(8.394Å). That these lines are not due to a second phase is established by plotting the variation of d spacing as a function of titanium substitution. The systematic change of d_{531} and d_{662} is shown in Fig. 1. Maximum titanium substitution results in the compound ulvöspinel, Fe_2TiO_4, and the pattern obtained differs from that of Forster & Hall (1965) in that they do not record the four weak reflexions. In the present investigation the spacings of all four reflexions varied systematically with composition x in the solid solution $(1-x)$ $Fe_3O_4-xFe_2TiO_4$. For values of x greater than 0.4, the 664 reflexion also became visible on the film. For $x<0.4$ this reflexion occurs at too high an angle to appear on the film (for Co$K\alpha$). This may provide mineralogists with a method of detecting ulvöspinel in magnetite.

Structure factor calculations

The observed structure factors F_{OBS}, were calculated from the experimental intensities, which were corrected in the usual way for multiplicity, absorption and by the Lorentz-polarization factor. F_{OBS} was put on an approximately absolute scale by making the maximum value equal to one-third of the total electrons in the unit cell. A Glasgow structure-factor least-squares computer program was used to calculate theoretical structure factors F_{CALC} and match them to F_{OBS} taking the oxygen parameter, u, as the variable. Initially F_{OBS} for individual members of the five combined reflexions were obtained by splitting the observed intensities into two equal parts. In later cycles of computation these were recalculated by splitting the observed intensities into the ratios required by the ratios of F_{CALC}. The deviation of the u parameter from the ideal value of 0·375 is a measure of the anion sublattice distortion from cubic close packing. The results of the calculation are shown in Table 1. Good agreement was obtained except for the two lowest angle lines 111 and 220. An overall fit of 13% was obtained for a u parameter of 0·381 in reasonable agreement with the value of 0·379 reported by Abrahams & Calhoun (1953).

Good agreement was found for 531 and 551–711. The calculated structure factors for 662 and 753 were also in reasonable agreement and all four lines should be expected to be found experimentally. Whether or not they are observed in practice presumably depends on the background being at a suitably low level. It is also possible that the lines may be dismissed as due to a second phase, unless the investigation being undertaken is a study of the effect of the addition of impurities (in this case titanium).

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Crystal and Molecular Structure of $[RuBr_2(CO)_3]_2$

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A three-dimensional structural analysis of a new bromocarbonyl compound of Ru^{II} shows that the compound is to be assigned the formula $[RuBr_2(CO)_3]_2$. It crystallizes in space group $C2/m$, with unit-cell dimensions $a=10·74$, $b=7·44$, $c=9·42$ Å, $\beta=106°32'$. Least-squares refinement led to a final agreement factor for the observed reflexions $R=0·103$. The molecule possesses molecular point group symmetry $2/m$ (C_{2h}); the Ru atoms are not bonded to each other directly but by means of two bromine bridges. The observed lengthening of non-bridging metal halide bond has been tentatively interpreted as due to the *trans* effect of the carbonyl ligand.

Introduction

Very recently Braca, Sbrana, Pino & Benedetti (1967) reported the preparation of a bromine carbonyl compound of Ru^{II}. We have carried out a structure analysis on a sample of the compound, obtained in minute yellow crystals, particularly suitable for single-crystal diffraction examination. The compound was proved to have a dimeric molecular structure, as shown by the formula $[RuBr_2(CO)_3]_2$; the calculated composition (Ru 29·3%, Br 46·3%, C 10·4%) is in good agreement with the experimental data of Braca *et al.* (1967). Recently Johnson, Johnston, Josty, Lewis & Williams (1967) have proposed a formula of this type for a product of oxidation of triruthenium dodecacarbonyl with bromine, on the basis of the molecular weight determination.

Experimental

Morphological and optical crystallography

On the basis of two-circle goniometer measurements we assigned the crystals to the monoclinic system, prismatic class; this was subsequently confirmed by structural data. The form development is: $\{001\}$, $\{\bar{2}01\}$, $\{101\}$, $\{\bar{1}11\}$, $\{100\}$; the habit is prismatic *b*. Form $\{100\}$ often does not appear or is very little developed. Parametric ratios $a:b:c = 1{\cdot}442:1:1{\cdot}24$, with $\beta = 106°38'$. Faces $\{\bar{2}01\}$ and $\{\bar{1}11\}$ are always streaked and curved: for this reason it was not possible to obtain a more precise value for the parametric c/b ratio.

The crystals are light yellow, quite transparent, with no perceptible pleochroism, and are optically negative with $2V = 80°$. From $(100) \wedge (\bar{2}01)$ prism with the least deviation method we measured n_α and an index of refraction intermediate between n_β and n_γ. From our measurements we obtained for the indices of refraction and optical orientation: $n_\alpha = 1{\cdot}564$ (**b**), $n_\beta = 1{\cdot}61$ (0° to **c**), $n_\gamma = 1{\cdot}64$ (+17° to **a**).

X-ray crystallography and intensity measurement

Making use of rotation and Weissenberg spectra obtained with Cu $K\alpha$ radiation and of precession spectra taken with Mo $K\alpha$ radiation, the values of cell constants have been determined:

$$\begin{aligned} a &= 10{\cdot}74 \pm 0{\cdot}02 \text{ Å} \\ b &= 7{\cdot}44 \pm 0{\cdot}01 \\ c &= 9{\cdot}42 \pm 0{\cdot}02 \\ \beta &= 106°32' \pm 10' . \end{aligned}$$

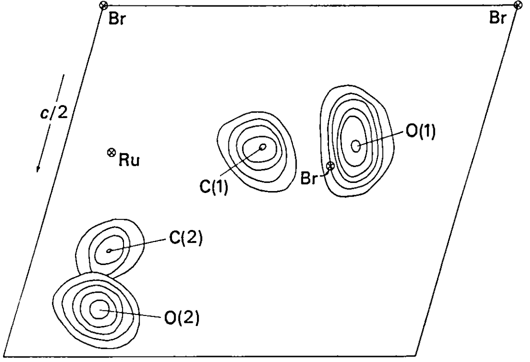

Fig. 1. A composite three-dimensional difference synthesis showing the two carbonyl groups in one asymmetric unit. The positions of the ruthenium and bromine atoms are indicated. Contours are at intervals of 1 e.Å^{-3} with the lowest contour at 2 e.Å^{-3}.

Taking into account the systematic absences of reflexions the possible space groups are: $C2/m$, Cm and $C2$. The morphology of the crystals does not show any sign of absence of a centre of symmetry and a thorough search for a piezoelectric effect gave a negative result; we thus assumed the centrosymmetric space group $C2/m$ as the most probable: this choice was subsequently confirmed by the structure analysis. The volume of the unit cell is 722 Å^3. The density of the crystals, determined by a microbalance of the Westphal type, was $D_m = 3{\cdot}11$ g.cm^{-3}. With four $RuBr_2(CO)_3$ stoichiometric units in the unit cell, the calculated density is $D_c = 3{\cdot}17$ g.cm^{-3}. $F(000) = 624$. The linear absorption coefficient for the Cu $K\alpha$ radiation is $\mu = 321$ cm^{-1}.

For the collection of intensity data a nearly cylindrical crystal was chosen, which had a mean cross-sectional diameter of 0·10 mm. The intensity data for the determination of the structure have been recorded with Cu $K\alpha$ radiation by means of equi-inclination Weissenberg photographs about **b** for $k = 0$ to 4, with the multiple film technique and integration process. A total of 579 independent reflexions (479 observable) was collected. The intensities, measured with a Nonius microdensitometer, have been corrected for Lorentz and polarization factors, and for the absorption factor using the three-constant formula proposed by Palm (1964) for cylindrical crystals.

With the same crystal we collected the $0kl$ reflexions, by means of precession photographs with the multiple exposure technique and integration process, using Mo $K\alpha$ radiation. The intensities of such reflexions, corrected for the Lorentz and polarization factors, were used to determine the y and z coordinates of the heavy atoms and to put initially on a common scale the corrected Weissenberg intensity data.

Determination of the structure

The structure determination was carried out by means of the two-dimensional Patterson syntheses projected along [010] and [100]. From the positions and heights of the relevant peaks in Patterson projections we were able to obtain a trial structure for the heavy atoms: accordingly the molecule was dimeric with two bromine bridges between the ruthenium atoms. Among the three heavy atoms of the $RuBr_2(CO)_3$ stoichiometric unit, the Ru atom and one of the Br atoms are in special positions on the symmetry plane (4*i*); the second Br atom, which completes the bridging bond, is in another special position along the twofold axis passing through the origin (4*h*). The parameters obtained for the three heavy atoms have been refined by a full-matrix least-squares program (Busing, Martin & Levy, 1962) with individual isotropic temperature factors and constant weights. For the refinement we made use only of the Weissenberg intensity data, putting also among the refined parameters the five scale factors, whose starting values were determined with use of the precession intensity data.

Table 1. *Observed and calculated structure factors*

Reflexions marked with *E* are apparently affected by extinction.

H	K	L	F_o	F_c
0	0	1	99.6	133.1
0	0	2	130.9	138.7
0	0	3	64.5	-54.6
0	0	4	192.0	218.1
0	0	5	232.0	268.7
0	0	6	51.4	41.3
0	0	7	70.1	-67.9
0	0	9	113.9	116.4
0	0	10	68.2	71.9
2	0	0	151.2	167.0
2	0	1	101.3	82.9
2	0	2	158.5	140.0
2	0	4	120.4	110.3
2	0	5	131.2	121.9
2	0	6	65.6	60.7
2	0	9	76.9	68.9
2	0	10	43.3	43.9
2	0	-1	107.2	147.4
2	0	-2	48.1	56.2
2	0	-3	141.9	163.3
2	0	-4	42.9	45.6
2	0	-5	101.8	98.5
2	0	-6	115.3	108.3
2	0	-7	83.0	76.4
2	0	-10	68.1	63.2
2	0	-11	50.9	51.2
4	0	1	130.7	-109.1
4	0	2	43.5	29.8
4	0	3	192.5	199.7
4	0	4	156.6	166.2
4	0	6	45.3	-44.7
4	0	7	37.4	34.5
4	0	8	92.4	92.6
4	0	9	38.2	40.3
E 4	0	-1	230.7	373.1
4	0	-2	157.5	187.6
4	0	-3	60.5	-54.8
4	0	-4	85.1	-90.6
4	0	-5	109.8	122.1
4	0	-6	188.4	241.0
4	0	-7	76.0	81.8
4	0	-8	57.1	-57.6
4	0	-9	22.2	-17.2
4	0	-10	95.3	95.4
4	0	-11	71.1	78.8
6	0	0	61.0	48.7
6	0	1	29.7	17.3
6	0	3	110.5	106.4
6	0	4	106.1	102.8
6	0	6	36.0	-32.3
6	0	7	29.2	30.2
6	0	8	58.3	60.2
6	0	-1	131.7	146.2
6	0	-2	113.2	111.0
6	0	-4	71.0	55.9
6	0	-5	52.0	47.0
6	0	-6	91.9	86.0
6	0	-7	86.6	80.4
6	0	-8	54.2	45.9
6	0	-10	14.6	21.0
6	0	-11	48.8	50.8
8	0	0	64.1	-60.3
8	0	1	63.9	59.6
8	0	2	115.3	121.1
8	0	3	62.3	62.5
8	0	4	29.8	-26.2
8	0	5	23.5	-21.9
8	0	6	34.8	35.3
8	0	7	46.4	54.2
8	0	-1	60.9	-49.9
8	0	-2	171.2	166.4
8	0	-3	155.8	151.3
8	0	-4	16.9	7.1
8	0	-5	89.5	-77.1
8	0	-6	31.6	22.7
8	0	-7	143.5	144.6
8	0	-8	87.0	87.2
8	0	-9	45.4	-30.6
8	0	-10	36.0	-34.2
8	0	-11	45.8	48.3
10	0	2	68.8	73.7
10	0	3	54.1	55.4
10	0	4	24.5	-15.7
10	0	5	26.1	-28.4
10	0	-2	100.3	89.1
10	0	-3	82.0	75.2
10	0	-4	27.4	-12.5
10	0	-6	29.6	24.3
10	0	-7	61.0	57.1
10	0	-8	50.4	50.0
12	0	0	42.0	40.0
12	0	1	54.3	56.0
12	0	2	20.8	18.5
12	0	-1	31.2	-30.4
12	0	-2	53.6	-45.7
12	0	-3	61.8	58.0
12	0	-4	90.5	86.7
12	0	-5	21.9	17.9
12	0	-6	50.7	-50.2
12	0	-8	58.8	67.9
1	1	0	141.5	208.5
1	1	1	83.9	67.0
1	1	2	144.8	-175.2
1	1	3	97.6	-93.1
1	1	4	100.2	90.1
1	1	5	139.9	146.0
1	1	7	116.6	-108.3
1	1	8	23.1	-14.5
1	1	9	69.2	67.0
1	1	10	46.7	41.2
1	1	11	23.7	-24.9
1	1	-1	53.7	53.7
1	1	-2	112.4	-146.3
1	1	-3	68.2	65.7
1	1	-4	81.0	75.9
1	1	-5	78.9	77.7
1	1	-7	63.8	56.0
1	1	-9	34.7	25.5
3	1	0	27.0	-15.8
3	1	1	126.6	-113.8
3	1	2	18.8	-13.3
3	1	3	83.2	72.1
3	1	4	47.6	47.1
3	1	6	45.3	-43.6
3	1	8	26.2	24.4
3	1	9	20.4	26.8
3	1	-1	110.4	137.4
3	1	-2	93.6	110.3
3	1	-3	87.4	-96.0
3	1	-4	101.9	-111.0
3	1	-5	31.0	27.0
3	1	-6	120.1	137.1
3	1	-7	38.4	29.2
3	1	-8	94.4	-90.7
3	1	-9	44.6	-40.2
3	1	-10	50.8	49.3
3	1	-11	51.6	51.5
5	1	0	33.1	21.4
5	1	1	150.2	-156.2
5	1	2	71.1	-57.7
5	1	3	105.7	98.3
5	1	4	101.4	105.0
5	1	5	43.4	-37.1
5	1	6	88.9	-85.4
5	1	8	59.1	56.5
5	1	9	22.8	23.3
5	1	-1	135.0	175.7
5	1	-2	73.0	70.0
5	1	-3	124.2	-127.4
5	1	-4	96.3	-90.7
5	1	-5	71.1	64.8
5	1	-6	91.5	95.7
5	1	-8	68.6	64.7
5	1	-9	32.5	-30.8
5	1	-11	36.9	37.7
7	1	0	67.8	-70.0
7	1	2	46.7	52.2
7	1	3	35.0	30.0
7	1	5	29.5	-35.9
7	1	8	15.8	21.6
7	1	-1	44.4	-38.8
7	1	-2	74.7	67.8
7	1	-3	101.1	94.0
7	1	-4	36.9	-25.7
7	1	-5	102.4	-90.4
7	1	-7	93.8	91.4
7	1	-8	54.7	53.7
7	1	-9	60.4	-52.8
7	1	-10	53.0	-51.3
7	1	-11	20.4	21.0
9	1	0	96.2	-100.6
9	1	2	69.3	75.0
9	1	3	45.8	48.1
9	1	4	36.7	-39.5
9	1	5	48.1	-47.1
9	1	6	22.8	14.6
9	1	-1	29.9	-22.1
9	1	-2	107.2	103.7
9	1	-3	81.0	72.7
9	1	-4	81.6	-67.5
9	1	-5	93.8	-83.3
9	1	-7	82.7	78.6
9	1	-8	30.6	26.6
9	1	-9	51.6	-49.2
9	1	-10	36.4	-35.1
11	1	1	19.4	24.9
11	1	2	18.3	20.5
11	1	4	22.6	-25.2
11	1	-1	29.6	-32.8
11	1	-2	25.6	-20.8
11	1	-3	23.2	28.4
11	1	-4	52.4	46.4
11	1	-6	49.0	-46.9
11	1	-7	27.4	-22.2
11	1	-8	44.7	45.2
11	1	-9	38.9	40.6
13	1	0	12.9	13.8
13	1	-1	49.0	-51.8
13	1	-2	37.4	-38.4
13	1	-3	43.2	42.7
13	1	-4	55.8	60.1
13	1	-5	19.2	-15.9
13	1	-6	49.8	-58.7
E 0	2	2	207.2	364.1
0	2	3	192.8	-256.5
0	2	4	59.8	52.5
0	2	5	84.7	79.7
0	2	6	90.2	-88.4
0	2	7	162.4	-172.5
0	2	8	72.4	-72.7
0	2	10	19.8	21.8
0	2	11	34.3	-45.1
2	2	0	113.7	-104.3
2	2	1	58.4	-42.3
2	2	2	160.5	-154.0
2	2	3	102.1	-104.7
2	2	4	71.5	-60.7
2	2	6	71.7	-61.3
2	2	7	99.3	-87.5
2	2	8	57.4	-54.2
2	2	-1	113.3	-131.1
2	2	-2	63.9	-66.0
2	2	-3	117.2	-137.2
2	2	-4	81.2	-88.9
2	2	-5	77.8	-77.3
2	2	-7	62.6	-56.2
2	2	-8	92.8	-79.2
2	2	-9	68.6	-64.9
4	2	0	87.7	-84.0
4	2	1	233.1	-288.1
4	2	2	138.0	-127.4
4	2	3	84.3	73.8
4	2	5	103.4	-102.5
4	2	6	121.2	-122.1
4	2	-1	78.9	78.1
4	2	-2	77.4	67.5
4	2	-3	183.5	-236.5
4	2	-4	183.2	-251.5
4	2	-6	79.1	84.9
4	2	-7	35.7	-36.9
4	2	-8	136.7	-149.5
4	2	-9	82.7	-90.4
4	2	-11	28.9	30.7
6	2	1	136.7	-141.6
6	2	2	87.2	-79.3
6	2	5	56.2	-58.0
6	2	6	79.3	-77.4
6	2	8	29.3	22.5
6	2	-2	63.8	-52.3
6	2	-3	86.3	-77.2
6	2	-4	119.9	-113.3
6	2	-5	59.8	-52.6
6	2	-6	37.5	-29.5
6	2	-8	51.1	-47.8
6	2	-9	69.0	-64.0
6	2	-10	54.2	-50.7
8	2	0	123.4	-149.4
8	2	1	34.4	-25.0
8	2	2	59.5	58.9
8	2	4	65.2	-76.2
8	2	5	59.0	-58.7
8	2	7	17.8	15.7
8	2	-1	92.7	-96.4
8	2	-3	84.3	77.0
8	2	-4	92.9	-85.6
8	2	-5	156.6	-166.7
8	2	-6	48.3	-46.6
8	2	-7	62.5	58.7
8	2	-9	83.9	-84.2
8	2	-10	70.9	-78.3
10	2	0	88.8	-92.6
10	2	1	30.0	-32.5
10	2	2	27.0	30.1
10	2	4	41.7	-43.2
10	2	5	44.6	-45.9
10	2	-1	55.4	-30.4
10	2	-4	56.8	-47.6
10	2	-5	79.8	-76.2
10	2	-6	32.6	-27.2
10	2	-9	29.5	-31.0
10	2	-10	38.3	-41.9
12	2	1	34.5	36.1
12	2	-1	62.2	-62.9
12	2	-2	58.3	-60.1
12	2	-4	57.6	55.8
12	2	-6	80.3	-87.7
12	2	-7	36.7	-42.4
12	2	-8	36.5	34.3
1	3	0	123.4	130.2
1	3	1	19.9	12.5
1	3	2	130.6	-136.5
1	3	3	133.5	-149.7
1	3	4	82.3	86.1
1	3	5	90.5	85.9
1	3	6	46.8	-37.6
1	3	7	89.1	-93.3
1	3	8	48.0	-39.4
1	3	9	51.5	52.2
1	3	10	27.8	29.5
1	3	-1	13.7	-14.3
1	3	-2	102.9	-120.5
1	3	-3	85.6	-99.6
1	3	-4	28.1	27.9
1	3	-5	73.4	71.2
1	3	-6	47.4	-40.8
1	3	-7	52.2	-46.7
1	3	-8	39.5	-39.4
1	3	-10	26.1	25.7
3	3	0	58.7	-55.4
3	3	1	114.0	-98.3
3	3	2	60.8	-53.7
3	3	3	36.7	32.9
3	3	4	46.8	43.3
3	3	5	50.5	-44.6
3	3	6	39.1	-34.1
3	3	7	31.7	-28.2
3	3	9	21.4	21.6
3	3	-1	72.5	84.6
3	3	-2	50.4	50.7
3	3	-3	69.0	-79.4
3	3	-4	128.4	-157.0
3	3	-5	29.4	30.3
3	3	-6	81.0	83.4
3	3	-8	73.5	-78.9
3	3	-9	61.5	-59.9
3	3	-10	36.6	35.6
3	3	-11	32.5	38.9
5	3	1	137.0	-136.9
5	3	2	93.5	-94.2
5	3	3	87.4	92.4
5	3	4	67.5	61.9
5	3	5	51.9	-48.1
5	3	6	72.3	-73.6
5	3	8	43.5	46.3
5	3	-1	108.0	124.7
5	3	-2	27.2	23.5
5	3	-3	108.2	-110.8
5	3	-4	104.3	-109.4
5	3	-5	29.8	26.9
5	3	-6	81.7	84.8
5	3	-7	27.9	-24.2
5	3	-8	58.4	-57.1
5	3	-9	44.6	-41.8
5	3	-10	9.6	8.9
5	3	-11	32.3	30.0
7	3	0	65.1	-63.7
7	3	1	24.6	-21.3
7	3	2	31.0	32.4
7	3	3	28.8	26.5
7	3	4	30.7	-32.6
7	3	5	25.0	-28.0
7	3	6	17.2	-17.6
7	3	-1	50.8	-53.1
7	3	-2	45.3	39.4
7	3	-3	65.5	59.9
7	3	-4	29.6	-26.1
7	3	-5	115.2	-113.7
7	3	-7	64.7	59.7
7	3	-8	31.7	28.3
7	3	-9	44.5	-46.2
7	3	-10	53.0	-61.4
7	3	-11	13.7	12.4
9	3	0	88.9	-94.0
9	3	1	29.6	-30.4
9	3	2	63.0	70.8
9	3	3	28.9	26.5
9	3	4	39.2	-41.6
9	3	5	43.2	-39.5
9	3	-1	34.1	-27.5
9	3	-2	79.2	76.6
9	3	-3	49.5	46.4
9	3	-4	62.9	-59.1
9	3	-5	84.0	-90.5
9	3	-7	68.0	69.9
9	3	-9	40.7	-44.1
9	3	-10	34.6	-37.8
11	3	0	11.2	-12.9
11	3	1	15.6	19.8
11	3	2	16.1	18.2
11	3	3	11.4	-15.5
11	3	-1	29.8	-30.4
11	3	-2	25.0	-24.2
11	3	-3	15.8	14.8
11	3	-4	36.5	35.0
11	3	-5	8.5	-5.9
11	3	-6	51.6	-58.1
11	3	-7	17.1	-16.7
11	3	-8	35.1	31.8
13	3	-3	31.4	31.4
13	3	-4	40.1	46.3
0	4	1	94.0	122.8
0	4	2	93.5	-95.0
0	4	3	56.5	-42.4
0	4	4	149.8	160.5
0	4	5	162.2	182.1
0	4	6	35.6	29.5
0	4	7	53.4	-49.0
0	4	9	71.2	81.0
0	4	10	54.0	62.2
2	4	0	107.9	95.4
2	4	1	101.2	85.8
2	4	2	67.9	47.8
2	4	3	33.5	29.4
2	4	4	91.8	77.9
2	4	5	95.9	88.6
2	4	6	43.5	39.5
2	4	8	22.6	20.8
2	4	9	49.3	54.6
2	4	-1	81.3	80.2
2	4	-2	66.8	70.9
2	4	-3	66.8	63.4
2	4	-4	41.4	46.2
2	4	-5	80.3	70.3
2	4	-6	84.8	80.4
2	4	-7	56.2	51.1
2	4	-10	45.8	49.8
4	4	0	43.5	36.4
4	4	1	94.5	-85.2
4	4	2	20.2	14.1
4	4	3	144.1	151.1
4	4	4	106.4	115.8
4	4	5	16.6	-4.9
4	4	6	35.8	-32.0
4	4	7	23.0	26.2
4	4	8	54.3	65.1
4	4	-1	163.1	221.8
4	4	-2	140.4	154.3
4	4	-3	48.8	-44.2
4	4	-4	76.1	-70.3
4	4	-5	92.6	96.9
4	4	-6	139.2	170.5
4	4	-7	59.0	58.1
4	4	-8	44.5	-42.1
4	4	-10	58.2	66.2
6	4	0	58.6	50.7
6	4	2	14.5	9.1
6	4	3	81.9	78.5
6	4	4	71.7	73.8
6	4	6	23.1	-20.9
6	4	7	17.5	19.0
6	4	-1	91.0	97.2
6	4	-2	78.0	69.9
6	4	-3	25.2	24.0
6	4	-5	38.3	39.4
6	4	-6	73.3	64.5
6	4	-7	65.1	60.5
6	4	-8	37.1	31.4
8	4	0	56.4	-50.2
8	4	1	39.5	38.9
8	4	2	86.5	96.5
8	4	3	43.7	45.1
8	4	4	20.1	-21.0
8	4	5	16.7	-15.1
8	4	6	24.5	26.0
8	4	-1	30.4	-20.9
8	4	-2	101.4	105.4
8	4	-3	117.7	121.4
8	4	-5	69.1	-63.2
8	4	-6	28.7	23.0
8	4	-7	101.0	107.9
8	4	-8	59.1	63.0
8	4	-9	23.4	-21.9
8	4	-10	24.0	-25.3
10	4	0	32.6	-29.3
10	4	1	13.8	6.0
10	4	2	50.0	57.6
10	4	3	42.3	39.1
10	4	-2	69.5	64.5
10	4	-3	56.2	52.1
10	4	-4	7.9	0.9
10	4	-6	18.2	17.8
10	4	-7	49.2	46.2
12	4	0	25.0	27.2
12	4	-1	26.7	-26.2
12	4	-2	26.9	-28.5
12	4	-3	33.9	37.9
12	4	-4	66.4	69.8
12	4	-5	16.8	14.1
12	4	-6	37.0	-43.0

After the third cycle we obtained the following value for the agreement index:

$$R_1 = \Sigma\ ||F_o| - |F_c|| / \Sigma\ |F_o| = 0{\cdot}171\ .$$

The positions of the light atoms were determined by a three-dimensional Fourier difference synthesis, with coefficients $\Delta F = F_o - F_c$ where F_c are the structure factors obtained from the preceding least-squares calculation, with only the contributions of the heavy atoms.

The synthesis clearly disclosed the positions of the carbon and oxygen atoms. Fig. 1 shows the superimposed contoured sections along [010] corresponding to the two carbonyl groups of the asymmetric unit. After a first cycle of least-squares refinement of all parameters, the 022 and $40\bar{1}$ reflexions were rejected because they appeared to be affected by extinction. Two more least-squares cycles were performed and the residual decreased to $R_1 = 0{\cdot}122$.

At this point anisotropic temperature factors for Ru and Br atoms were introduced in the form

$$\exp\ \{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}\ .$$

For the special positions occupied by Ru and Br atoms, the Levy (1956) rules show that $\beta_{12} = \beta_{23} = 0$.

Two further least-squares cycles reduced the residual to $R_1 = 0{\cdot}103$, whereas $R_2 = [\Sigma w ||F_o| - |F_c||^2 / \Sigma w |F_o|^2]^{\frac{1}{2}}$ was 0·116.

In the final four refinement cycles the following weighting system was introduced:

$$w_{hkl} = \frac{1}{(2/|F_{\max}|)\ |F_o|^2 + |F_o| + 2|F_{\min}|} \quad \text{if } |F_o| \geq 2|F_{\min}|$$

$$w_{hkl} = a|F_o|^2 \quad \text{if } |F_o| < 2|F_{\min}|$$

where $|F_{\min}| = 15{\cdot}0$, $|F_{\max}| = 225{\cdot}0$ and the a constant was such as to assure that the two weighting functions assumed the same value for $|F_o| = 2|F_{\min}|$.

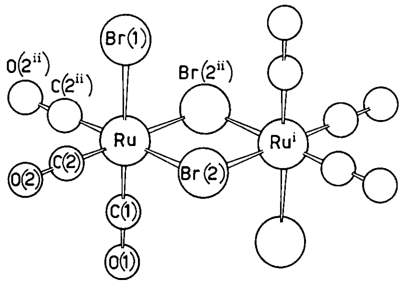

Fig. 2. The molecular structure of $[RuBr_2(CO)_3]_2$.

Scattering factors of Thomas & Umeda (1957) were used for Ru and Br atoms, and the Freeman (1959) values for carbon and oxygen. The observed and calculated structure factors are compared in Table 1. Table 2 gives the final positional and thermal parameters with their standard deviations.

Description and discussion of the structure

The structure consists of dimeric molecules $[RuBr_2(CO)_3]_2$ (Fig. 2). The interatomic distances and bond angles have been calculated by the *ORFFE* program of Busing, Martin & Levy (1964). Intramolecular distances and bond angles are reported respectively in Tables 3 and 4. The intermolecular distances of the closest neighbouring atoms are given in Table 5 and Fig. 3.

In the above mentioned Tables and Figures the atoms of the different asymmetric units are related to the symmetry equivalent atoms of the fundamental unit as follows:

i	atom at	$-x$	y	$-z$
ii	atom at	x	$-y$	z
iii	atom at	$\frac{1}{2}+x$	$\frac{1}{2}+y$	z
iv	atom at	$\frac{1}{2}+x$	$\frac{1}{2}-y$	z
v	atom at	x	$1-y$	z

Fig. 3 illustrates the arrangement of the molecules in the unit cell as seen along [001]. The packing of the molecules does not present outstanding peculiarities; as the closest intermolecular distances show, the interactions are exclusively of the van der Waals type.

The molecular structure is very similar to that of $[MnBr(CO)_4]_2$ determined by Dahl & Wei (1963). It

Table 3. *Intramolecular distances, with standard deviations*

Ru – Br(1)	2·543 ± 0·004 Å
Ru – Br(2)	2·571 ± 0·004
Ru – C(1)	1·97 ± 0·03
Ru – C(2)	1·90 ± 0·03
C(1) – O(1)	1·07 ± 0·04
C(2) – O(2)	1·18 ± 0·03
Ru .... Ru^{i}	3·752 ± 0·004
Br(2)... Br(2^{ii})	3·517 ± 0·009
Br(1)... Br(2)	3·632 ± 0·004

Table 2. *Final atomic parameters and, in parenthesis, the significant figures of standard deviations*

For the numbering of atoms see Fig. 2.

	x	y	z	B	β_{11}	β_{22}	β_{33}	β_{13}
Ru	0·0608(2)	0	0·2074(2)		0·0044(2)	0·0103(65)	0·0058(3)	0·0023(2)
Br(1)	−0·1709(3)	0	0·2254(4)		0·0067(3)	0·0131(67)	0·0137(5)	0·0047(3)
Br(2)	0	0·2363(6)	0		0·0105(4)	0·0083(65)	0·0074(4)	0·0033(3)
C(1)	0·2424(29)	0	0·2005(32)	2·37(53)				
C(2)	0·0920(18)	0·1867(39)	0·3509(21)	2·30(43)				
O(1)	0·3430(22)	0	0·2063(24)	2·65(49)				
O(2)	0·1105(19)	0·3045(33)	0·4380(24)	4·71(51)				

Table 4. *Bond angles with standard deviations*

Br(2) – Ru – Br(2^{ii})	86·3 ± 0·2°
Br(1) – Ru – Br(2)	90·5 ± 0·1
Ru – Br(2) – Ru^{i}	93·7 ± 0·2
Br(1) – Ru – C(2)	86·0 ± 0·6
Br(2) – Ru – C(1)	90·8 ± 0·6
Br(2) – Ru – C(2)	89·8 ± 0·7
C(1) – Ru – C(2)	92·8 ± 0·8
C(2) – Ru – C(2^{ii})	93·9 ± 1·5
Br(2) – Ru – C(2^{ii})	174·7 ± 0·7
C(1) – Ru – Br(1)	178·2 ± 0·9
O(1) – C(1) – Ru	175·3 ± 2·6
O(2) – C(2) – Ru	178·9 ± 2·2

Table 5. *Intermolecular distances less than* 3·8 Å

O(1) ... Br(1^{iii})	3·73 Å
O(1) ... Br(2^{iv})	3·51
O(1) ... C(2^{iv})	3·52
O(1) ... O(2^{iv})	3·40
O(2) ... Br(1^{iii})	3·78
O(2) ... O(2^{v})	2·91

can be described as a pair of octahedra sharing an edge formed by the two bridging bromine atoms. The two remaining Br atoms are bonded each to a Ru atom and are *trans* to one another. The molecular point group symmetry is $2/m$ (C_{2h}).

The two independent C–O bond lengths do not differ significantly; the mean value 1·13 Å is the same as in carbon monoxide and does not disagree with the values obtained for similar metal–carbonyl compounds. The two independent Ru–C bond lengths also do not differ significantly, and their mean value is 1·93 Å.

As in the case of [MnBr(CO)$_4$]$_2$, the electronic configuration of the inert gas is attained by each metal atom with the formation of the usual electron pair metal–halide bonds without need of metal–metal interactions; in fact the Ru$\cdots$Ru intramolecular distance is 3·75 Å.

The most striking feature in the molecule is the low difference between bond length values of Ru–Br(1), 2·543 Å, and Ru–Br(2), 2·571 Å. In view of our data this difference appears highly significant; however, it is still less than the difference which we should expect, and which was actually found in different compounds which had both bridging and non-bridging metal–halide bonds. The fact may be explained by the large '*trans* effect' of the carbonyl group on the Ru–Br(1) bond; this type of effect is known to play an important role in metal complexes (Basolo & Pearson, 1962). As assumed by Chatt, Duncanson & Venanzi (1955), the ligands of high *trans*-influence have a great effect on the molecular π-bonding system involving the *d*-orbitals of the metal; if the *trans* bond has some amount of

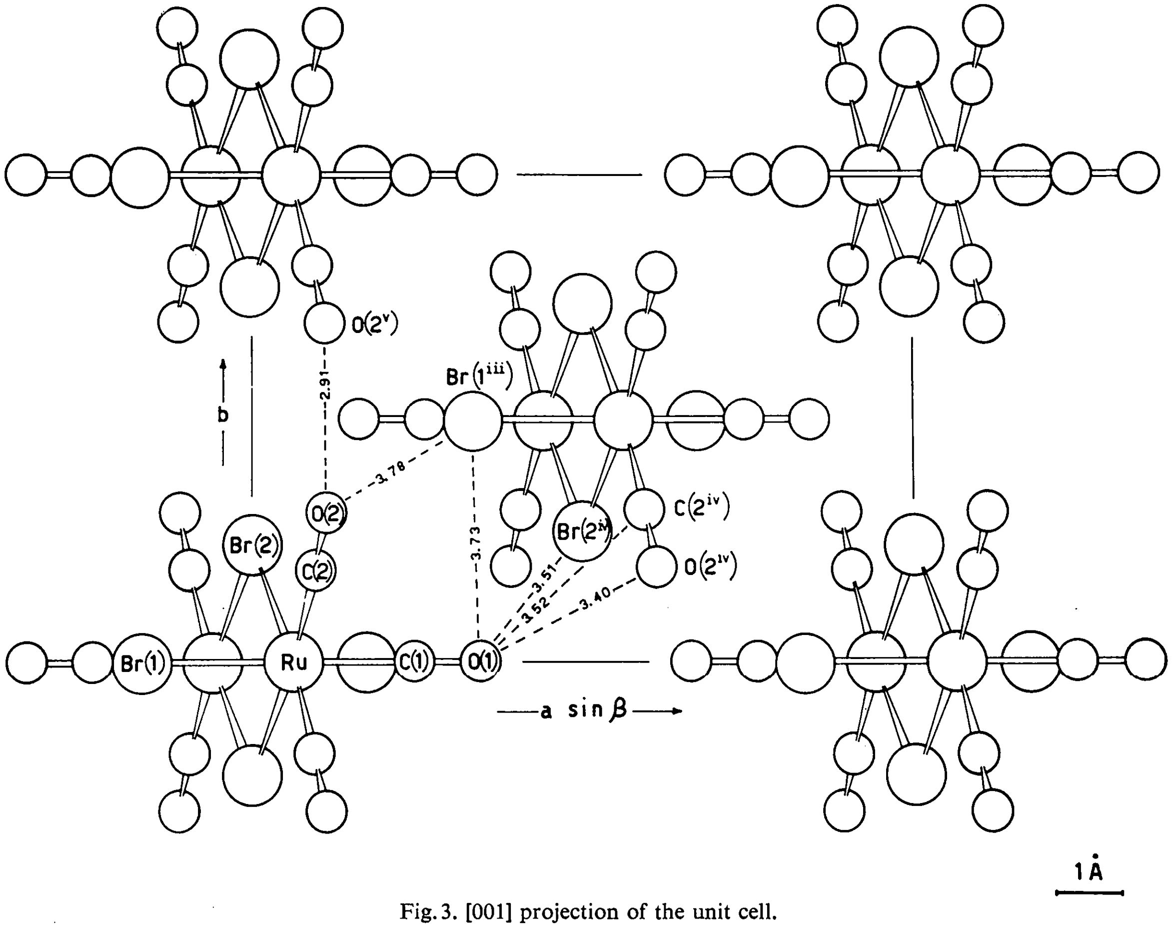

Fig. 3. [001] projection of the unit cell.

double bond character (as commonly it occurs for transition metal–chlorine or metal–bromine bonds) this amount will be reduced. The effect was demonstrated in lengthening Me–X bonds in square planar complexes of platinum and palladium, for some of which the structure is known: the anion of Zeise's salt $[Pt(C_2H_4)Cl_3]^-$ (Wunderlich & Mellor, 1954, 1955), the corresponding bromo complex $[Pt(C_2H_4)Br_3]^-$ (Bokij & Kukina, 1957), *cis*-$[Pt(C_2H_4)NH_3Br_2]$ (Kukina, Bokij & Brusentsev, 1964), the ethylene–palladium chloride complex (Dempsey & Baenziger, 1955) and the styrene–palladium chloride complex (Holden & Baenziger, 1955). This effect can probably be generalized to the present case, because Jenkins, Lupin, Shaw & Smithies (1966) have obtained infrared and nuclear magnetic resonance spectroscopic evidence for the *trans* effect in octahedral complexes of ruthenium(II). Noticing that the compound $[RuBr_2(CO)_3]_2$ examined may be considered as a dimeric form of a *cis*-bromocarbonyl complex of Ru^{II}, our suggestion can be proved analysing the structure of a *trans*-bromo compound of the metal.

We are indebted to Prof. P. Pino for having supplied us with crystals of the compound, and to Prof. S. Bonatti for his encouragement and help throughout the course of the structure determination. The valuable criticism and discussion of the data by Prof. P. Corradini and Prof. O. S. Mills are gratefully acknowledged.

The three-dimensional Fourier difference synthesis was calculated with a program written by A. Domenicano and D. Giucci. All the calculations were performed on the IBM 7090 computer of the Centro Nazionale Universitario di Calcolo Elettronico (Pisa).

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The Crystal Structure of Iodine Monobromide, IBr

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The crystal structure of iodine monobromide has been determined and refined to $R=6\cdot5\%$. The crystal is orthorhombic, $Ccm2_1$ (no. 36), with four molecules in a unit cell of dimensions $a=4\cdot90$, $b=6\cdot99$, $c=8\cdot93$ Å. All atoms lie on mirror planes and the molecules form a herringbone pattern similar to that in crystalline iodine. The intramolecular I–Br distance is 2·52 Å and the shortest intermolecular I···Br distances are 3·18 and 3·76 Å.

Introduction

The structure of iodine monobromide was studied in order to compare it with the structures of iodine and iodine monochloride. In both of the latter there are short intermolecular distances which suggest unusually strong interaction between adjacent molecules. Iodine monobromide is apparently the only iodine–bromine interhalogen compound. Its approximate structure was inferred (Heavens & Cheesman, 1950) on the basis of powder data from a series of solid solutions (0–38 mole % Br). No actual structure determination has been reported.

Experimental

Iodine bromide was formed by direct combination of the elements. Iodine and bromine form a nearly continuous series of solid solutions with iodine bromide.