

Gradual Anionic Character of Gold in Ternary Perovskite Type Oxides

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X-ray structure determination of novel Rb_3AuO and XANES (X-ray absorption near edge structure) spectra monitoring the anionic character of gold.

Gold, being a typical metal, preferentially adopts positive oxidation states. However, considering its electron affinity which is very similar to iodine,¹ the existence of anionic gold in CsAu containing the auride anion (Au^-) is not surprising. Furthermore, some alloys M_xAu_y ($\text{M} = \text{alkali metal, Mg, Zn}$)² and two ternary compounds Ca_3AuN^3 and Cs_3AuO^4 have been reported to contain negatively charged gold. Out of these only CsAu and Cs_3AuO are non-metallic. Their physical features are consistent with the ionic descriptions $\text{Cs}^+\text{Au}^{5-}$ and $(\text{Cs}^+)_3\text{Au}^{2-}$.^{4,6}

To gain further insight into the chemistry of aurides and their bonding features we have continued to examine the opportunities for obtaining anionic gold in ternary oxides. We are especially interested in the influence of the constituent alkali metal with respect to the amount of ionic and metallic character of chemical bonding. For this purpose we reacted Rb_2O with gold in excess rubidium at 100 °C. After six weeks the excess rubidium was distilled off leaving a blackish-grey solid. Wedge-shaped, transparent crystals can be isolated but they are extremely oxygen- and moisture-sensitive.

X-Ray powder patterns can be indexed assuming a cubic unit cell [$a = 5.501(2) \text{ \AA}$]. According to the results of a single-crystal structure determination the novel compound is identified to be Rb_3AuO .[†] Rb_3AuO crystallizes in the ideal cubic anti-perovskite structure type (anti- CaTiO_3). Gold adopts the Ca-position, oxygen the Ti-position (Fig. 1). If the changes of the coordination numbers of oxygen are considered the O-Rb distance [$2.751(1) \text{ \AA}$] agrees satisfactorily with the corresponding one in Rb_2O (2.92 \AA),⁷ while the Rb-Au distance [$3.889(1) \text{ \AA}$] is lengthened in contrast to Rb-Au [3.55 \AA]⁸ and becomes equal to the sum of the metallic radii (3.92 \AA).⁹ On the one hand this is at least in part an effect of coordination number increase from 8 (RbAu) to 12 (Rb_3AuO), but also it must be attributed to a reduced ionic character of the bond in favour of more metallic contribution.

A comparison of the molar volumes lends further support to this interpretation. The molar volume of Rb_3AuO ($100.3 \text{ cm}^3 \text{ mol}^{-1}$) is larger than the sum of RbAu and Rb_2O ($91.6 \text{ cm}^3 \text{ mol}^{-1}$),^{8,10} but lower than the sum of Rb_2O and the metallic components Rb and Au ($116.2 \text{ cm}^3 \text{ mol}^{-1}$).⁹ In contrast, the molar volume of the ionic Cs_3AuO (112.9

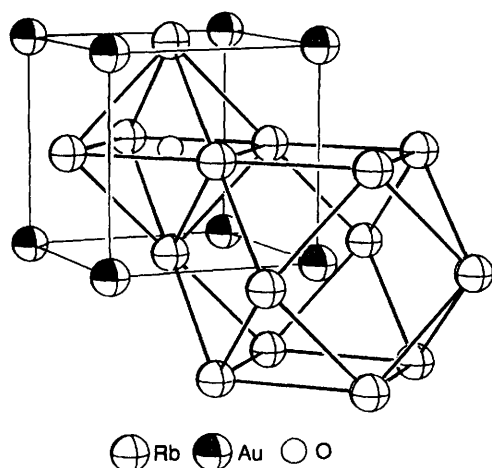


Fig. 1 Unit cell of Rb_3AuO with accentuated polyhedrons around gold and oxygen

$\text{cm}^3 \text{ mol}^{-1}$) is equal to the sum of the constituting binaries CsAu and Cs_2O ($111.3 \text{ cm}^3 \text{ mol}^{-1}$).^{8,10} Thus, the ionic character of ternary alkali metal gold oxides decreases with the introduction of lighter and more electronegative alkali metals.

The anionic character of gold can be established independently by comparing the gold L_1 XANES spectra of Rb_3AuO and suitable references (Au_2O_3 , AuCN, Au, CsAu, Cs_3AuO) (Fig. 2).⁶ The dependence between the oxidation state of gold and the ionisation energy of the Au 2s electron is marked by the turning point of the absorption edge. In the case of Rb_3AuO the ionisation energy is higher than in CsAu and Cs_3AuO , but lower than in metallic gold (Table 1). Thus, the anionic character, even though less pronounced than in the caesium compounds, is confirmed.

In conclusion, the question whether gold is in an anionic state or not, obviously can not be answered simply by 'yes' or 'no': the anionic character seems to vary with, and to be decided by, the choice of the alkali metal component. How

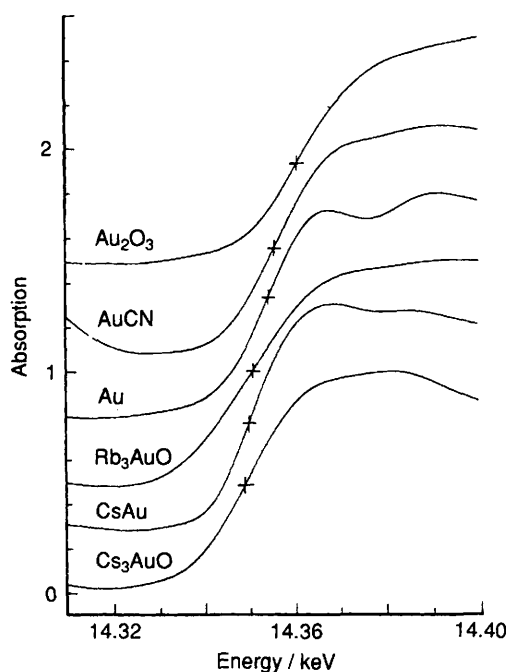


Fig. 2 Au- L_1 -XANES spectra of Rb_3AuO and references (turning points are marked by crosses)

Table 1 Ionisation energies of the Au 2s electrons (I) depending on the oxidation state of gold and their difference from the ionisation energy of metallic gold (I_0)

Compound	Oxidation state of gold	I/eV	$I - I_0/\text{eV}$
Au_2O_3	+3	14360.3	+6.9
AuCN	+1	14355.0	+1.6
Au	± 0	14353.4	± 0.0
Rb_3AuO	(-1)	14350.3	-3.1
CsAu	-1	14349.9	-3.5
Cs_3AuO	-1	14349.8	-3.6

these gradual changes in the electron distribution express themselves microscopically has not been clarified, so far. There are some indications favouring the local picture of decreasing strength of attractive interactions between core and excess electrons in Au^- with decreasing atomic number of the alkali metal resulting in an increase in the size of Au^- .

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Footnote

† Crystal data for Rb_3AuO : $M_r = 469.38 \text{ g mol}^{-1}$, cubic, $a = 5.501(2) \text{ \AA}$, $V = 166.55(9) \text{ \AA}^3$, space group $Pm\bar{3}m$, $Z = 1$, $D_c = 4.680 \text{ g cm}^{-3}$, $F(000) = 198$, $\mu(\text{Mo-K}\alpha) = 43.731 \text{ mm}^{-1}$. Data were collected on an Enraf Nonius CAD 4. 2258 data were recorded and merged to give 137 unique reflections. The structure was solved via Patterson method and refined by least-squares analysis. Rb on 3c, Au on 1a, O on 1b, $R = 0.039 [F_o > 3\sigma(F)]$.

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Fachinformationszentrum Karls-

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