361. *The Stereochemistry of Quadricovalent Atoms: Tervalent Gold.*

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No attempt has apparently been made to determine the configuration of a quadricovalent compound of gold; we have now carried out an *X*-ray examination of *potassium auribromide dihydrate*, $K[AuBr_4],2H_2O$, and find that the ion $[AuBr_4]'$ possesses a planar configuration. The work of Gibson and his collaborators has shown that the co-ordination number of tervalent gold in complex compounds is almost invariably 4; in agreement with this, the *X*-ray evidence shows that the water in the auribromide is held merely as water of crystallisation, *i.e.*, that the substance has the above constitution and does not contain the sexacovalent complex $[AuBr_4,(H_2O)_2]$. Tervalent gold must thus be added to those elements which can exhibit a planar distribution of valencies in their quadricovalent derivatives; it appears to be the first example of a metal other than bivalent in this category.

Potassium auribromide crystallises in dark red, elongated, monoclinic, holohedral prisms. The unit cell has dimensions $a = 9{\cdot}51$, $b = 11{\cdot}93$, $c = 8{\cdot}46$ A., with $\beta = 94°\ 24'$, and thus contains four molecules of $KAuBr_4,2H_2O$, the space-group being $P2_1/n$ (C_{2h}^5). In addition to the space-group halvings, however, it is found that all planes having l odd are extremely weak; *i.e.*, on the rotation photograph about the *c*-axis the odd layer lines are very nearly absent, so that unless close inspection is made, the length of the *c*-axis appears to be 4·23 A. Since the intensity of the strongest ($hk\overline{2n+1}$) reflection is not more than one-fiftieth of that of (004) (Table I), we have felt justified in adopting a smaller

Table I.

hkl.	*F*(obs.).	*F*(calc.).	*hkl.*	*F*(obs.).	*F*(calc.).	*hkl.*	*F*(obs.).	*F*(calc.).	*hkl.*	*F*(obs.).	*F*(calc.).
200	49	37	003	53	45	040	8	16	220	62	74
400	30	26	004	21	9	060	66	82	330	93	115
600	96	113	$\bar{2}02$	<13	5	080	71	64	440	57	84
800	36	42	$\bar{4}10$	<10	7	0100	77	77	550	4	2
001	58	64	$\bar{4}01$	<10	14	110	60	96	402	<16	14
002	49	51	020	50	63						

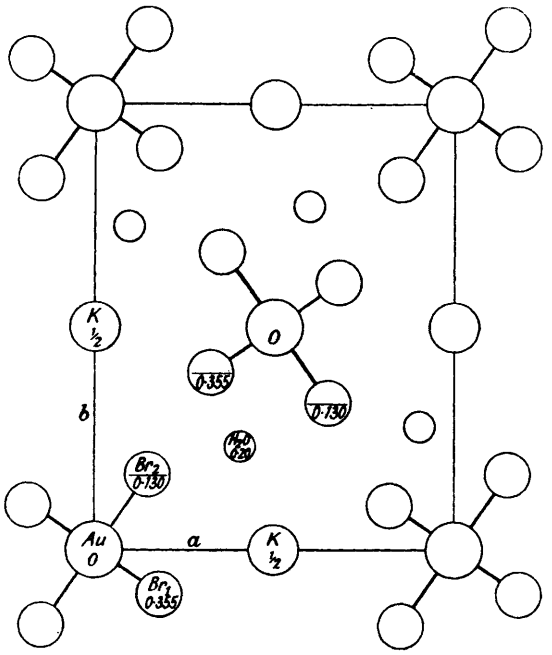
unit cell containing two molecules for the purpose of the structure determination. In the following discussion, therefore, the cell dimensions are taken as $a = 9{\cdot}51$, $b = 11{\cdot}93$, $c = 4{\cdot}23$ A., and the space-group as $P2_1/a$ (C_{2h}^5). In this cell the space-group conditions require each gold atom to lie on a centre of symmetry, with four bromine atoms in a plane around it.

If one gold atom is placed at the origin of co-ordinates (000), the other lies at $(\frac{1}{2}\frac{1}{2}0)$. With such an arrangement it is to be expected that all planes for which $h + k$ is odd will be weak, since the contributions of the two gold atoms to the structure factors of such planes will cancel each other; in accordance with this it is observed that the rotation photograph about the [110] axis shows weak odd layer lines. The potassium ions lie on symmetry centres, either $(\frac{1}{2}00)$ and $(0\frac{1}{2}0)$, or $(\frac{1}{2}0\frac{1}{2})$ and $(0\frac{1}{2}\frac{1}{2})$, while the bromine atoms are divided into two sets of four on general positions. The four equivalent oxygen atoms also lie on general positions, so that nine parameters in all are required to determine the structure. These parameters have been found by means of absolute intensity measurements, the atomic positions being adjusted by trial to obtain the best possible agreement (Table I) between the calculated structure factors, *F* (calc.), and those obtained from the absolute intensities, *F* (obs.). The atomic co-ordinates finally deduced in this way are as follows, only those for the representative bromine and oxygen atoms near the origin being given;

Au	(000)	$(\frac{1}{2}\frac{1}{2}0)$	Br_1	(0·189, $\overline{0{\cdot}104}$, 0·355), etc.
K	$(\frac{1}{2}0\frac{1}{2})$	$(0\frac{1}{2}\frac{1}{2})$	Br_2	(0·142, 0·168, $\overline{0{\cdot}130}$), etc.
			O	($\overline{0{\cdot}09}$, 0·28, 0·20), etc.

(Owing to its relatively small scattering power, the oxygen atom cannot be fixed with the same accuracy as the other atoms.)

Calculations show that if the co-ordinates of the five atoms in the $[AuBr_4]$ complex are varied independently, variations of 0·01 from the above co-ordinates lead to appreciable discrepancies between observed and calculated F values. We may therefore conclude that the displacement (if any) of an atom in the complex ion from the plane of the other four is less than 0·2 A. The intensity measurements thus confirm the deduction from space-group considerations that to a very close approximation the ion $[AuBr_4]'$ is planar.



A projection of the structure on the (001) plane is shown in the figure, and the principal (minimum) atomic distances are recorded (in A.) in Table II. The complex ion $[AuBr_4]$ is clearly shown; as would be anticipated the Au–Br distances, owing to the existence of covalent bonds, are considerably less than any others in the structure. There is evidently no question of co-ordination between the water molecules and the gold atoms.

TABLE II.

$Au–Br_1$	2·65	Br–Br	3·34	Br–O	3·0
$Au–Br_2$	2·48	Au–O	3·6	K–O	3·1
K–Br	3·26				

We have also examined potassium aurichloride, $KAuCl_4$. On account of difficulties in the measurement of intensities, the structure has not been determined in detail, but the general nature of the halvings suggests that the ion $[AuCl_4]$ is probably planar.

EXPERIMENTAL.

The X-ray data were obtained in the usual manner from single crystals, copper-K α radiation being used. The measurement of the absolute intensities and the calculation of the structure factors were carried out as previously described (this vol., p. 775).

Potassium auribromide dihydrate. The commercial salt was recrystallised from ethyl alcohol (Found: K, 6·80; Au, 33·43. $KAuBr_4,2H_2O$ requires K, 6·61; Au, 33·32%). The monoclinic crystals are elongated parallel to the c-axis, and exhibit the forms $a\{100\}$, $b\{010\}$, $c\{001\}$, $m\{110\}$, $o\{111\}$, and $s\{10\bar{2}\}$; their habit and the absence of pyroelectric effects show that they are to be assigned to the prismatic class. This salt is erroneously described by Muthmann and by Schottländer (Groth, "Chemisches Krystallographie," Vol. 1, 442) as anhydrous. The cell dimensions are as given above, whence $a : b : c = 0·797 : 1 : 2 \times 0·355$ [cf. 0·797 : 1 : 0·361 (Groth, *op. cit.*)], and with four molecules in the unit cell d (calc.) = 4·08 g./c.c. (obs., 4·1 approx.). The abnormal spacings are $\{0k0\}$ absent for k odd, and $\{h0l\}$ absent for $h + l$ odd, so that the space-group is $P2_1/n$. In addition, all planes with l odd are very weak. The crystals have very high birefringence and appear to be optically negative; the minimum refractive index is 1·67 inclined at 20° to $[c]$ in the acute angle β. This direction is approximately perpendicular to the mean plane of the $AuBr_4$ groups.

Potassium aurichloride. In contrast to the bromide, the aurichloride dihydrate recrystallises anhydrous from ethyl alcohol (Found: Au, 51·4; K, 10·1. Calc.: Au, 52·2; K, 10·4 %). It occurs in golden-yellow monoclinic combinations of $a\{100\}$, $c\{001\}$, and $m\{110\}$; its holohedral symmetry is shown by its habit and the absence of pyroelectric effects. The cell dimensions are $a = 12·18$, $b = 6·35$, and $c = 8·67$ A., with $\beta = 95° 24'$, whence $a : b : c = 1·916 : 1 : 1·364$ [cf. 1·918 : 1 : 1·361 (Groth, *op. cit.*)]. With four molecules in the unit cell, d (calc.) = 3·75 g./c.c. (obs., 3·3—3·9). The abnormal halvings are $\{0k0\}$ absent for k odd, and $\{h0l\}$ absent for h odd, so that the space-group is $P2_1/a$. As with the bromide, both the c-axis and the [110]

axis show weak odd layer lines, although not so markedly, and it is therefore probable that the symmetry of the $[AuCl_4]'$ ion approximates to C_{2h}, *i.e.*, that it is planar. With crystals having such high absorption ($\mu = 618$ cm.$^{-1}$) accurate measurement of intensities is only possible from developed or ground faces, and in this case it was not possible to obtain sufficient measurements to determine the structure in detail.

SUMMARY.

The structure of potassium auribromide dihydrate has been determined by *X*-ray methods. The tervalent gold atom in the quadricovalent ion $[AuBr_4]'$ exhibits a planar distribution of valencies.

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