anionic amide dbabh. U: triple-ζ basis set with polarization functions frozen core (5d); N: triple-ζ basis set with polarization functions frozen core (1s); H: double-ζ basis set with polarization functions including H polarization.
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Base-Induced Disproportionation of Elemental Gold**

Anja-Verena Mudring and Martin Jansen*

Elemental gold is the paragon of precious, not only in a chemical sense. This evaluation is based on its general chemical inactivity which seems to weaken, however, with respect to extremely electron-rich reaction partners. Thus, in spite of its high melting point, gold reacts under mild conditions with molten alkali metals. Particularly the formation of Cs_3AuO from CsAu and Cs_2O by interdiffusion in the solid state indicates that in such compounds gold is able to exist as an anion with an excess, localized electron.[1] Here, a decisive role is played by the high-electron affinity of gold, which comes close to that of iodine. This obvious relationship to the chemistry of halogens is well supported by crystal-chemical arguments. Thus, there are a number of isotypic alkali auride oxides and alkali halogenide oxides in which Au^- takes over the same crystal-chemical function as a halogenide.[2]

We have now observed another amazing parallel to the chemistry of halogens: like these, gold seems to disproportionate under the influence of bases. In reactions of gold with the alkali metals cesium, rubidium, or potassium, and the corresponding alkali metal oxides in ratios of alkali metal to gold of three or higher, anti-perovskites of formula type M_3AuO develop.[3] If less alkali metal is used, the disproportionation of gold into Au^+ and Au^- is observed and the novel alkali metal auride aurates(I) $Rb_7Au_5O_2$ ($[RbAu]_4[Rb_3AuO_2]$) and $Cs_7Au_5O_2$ ($[CsAu]_4$-$[Cs_3AuO_2]$) are formed. The structural features clearly indicate the presence of monovalent gold in the form of characteristic AuO_2^{3-} dumbbells along with Au^- with its typical distances between alkali metal and Au^-. Independent of this, the presence of gold in the two mentioned valence states was confirmed by Mössbauer spectroscopy; both the isomeric shift and the quadrupolar splitting confirm the presence of Au^+ and Au^- next to each other.[4]

At first glance it seems paradox that gold, in a positive oxidation state, can form during the reducing influence of the alkali metals. The effect of some oxidizing agents can be excluded since—even when handling the extremely oxidation-sensitive reactants in inadequate working conditions—traces of oxygen are immediately absorbed by the alkali metal. Thus, the positively charged gold must have formed through disproportionation, whereas in strong analogy to the disproportionation of halogens, as induced by bases, the stabilization of the positive oxidation state by complexation is the most important contribution to the driving force of this reaction. But, also the high electron affinity of gold, as well as the stabilization of Au^- by coulombic interactions with the alkali ions are significant components for the stabilization.

According to the results of single-crystal structure analyses,[5, 6] which have been confirmed by powder X-ray diffraction, $Rb_7Au_5O_2$ and $Cs_7Au_5O_2$ crystallize as representatives of a completely new structure type (Pearson Code oI28), which unites both the characteristic structural features of oxoaurates(I) and ionic aurides. Remarkably, both corresponding structure parts are spatially separated in such a way that the complete structure can be regarded as an intergrowth of layers of composition Cs_3AuO_2 and $(CsAu)_4$ (Figure 1).

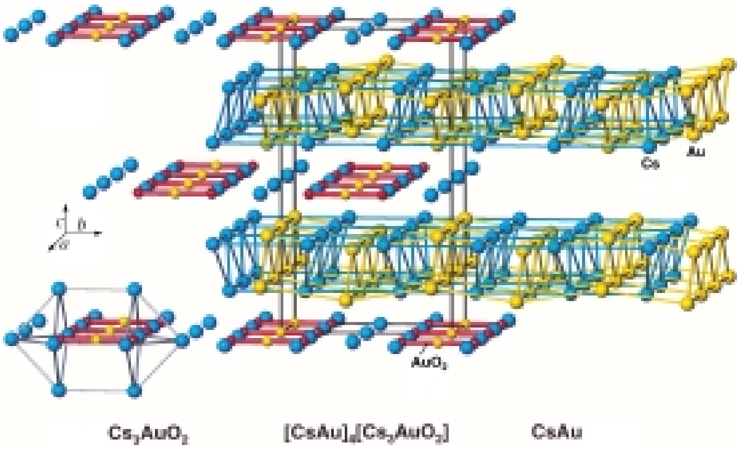

Figure 1. Perspective representation of the crystal structure of $Cs_7Au_5O_2$, (left: Cs_3AuO_2 partial structure, right: CsAu partial structure, center: $[CsAu]_4[Cs_3AuO_2]$ with unit cell). The connecting lines between Cs (blue) and Au (yellow) highlight the layered-type of structure and emphasize the connection to the tungsten carbide type. Mean bond lengths in $Cs_7Au_5O_2$: $d(Au^+{-}O) = 200$, $d(Au^-{-}Cs) = 375$ pm. For the isotypic compound $Rb_7Au_5O_2$: $d(Au^+{-}O) = 200$, $d(Au^-{-}Rb) = 372$ pm.

According to the site symmetry (*mmm*), the AuO_2^{3-} ions, which show the expected bond lengths, are exactly linear[7] ($d(Au{-}O) = 200$ pm), and are surrounded by a bicapped cube of ten alkali metal ions. An analogue of this building unit is found in pure Cs_3AuO_2.[8] In the auride partial structure, the alkali metals and gold form approximately the same nets of trigonal prisms, interpenetrating each other. Thus, this part of the structure corresponds to a distorted section of the

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tungsten carbide type. In an alternative approach, the Cs^+/Au^- partial structure can be derived from the binary component CsAu[9] (CsCl-type), by cutting out a disk which is oriented along (101), and is of a half a face diagonal of the unit cell of CsAu in thickness. The latter description seems in this respect more suitable because gold is located rather on the faces of the trigonal-prismatic cesium polyhedra than in their centers. In addition, these prisms are completed to give cubes by cesium atoms from the Cs_3AuO_2 layer.

The two auride aurates introduced here complement the group of compounds carrying the same element in a positive, as well as a negative oxidation state by representatives being remarkably stable. In spite of the proximity in space of Au^- and Au^+ (shortest distance $d(Au^+{-}Au^-) = 428$ pm), no redox lability is found.

Experimental Section

$Rb_7Au_5O_2$ and $Cs_7Au_5O_2$ were obtained as single-phase solids by reaction of the required amounts of alkali metal aurides MAu (M = Rb, Cs) with gold, and the corresponding alkali oxides under argon at $T = 425\,^\circ C$ for one day. Samples of higher crystallinity were obtained by starting from alkali metal, gold, and alkali metal oxide, and by using an excess of alkali metal which is distilled off in dynamic vacuum on completion of the reaction. The alkali metals themselves were prepared by reducing the corresponding chlorides with calcium, and were distilled before usage.[10] The alkali metal monoxides were made by oxidizing the respective alkali metal with the appropriate amount of oxygen.[11] Elemental gold was precipitated by reducing tetrachloric gold acid with sodium oxalate.[12]

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[5] Crystallographic data of $Rb_7Au_5O_2$: orthorhombic, space group *Immm* (no. 71), $a = 567.1(1)$, $b = 930.1(2)$, $c = 1659.3(3)$ pm, $V = 875.3(3) \times 10^6\,pm^3$, $\rho_{calcd} = 6.128\,g\,cm^3$, $Z = 2$, $\mu Mo_{K\alpha} = 61.071\,mm^{-1}$, $F(000) = 1340$, $\lambda = 71.073$ pm, Enraf-Nonius CAD4 diffractometer, graphite monochromator, $T = 293$ K, $\omega/2\theta$ scan, 1014 measured reflections, 265 symmetry-independent reflections, 30 refined parameters. Empirical absorption correction (psi-scans). Structure solution (heavy atoms) with direct methods.[13] Subsequent difference Fourier analysis provided the positions of oxygen atoms. All positions can be refined anisotropically giving $R_1 = 0.043$ and $wR_2 = 0.1110$.[14]

[6] Crystallographic data of $Cs_7Au_5O_2$: orthorhombic, space group *Immm* (no. 71), $a = 599.4(1)$, $b = 960.6(3)$, $c = 1721(1)$ pm, $V = 990.8(8) \times 10^6\,pm^3$, $\rho_{calcd} = 6.572\,g\,cm^3$, $Z = 2$, $\mu Mo_{K\alpha} = 49.54\,mm^{-1}$, $F(000) = 1592$, $\lambda = 71.073$ pm, Enraf-Nonius CAD4 diffractometer, graphite monochromator, $T = 293$ K, $\omega/2\theta$ scan, 3395 measured reflections, 476 symmetry-independent reflections, 30 refined parameters. Empirical absorption correction (psi-scans). Structure solution (heavy atoms) with direct methods.[13] Subsequent difference Fourier analysis provided the positions of oxygen atoms. All positions can be refined anisotropically giving $R_1 = 0.0431$ and $wR_2 = 0.0756$. Further details on the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-411333 ($Rb_7Au_5O_2$) and CSD-411334 ($Cs_7Au_5O_2$).

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Unusual C–H···Se=C Interactions in Aldols of Chiral *N*-Acyl Selones Detected by Gradient-Selected $^1H-^{77}Se$ HMQC NMR Spectroscopy and X-ray Crystallography**

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During the past decade we have been exploring the uses of the selenocarbonyl group both as an analytical tool to interrogate chiral centers[1] (using ^{77}Se NMR spectroscopy) and as a platform for the development of new asymmetric chemical methods associated with selone-based chiral derivatizing agents (CDAs). In the course of these studies, we have uncovered a new type of aldol reaction using chiral *N*-acyl selone reagents (Scheme 1), in which the selenocarbonyl group plays a pivotal role in the stereoselectivity of these reactions.[2] An unexpected observation in the aldol products was proton couplings to the selenium atom of the CDA.

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