of three are vacant.

TABLE II

ATOMIC POSITIONS FOR $BaRuO_3$

Space Group $R\bar{3}m$[a]

Hexagonal Axes

$(0, 0, 0;\ ^1/_3, ^2/_3, ^2/_3;\ ^2/_3, ^1/_3, ^1/_3) +$

| | | |
|---|---|---|
| 3 $Ba_I$ in (a) | 0, 0, 0 | |
| 6 $Ba_{II}$ in (c) | $0, 0, z;\ 0, 0, \bar{z}$ | $z = 0.2181 \pm 0.0002$ |
| 3 $Ru_I$ in (b) | $0, 0, ^1/_2$ | |
| 6 $Ru_{II}$ in (c) | $0, 0, z;\ 0, 0, \bar{z}$ | $z = 0.3819 \pm 0.0003$ |
| 9 $O_I$ in (e) | $^1/_2, 0, 0;\ 0, ^1/_2, 0;$<br>$^1/_2, ^1/_2, 0$ | |
| 18 $O_{II}$ in (h) | $x, \bar{x}, z;\ x, 2x, z;\ 2\bar{x}, \bar{x}, z;$<br>$\bar{x}, x, \bar{z};\ \bar{x}, 2\bar{x}, \bar{z};\ 2x, x, \bar{z}$ | $x = 0.156 \pm 0.004$<br>$z = 0.558 \pm 0.001$ |

[a] Although the X-ray data were consistent with the space groups R32, R3m, and $R\bar{3}m$, the last was assumed. It is the space group for the rhombohedral nine-layer close-packed stacking.

A check on whether the "central" octahedra were completely occupied was made by using the fraction of these sites occupied as a parameter of the refinement. The $R$ factor decreased steadily with increas-

Table III

Observed and Calculated Structure Factors

| H | K | L | FOBS | FCAL | H | K | L | FOBS | FCAL | H | K | L | FOBS | FCAL | H | K | L | FOBS | FCAL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 6 | 68 | 52 | 2 | 2 | 24 | 97 | 83 | 4 | 0 | 16 | 72 | 34 | -1 | 0 | 23 | 155 | 137 |
| 0 | 0 | 9 | 169 | 161 | 3 | 0 | 0 | 288 | 373 | 4 | 0 | 19 | 83 | 78 | -1 | 0 | 26 | 138 | 191 |
| 0 | 0 | 12 | 101 | 74 | 3 | 0 | 6 | 57 | 41 | 4 | 0 | 22 | 91 | 73 | -1 | 0 | 29 | 34 | 44 |
| 0 | 0 | 18 | 351 | 333 | 3 | 0 | 9 | 53 | 39 | 4 | 1 | 0 | 220 | 254 | -2 | 0 | 4 | 205 | 217 |
| 0 | 0 | 24 | 169 | 132 | 3 | 0 | 12 | 82 | 62 | 4 | 1 | 6 | 44 | 36 | -2 | 0 | 7 | 194 | 215 |
| 0 | 0 | 27 | 82 | 81 | 3 | 0 | 18 | 250 | 244 | 4 | 1 | 12 | 62 | 52 | -1 | 0 | 23 | 155 | 137 |
| 0 | 0 | 30 | 78 | 70 | 3 | 0 | 24 | 155 | 133 | 4 | 1 | 18 | 195 | 186 | -2 | 0 | 13 | 224 | 234 |
| 1 | 0 | 1 | 85 | 66 | 3 | 0 | 27 | 45 | 47 | 4 | 1 | 24 | 105 | 101 | -2 | 0 | 16 | 50 | 42 |
| 1 | 0 | 4 | 124 | 127 | 3 | 1 | 5 | 163 | 173 | 4 | 1 | -6 | 52 | 28 | -2 | 0 | 22 | 105 | 88 |
| 1 | 0 | 7 | 184 | 201 | 3 | 1 | 8 | 152 | 158 | 4 | 1 | -12 | 56 | 44 | -2 | 0 | 22 | 105 | 88 |
| 1 | 0 | 10 | 229 | 250 | 3 | 1 | 11 | 62 | 44 | 4 | 1 | -18 | 175 | 183 | -2 | 0 | 25 | 176 | 162 |
| 1 | 0 | 13 | 185 | 183 | 3 | 1 | 14 | 125 | 132 | 4 | 2 | 5 | 181 | 182 | -2 | 0 | 28 | 150 | 131 |
| 1 | 0 | 16 | 92 | 63 | 3 | 1 | 17 | 111 | 86 | 4 | 2 | 8 | 169 | 160 | -2 | 1 | 6 | 47 | 47 |
| 1 | 0 | 19 | 97 | 85 | 3 | 1 | 23 | 126 | 102 | 4 | 2 | 11 | 62 | 55 | -2 | 1 | 9 | 32 | 34 |
| 1 | 0 | 22 | 68 | 51 | 3 | 1 | 26 | 106 | 78 | 4 | 2 | 14 | 128 | 143 | -2 | 1 | 12 | 69 | 65 |
| 1 | 0 | 25 | 184 | 154 | 3 | 1 | -1 | 56 | 33 | 4 | 2 | 17 | 86 | 68 | -2 | 1 | 18 | 206 | 223 |
| 1 | 0 | 28 | 153 | 134 | 3 | 1 | -4 | 99 | 86 | 4 | 2 | 23 | 117 | 114 | -2 | 1 | 24 | 117 | 118 |
| 1 | 1 | 0 | 271 | 302 | 3 | 1 | -7 | 138 | 124 | 4 | 2 | 26 | 109 | 85 | -2 | 1 | 30 | 82 | 63 |
| 1 | 1 | 6 | 53 | 39 | 3 | 1 | -10 | 160 | 165 | 4 | 2 | -4 | 122 | 109 | -3 | 2 | 28 | 134 | 121 |
| 1 | 1 | 9 | 37 | 28 | 3 | 1 | -13 | 135 | 128 | 4 | 2 | -7 | 147 | 128 | -3 | 2 | -26 | 108 | 89 |
| 1 | 1 | 12 | 74 | 53 | 3 | 1 | -16 | 65 | 41 | 4 | 2 | -10 | 174 | 161 | -4 | 0 | 5 | 232 | 237 |
| 1 | 1 | 18 | 209 | 183 | 3 | 1 | -19 | 62 | 62 | 4 | 2 | -13 | 153 | 147 | -4 | 0 | 8 | 221 | 206 |
| 1 | 1 | 24 | 127 | 97 | 3 | 1 | -22 | 40 | 38 | 4 | 2 | -16 | 34 | 32 | -4 | 0 | 11 | 93 | 80 |
| 1 | 1 | 27 | 47 | 33 | 3 | 1 | -25 | 125 | 116 | 4 | 2 | -19 | 44 | 64 | -4 | 0 | 14 | 183 | 179 |
| 2 | 0 | 2 | 47 | 26 | 3 | 1 | -28 | 105 | 102 | 4 | 2 | -22 | 56 | 61 | -4 | 0 | 17 | 101 | 76 |
| 2 | 0 | 5 | 273 | 334 | 3 | 2 | 1 | 58 | 36 | 4 | 2 | -25 | 125 | 121 | -4 | 0 | 20 | 50 | 37 |
| 2 | 0 | 8 | 254 | 279 | 3 | 2 | 4 | 104 | 90 | 4 | 2 | -28 | 109 | 101 | -4 | 0 | 23 | 138 | 135 |
| 2 | 0 | 11 | 114 | 80 | 3 | 2 | 7 | 136 | 125 | 4 | 4 | 0 | 186 | 175 | -4 | -2 | 4 | 97 | 87 |
| 2 | 0 | 14 | 222 | 220 | 3 | 2 | 10 | 156 | 162 | 5 | 0 | 5 | 176 | 165 | -4 | -2 | 7 | 105 | 103 |
| 2 | 0 | 17 | 114 | 85 | 3 | 2 | 13 | 150 | 132 | 5 | 0 | 8 | 189 | 167 | -4 | -2 | 10 | 139 | 129 |
| 2 | 0 | 20 | 47 | 42 | 3 | 2 | 16 | 43 | 46 | 5 | 0 | 11 | 74 | 45 | -4 | -2 | 13 | 113 | 118 |
| 2 | 0 | 23 | 178 | 154 | 3 | 2 | 19 | 44 | 59 | 5 | 0 | 14 | 139 | 129 | -4 | -2 | 25 | 80 | 97 |
| 2 | 0 | 26 | 157 | 120 | 3 | 2 | 25 | 125 | 117 | 5 | 0 | 17 | 125 | 88 | -4 | -2 | 28 | 52 | 81 |
| 2 | 1 | 1 | 44 | 33 | 3 | 2 | 28 | 113 | 104 | 5 | 2 | 0 | 198 | 231 | -5 | 0 | 4 | 100 | 80 |
| 2 | 1 | 4 | 88 | 88 | 3 | 2 | -5 | 163 | 177 | 5 | 2 | 18 | 157 | 169 | -5 | 0 | 7 | 150 | 132 |
| 2 | 1 | 7 | 141 | 148 | 3 | 2 | -8 | 153 | 153 | 5 | 2 | 24 | 96 | 93 | -5 | 0 | 10 | 192 | 177 |
| 2 | 1 | 10 | 174 | 189 | 3 | 2 | -11 | 57 | 43 | 5 | 2 | -12 | 55 | 51 | -5 | 0 | 13 | 131 | 127 |
| 2 | 1 | 13 | 135 | 136 | 3 | 2 | -17 | 118 | 94 | 5 | 2 | -18 | 171 | 173 | -5 | 0 | 16 | 59 | 42 |
| 2 | 1 | 16 | 33 | 43 | 3 | 2 | -23 | 114 | 110 | 5 | 2 | -24 | 100 | 100 | -5 | 0 | 19 | 68 | 73 |
| 2 | 1 | 19 | 72 | 71 | 3 | 3 | 0 | 202 | 194 | 6 | 0 | 0 | 246 | 289 | -5 | 1 | 24 | 86 | 97 |
| 2 | 1 | 25 | 151 | 127 | 3 | 3 | 9 | 34 | 27 | 6 | 0 | 9 | 66 | 61 | -6 | 1 | 5 | 133 | 134 |
| 2 | 1 | 28 | 129 | 110 | 3 | 3 | 12 | 69 | 38 | 6 | 0 | 12 | 60 | 50 | -6 | 1 | 8 | 131 | 130 |
| 2 | 1 | -5 | 168 | 187 | 3 | 3 | 18 | 166 | 144 | 6 | 1 | 5 | 130 | 125 | -6 | 1 | 11 | 45 | 38 |
| 2 | 1 | -8 | 169 | 184 | 3 | 4 | -1 | 30 | 12 | 6 | 1 | 8 | 118 | 110 | -6 | 1 | 14 | 93 | 107 |
| 2 | 1 | -11 | 69 | 48 | 3 | 4 | -4 | 38 | 47 | 6 | 1 | 14 | 81 | 101 | -6 | 1 | 17 | 80 | 70 |
| 2 | 1 | -14 | 133 | 138 | 3 | 4 | -7 | 77 | 79 | 6 | 1 | 17 | 94 | 67 | -6 | 1 | 23 | 86 | 87 |
| 2 | 1 | -17 | 91 | 71 | 3 | 4 | -10 | 93 | 105 | 6 | 1 | -4 | 69 | 63 | -6 | 1 | 26 | 75 | 64 |
| 2 | 1 | -23 | 110 | 105 | 3 | 4 | -13 | 83 | 76 | 6 | 1 | -7 | 96 | 91 | -6 | 1 | -4 | 77 | 67 |
| 2 | 1 | -26 | 96 | 81 | 3 | 5 | -5 | 107 | 103 | 6 | 1 | -10 | 112 | 115 | -6 | 1 | -7 | 107 | 104 |
| 2 | 2 | 0 | 248 | 289 | 3 | 5 | -8 | 115 | 93 | 6 | 1 | -13 | 92 | 96 | -6 | 1 | -10 | 130 | 137 |
| 2 | 2 | 6 | 39 | 26 | 4 | 0 | 4 | 153 | 144 | -1 | 0 | 8 | 234 | 243 | -6 | 1 | -13 | 113 | 105 |
| 2 | 2 | 9 | 86 | 67 | 4 | 0 | 7 | 172 | 163 | -1 | 0 | 11 | 82 | 62 | -6 | 1 | -16 | 65 | 33 |
| 2 | 2 | 12 | 60 | 42 | 4 | 0 | 10 | 216 | 204 | -1 | 0 | 14 | 181 | 187 | -6 | 1 | -19 | 72 | 56 |
| 2 | 2 | 18 | 202 | 190 | 4 | 0 | 13 | 204 | 184 | -1 | 0 | 17 | 155 | 125 | -6 | 1 | -25 | 115 | 102 |

ing fraction of sites occupied and reached its lowest value at full occupancy.

The face sharing of the octahedra occupied by ruthenium atoms suggests metal–metal bonding. The Ru–Ru distance of 2.55 Å. is shorter than the closest approach distance in Ru metal, 2.65 Å. The two crystallographically different positions for ruthenium atoms would permit different oxidation states, as well as different environments, but no direct evidence concerning the oxidation states is available.

Bond distances and angles are shown in Table IV. The octahedra show some elongation which serves to increase the distance between ruthenium atoms. It is possible that cations smaller than barium in the $AO_3$

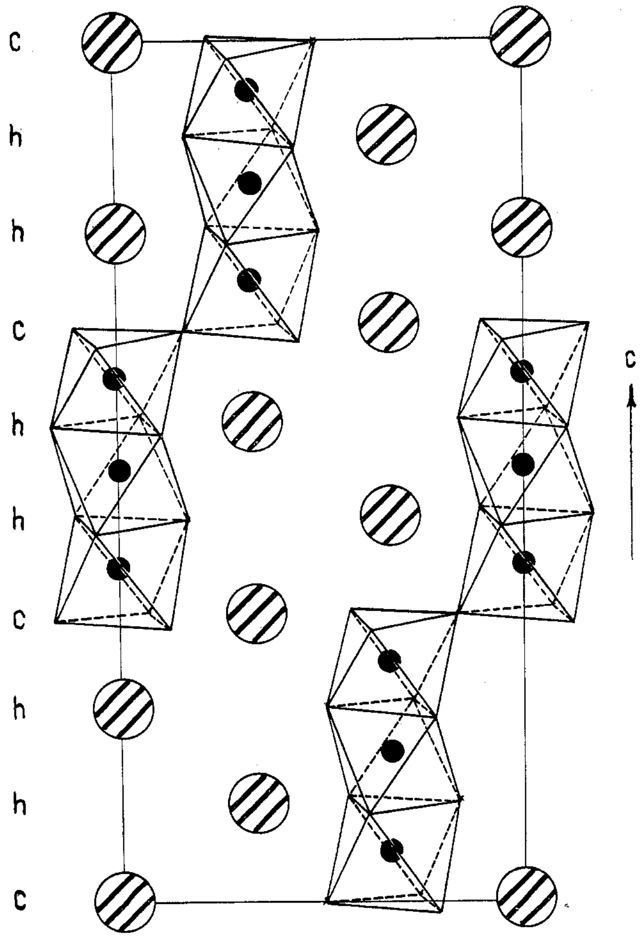

Figure 1.—Cation contents of the hexagonal 110 plane of $BaRuO_3$. Small black circles are Ru; large striped circles are Ba. Oxygen coordination around Ru is also shown. c and h represent "cubic" and "hexagonal" layers.

TABLE IV

BOND DISTANCES AND ANGLES FOR $BaRuO_3$[a]

| Atoms | Distances, Å. | | Angle, deg. |
|---|---|---|---|
| $O_1$–$Ru_1$–$O_2$ | 1.96 | 1.96 | 94.1 |
| $O_4$–$Ru_1$–$O_5$ | 2.02 | 2.02 | 83.5 |
| $O_4$–$Ru_1$–$O_3$ | 2.02 | 1.96 | 91.0 |
| $O_4$–$Ru_2$–$O_5$ | 2.00 | 2.00 | 84.7 |
| $O_4$–$Ru_2$–$O_8$ | 2.00 | 2.00 | 95.3 |
| $Ru_1$–$Ru_2$ | 2.55 | | |

[a] The standard error in the Ru–Ru distance is less than 0.01 Å. The standard errors in the $Ru_1$ to $O_1$, $O_2$, $O_3$ distances are also less than 0.01 Å. Other cation–oxygen distances have standard errors in the range 0.02–0.03 Å. The largest standard errors in the angles are about 1°.

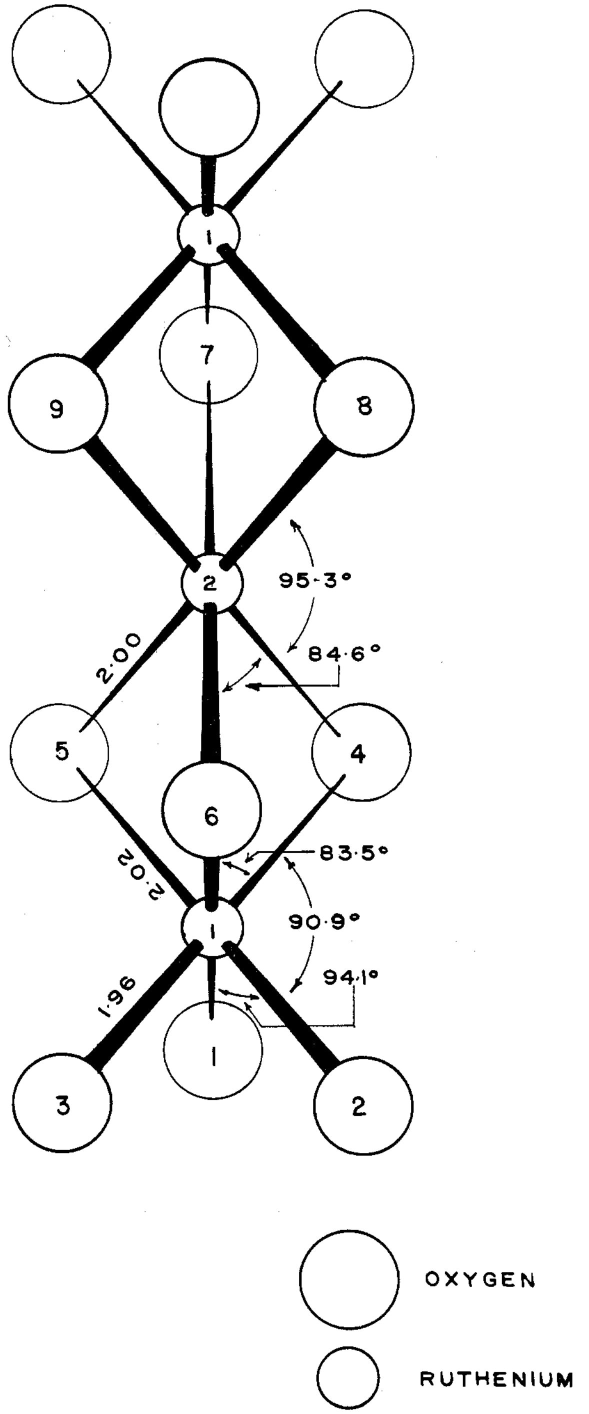

Figure 2.—Strings of three face-sharing $RuO_6$ octahedra in $BaRuO_3$.

layers would lead to instability in the structure due to reduced distances, and increased interionic repulsion, between ruthenium ions.

Other oxides which have been found to have X-ray powder patterns similar to $BaRuO_3$ are $BaIrO_3$ and $BaPtO_3$. Some attempts to replace part of the ruthenium with other ions were made. It was found that $Mn^{IV}$ will substitute for up to about 66% of the $Ru^{IV}$ with a continuous decrease in lattice parameters. Above 66% $Mn^{IV}$ lines of a new phase begin to appear in the diffraction pattern. Nickel, which forms continuous strings of $NiO_6$ octahedra-sharing faces in $BaNiO_3$, did not replace $Ru^{IV}$ but formed the hexagonal barium titanate structure when the nickel to ruthenium ratio was as small as 1:3. It is hoped that some of these results, together with findings about other nine-layer compounds, will be discussed in a later paper.

The occurrence of the sequence of three face-sharing octahedra is unusual but has been reported before. The structure of $Ba_4Ti_2PtO_{10}$[8] shows this feature. In this case the central octahedron contains platinum; the two outer octahedra contain titanium. Nickel(II)

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

acetylacetonate[9] also has a grouping of three face-sharing octahedra. These octahedra are quite elongated, however, and the Ni–Ni distances are long (2.89 Å.).

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[9] G. J. Bullen, R. Mason, and P. Pauling, *Nature*, **189**, 291 (1961).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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# Reactions of Molybdenum(V) Chloride and Molybdenum(V) Oxotrichloride with Some Oxygen and Sulfur Donor Molecules

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Complexes of the types $MoOCl_3 \cdot 2L$ and $MoOCl_3 \cdot L'$ have been prepared by the reactions of molybdenum(V) chloride and molybdenum(V) oxotrichloride with the ligands L = tetrahydrofuran, pentamethylene oxide, tetrahydrothiophene, and pentamethylene sulfide, and L' = 1,4-dioxane, 1,4-thioxane, ethylene glycol dimethyl ether, dimethyl sulfide, diethyl sulfide, and di-*n*-propyl sulfide. The compounds $MoO_2Cl_2 \cdot$2tetrahydrofuran and $MoCl_4 \cdot$2pentamethylene oxide have also been isolated. The visible and infrared spectra and the magnetic properties of these compounds have been examined and the results are discussed.

## Introduction

Very few complexes of molybdenum(V) oxotrichloride have been reported, presumably because the halide is rather difficult to prepare. Those compounds that have been characterized have been prepared from molybdenum(V) chloride. Thus Horner and Tyree[1] recently treated molybdenum(V) chloride with the oxygen-containing ligands LO (where L = $(C_6H_5)_3P$, $(C_6H_5)_3As$, and $(CH_3)_2S$) and obtained the complexes $MoOCl_3 \cdot 2LO$. It seems that oxygen is extracted from the ligand, with the transient formation of molybdenum(V) oxotrichloride, which reacts with excess of the ligand. Mitchell[2] studied the reaction of bipyridyl with the pentahalide in moist carbon tetrachloride and noted the formation of the compound $MoOCl_3 \cdot$bipy.

## Experimental

**Analysis.**—Molybdenum and chlorine were determined as described previously.[3] For sulfur determination, the compounds were fused with a $Na_2O_2$–$Na_2CO_3$ mixture in a bomb, and the sulfate formed was determined gravimetrically as $BaSO_4$. Carbon and hydrogen were determined by a professional analyst.

**Spectra.**—Visible spectra were determined on solutions in 1-cm. cells by means of a Unicam SP 600 spectrophotometer. Infrared spectra were examined on Nujol mulls with a Unicam SP 200 spectrophotometer.

**Molecular Weight.**—Determinations were made cryoscopically in benzene.[4]

**Magnetic Susceptibility and Oxidation State.**—Estimations were carried out in the usual manner.[5]

**Materials.**—$MoCl_5$ (Climax Molybdenum Co.) was purified by vacuum sublimation. $MoOCl_3$ was prepared as described by Edwards.[6] *Anal.* Calcd. for $MoOCl_3$: Cl, 48.7; Mo, 43.9. Found: Cl, 48.9; Mo, 43.8. The ligands were dried with calcium hydride and distilled several times from fresh potassium metal.

**Reactions** were carried out by standard procedures, using excess of ligand, without another solvent. Ampoules of the reactants were sealed at −80° and the contents allowed to react at room temperature. After a suitable reaction period the ampoule was opened under a nitrogen atmosphere and connected to an all-glass vacuum system incorporating a filtration unit. All compounds isolated were pumped under high vacuum for several hours prior to analysis.

(1) **Reactions of $MoCl_5$.** (i) **With $C_4H_8O$.**—The dark brown solution first formed slowly turned green and after 30 min. deposited a green solid. *Anal.* Calcd. for $MoOCl_3 \cdot 2C_4H_8O$: C, 26.5; H, 4.5; Cl, 29.4; Mo, 26.5. Found: C, 26.3; H, 4.6; Cl, 29.6; Mo, 25.9; $\mu$, 1.68 B.M.; oxidation state, 5.0. Reaction for a really prolonged period (2 years) gave a dark brown solid. *Anal.* Calcd. for $MoO_2Cl_2 \cdot 2C_4H_8O$: C, 28.0; H, 4.7; Cl, 20.7; Mo, 28.1. Found: C, 27.5; H, 4.8; Cl, 21.1; Mo, 28.1; $\chi_M'$, $-12 \times 10^{-6}$ c.g.s.

(ii) **With $C_5H_{10}O$.**—A mixture of yellow and green solids was deposited from solution. The yellow compound was obtained pure by washing out the green solid (and various ligand decomposition products) with benzene. *Anal.* Calcd. for $MoCl_4 \cdot 2C_5H_{10}O$: C, 29.3; H, 4.9; Cl, 34.6; Mo, 23.4. Found: C, 29.3; H, 5.3; Cl, 34.7; Mo, 23.3; $\mu$, 2.37 B.M.; oxidation state, 4.1. The green solid could not be isolated in a pure form.

(iii) **With $C_4H_8O_2$.**—After reaction for 20 days the brown solution deposited green crystals; the latter were isolated. *Anal.* Calcd. for $MoOCl_3 \cdot 1.5C_4H_8O_2$: C, 20.6; H, 3.5; Cl, 30.4; Mo, 27.4. Found: C, 20.1; H, 3.6; Cl, 30.5; Mo, 25.1; $\mu$, 1.66 B.M.; oxidation state, 5.0.

(2) **Reactions of $MoOCl_3$.**—Reactions with oxygen ligands were carried out in the absence of a solvent; the product was

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