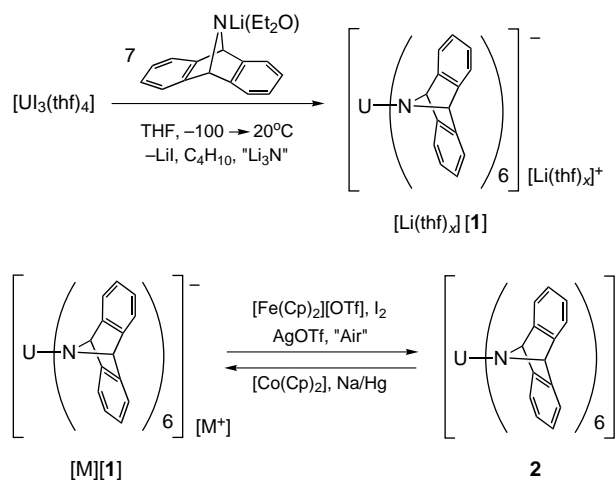


Uranium Hexakisamido Complexes**

Karsten Meyer, Daniel J. Mindiola, Thomas A. Baker, William M. Davis, and Christopher C. Cummins*

Here we report on the synthesis and characterization of the unique hexakisamidouranium(v) anion $[U(dbabh)_6]^-$ (**1**, Hdbabh = 2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene^[1]) and its one-electron oxidation product, namely the neutral homoleptic uranium(vi) derivative $[U(dbabh)_6]$ (**2**). Employed previously in the synthesis of terminal nitrido derivatives of chromium(vi), the dbabh ligand is redox-active such that elimination of anthracene from a complex containing it effects a two-electron oxidation.^[2] The latter feature is critical to the present synthesis of anion **1**, a synthesis beginning with uranium(III) and employing anthracene elimination as the means for oxidation to uranium(v).

Accordingly, treatment of a thawing solution of $[U(THF)_4]^{3+}$ in THF with a cold ethereal suspension of $[Li(dbabh)(OEt_2)]$ (7 equiv) provided an orange crystalline precipitate of the lithium salt $[Li(thf)_x][1]$ in 85% yield. Anthracene (ca. one equivalent per mol uranium) was shown by ¹H NMR spectroscopy to be a by-product of the reaction. Additionally, the yield of anion **1** was found to be maximized when seven equivalents of $[Li(dbabh)(OEt_2)]$ were employed, supporting the stoichiometry for the reaction as proposed in Scheme 1. Recrystallization of $[Li(thf)_x][1]$ from a saturated



Scheme 1. Synthesis of the homoleptic hexakisamidouranium(v) and (vi) complexes. Cp = C₅H₅, Tf = SO₂CF₃.

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solution of $[PPh_4][Br]$ in dichloromethane/hexane at $-40^\circ C$ afforded cube-shaped, exceedingly air-sensitive but thermally stable crystals of the salt $[PPh_4][1]$.

The hexakisamidouranium(v) complex $[Li(thf)_x][1]$ was found to be EPR-silent at room temperature, but its X-band EPR spectrum in a dilute frozen acetonitrile/toluene solution at 20 or 100 K evinced a single broad isotropic signal centered at $|g| = 1.12$ (Figure 1).^[4] The isotropic g value observed for **1** is unexceptional given that other pseudo-octahedral uranium(v) complexes exhibit a similar parameter, some exam-

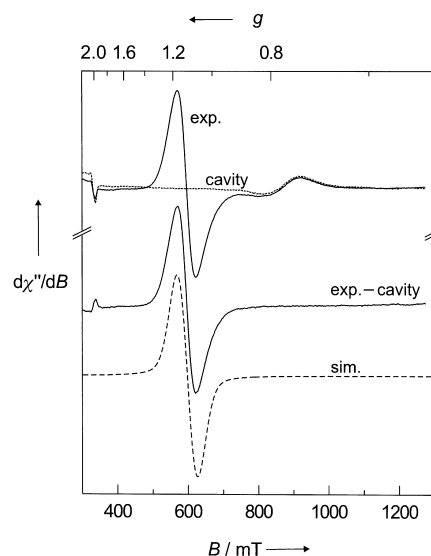


Figure 1. X-band EPR spectrum of $[Li(thf)_x][1]$ recorded in CH₃CN/toluene at 20 K. Shown are the measured spectrum (exp.), that of the sample chamber (cavity), the difference between the two spectra (exp. – cavity), and the simulated spectrum (sim.).

ples being $[UCl_5(SOCl_2)]$ ($g_{calcd} = -1.18$, $|g_{exp}| = 1.1(15)$) and $[U(OEt)_5]_2$ ($g_{calcd} = -1.16$).^[5] SQUID magnetometry revealed the magnetic moment for microcrystalline $[nBu_4N][1]$ to be $1.16 \mu_B$ in a temperature range between 5 and 35 K.^[6] The low g value together with the magnetic susceptibility data are characteristic of an ion with a 5f¹ electron configuration in a cubic crystal field, perturbed additionally by spin-orbit coupling.^[7] In contrast, it was shown recently that low-symmetry organometallic derivatives of uranium(v) supported by η^5 -C₅H₅ or η^8 -C₈H₈ ligation exhibit highly anisotropic g values ranging from 3.3–0.7.^[8]

While salts of the paramagnetic anion **1** are extremely air-sensitive, the corresponding neutral uranium(vi) derivative $[U(dbabh)_6]$ (**2**) is remarkably robust and is the only detectable product of air-oxidation of anion **1**. Salts of anion **1** were seen to exhibit a one-electron oxidation wave at -1.01 V versus the ferrocene/ferrocenium couple (see Supporting Information). Chemical oxidation of **1** thus was conveniently accomplished with silver triflate, a regimen providing **2** in 95% yield from $[Li(thf)_x][1]$. Recrystallization from toluene at $-40^\circ C$ over a few days delivered **2** as dark purple prisms.

Single-crystal X-ray diffraction studies were carried out for salt $[PPh_4][1]$ ^[9] and for neutral **2** (Figure 2).^[10] In both cases, two crystallographically independent but chemically equiv-

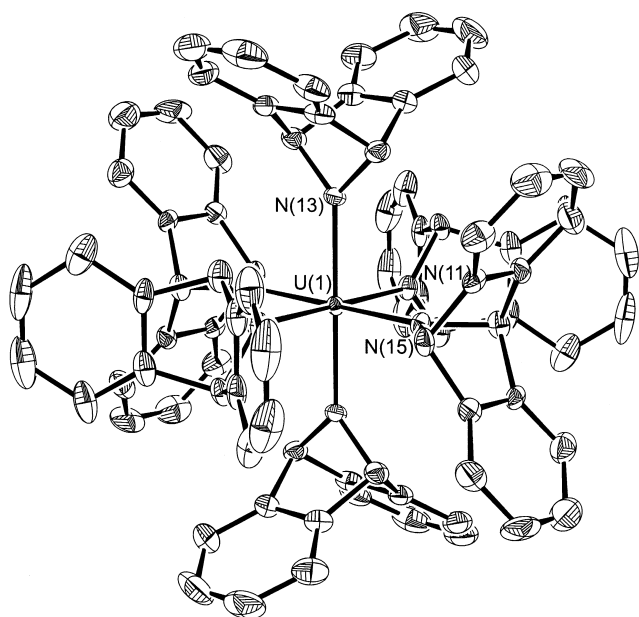


Figure 2. Molecular structure of $[U(dbabh)_6]$ (**2**) (see text for details).

alent molecules were found to be present in the asymmetric unit. Both uranium atoms in **1** and **2** reside at crystallographic inversion centers, such that there are three crystallographic U–N distances per uranium center. The six amido nitrogen atoms in the uranium(v) and (vi) species define a near-perfect octahedron, the U–N distances ranging from 2.230(11) to 2.267(13) Å in anion **1** and from 2.178(6) to 2.208(5) Å in neutral **2**. The observation of slightly shorter bond lengths in **2** than in **1** is explicable in terms of the higher formal oxidation state for the uranium center in the former. N–U–N angles for **1** and **2** are 90° to within experimental error, in accord with the point group symmetry T_h , which is approximated by the $[U(dbabh)_6]^{0/1-}$ molecules. A point of interest with respect to ligand conformation is that the angles about each of the nitrogen atoms sum to 360(11)° in **1** and 360(5)° in **2**, such that the dbabh ligands are disposed favorably for π donation to the respective uranium centers.

A single ligand environment is evidenced in the solution NMR spectra of **2**, consistent with the molecule's T_h symmetry.^[11] The line widths in the 1H NMR spectra of **2** were determined to be less than 1.5 Hz and the observed shifts are in a range typical for organic derivatives of the ligand, such as $H(dbabh)$ or $Br(dbabh)$.^[1] On the other hand, it is found that the 1H NMR spectra of mixtures of diamagnetic **2** and salts of paramagnetic anion **1** represent an average of the two independent spectra. This phenomenon, being indicative of self-exchange electron transfer in the **1/2** couple, warrants further investigation.

Two distinct absorption bands are observed in the electronic absorption spectrum of **2**, one at 353 nm ($\epsilon = 2200\text{ M}^{-1}\text{ cm}^{-1}$), the other at 501 nm ($\epsilon = 1200\text{ M}^{-1}\text{ cm}^{-1}$) (see Supporting Information).^[12]

Group theoretical considerations and density functional theory (DFT) calculations indicate that in anion **1** the ground state involves population of a nonbonding $5f_{xyz}$ orbital by the unpaired electron, while in neutral **2** the HOMO is triply

degenerate and consists of amido to uranium π -bonding molecular orbitals.^[13] In the latter orbitals, the character is largely nitrogen 2p, but contributions from uranium 5f and 6d functions also are indicated (Figure 3).

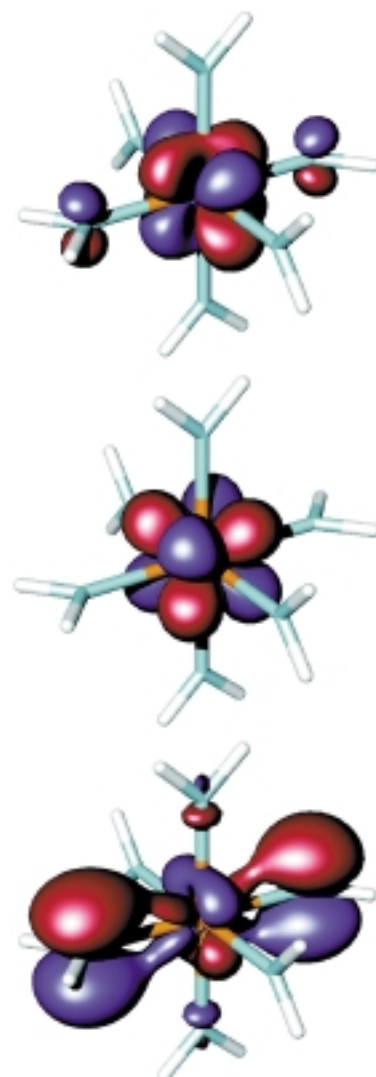


Figure 3. Antibonding LUMO (top), SOMO (middle), and HOMO (bottom) of the model $[U(NH_2)_6]^-$ ion (LUMO and HOMO are threefold degenerate).

Anion **1** and its redox partner, neutral **2** are unique in uranium chemistry for being isolable hexakisamido complexes, and also for providing a robust redox couple in which the addition or removal of an electron is accompanied by minimal structural change. Other examples of hexakisamido-uranium derivatives include $[U(NMe_2)_6]$, but the latter evidently has not been isolated, being characterized only by its proton NMR spectrum.^[14] Hexakisamido complexes are more common in transition metal chemistry, being exemplified by $[M(NMe_2)_6]$ ($M = Mo, W$);^[15, 16] however, the latter neutral complexes are not known to have well-defined anionic counterparts. The stability of $[U(dbabh)_6]$ in two states of charge is reminiscent of the behavior of other robust couples that retain their structural integrity, such as the archetypal ferrocene/ferrocenium couple.

Experimental Section

[Li(thf)₃][1], [nBu₄N][1], [Ph₄P][1]: A cold suspension of [Li(dbabh)]·Et₂O (350 mg, 1.28 mmol) in diethyl ether (7 mL) was added to a cold solution (−90 °C) of [U₃(thf)₄] (172 mg, 0.18 mmol) in THF (7 mL) and stirred. After 2 h at −50 °C the resulting greenish-brown solution was allowed to reach room temperature and was filtered. Within 36 h, orange crystals of [Li(thf)₃][U(dbabh)₆] were filtered off, washed with diethyl ether, and dried in vacuum (225 mg, *x* = 0, 0.16 mmol, 89 %). Recrystallization from a saturated solution of [nBu₄N][ClO₄] in THF yielded orange needle-shaped crystals of [nBu₄N][U(dbabh)₆]. Block-shaped single crystals of [Ph₄P][U(dbabh)₆] suitable for an X-ray diffraction analysis were obtained from a CH₂Cl₂/hexane solution containing [PPh₄][Br]. ¹H NMR (300 MHz, CD₃CN, 23 °C): δ = 4.42 (s, 2H, Δ*ν*_{1/2} = 110 Hz), 6.73 (s, 4H, Δ*ν*_{1/2} = 13 Hz), 6.86 (s, 4H, Δ*ν*_{1/2} = 10 Hz); elemental analysis (%) calcd for [nBu₄N][1]: C 73.47, H 5.92, N 6.03; found: C 73.28, H 6.08, N 6.03.

2: Reaction of a solution of [Li(thf)₃][1] (350 mg, 0.25 mmol) in acetonitrile (20 mL) with a solution of silver trifluoromethanesulfonate (AgOSO₂CF₃ (AgOTf); 72 mg, 0.28 mmol) or with stoichiometric amounts of [(C₅H₅)₂Fe][X] (X = SO₃CF₃ (OTf), B[3,5-(CF₃)₂C₆H₃]₄) in acetonitrile resulted in the spontaneous formation of colloidal silver metal and precipitation of **2**. After filtering off the residues and washing the solids with tetrahydrofuran, the filtrate was evaporated to dryness yielding **2** (330 mg; 0.24 mmol, 95 %). Recrystallization from toluene at −40 °C yielded dark purple prism-shaped crystals of **2** suitable for X-ray diffraction analysis. ¹H NMR (500 MHz, C₆D₆, 25 °C): δ = 5.72 (s, 2H, Δ*ν*_{1/2} = 1.3 Hz), 6.99 (q, 4H, Δ*ν*_{1/2} = 1.5 Hz), 7.14 (q, 4H, Δ*ν*_{1/2} = 1.5 Hz); ¹³C NMR (500 MHz, C₆D₆, 25 °C): δ = 71.5 (s), 122.3 (s), 126.6 (s), 159.9 (s); elemental analysis (%) calcd for **2**: C 72.51, H 4.35, N 6.04; found: C 73.11, H 4.49, N 5.85.

The X-band EPR spectra of [Li(thf)₃][1] were performed on a Bruker EMX spectrometer equipped with a helium flow cryostat (Oxford Instruments ESP 310) in the temperature range 20–300 K. The magnetization of crystalline powdered samples of [nBu₄N][1] was recorded between 5–300 K at 0.1, 0.3, 0.5, and 0.7 T with a SQUID magnetometer (Quantum Design). Values of the magnetic susceptibility were corrected for the underlying diamagnetic increment (*χ*_{dia} = −922.1 × 10^{−6} cm³mol^{−1}) by using tabulated Pascal constants and the effect of the blank sample holder (gelatine capsule/straw).

Cyclic voltammetry was performed under N₂ in dry THF containing predried and recrystallized tetra-*n*-butylammonium perchlorate (TBA-ClO₄; Aldrich, ca. 0.9 M). A platinum disk electrode (1.6 mm diameter, Bioanalytical Systems), a platinum wire, and a silver wire were employed as the working electrode. A one-cell compartment was used in the cyclic voltammetry measurements. The electrochemical response was collected with the assistance of an Eco-Chemie Autolab potentiostat (pgstat20) and the GPES 4.3 software package. The ferrocenium/ferrocene couple was used as internal standard. Scan rates varied between 25 and 160 mV s^{−1}.

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- [9] Crystallographic details for [Ph₄P][1]: Orange block-shaped crystals grown from a concentrated solution of [Li(thf)₃][U(dbabh)₆] and excess of [PPh₄][Br] in CH₂Cl₂/hexane at −40 °C were coated with Paratone N oil (Exxon) on a microscope slide. A crystal of approximate dimensions 0.1 × 0.1 × 0.1 mm was selected and mounted with wax on a glass fiber. A total of 27648 reflections (−10 ≤ *h* ≤ 15, −30 ≤ *k* ≤ 30, −28 ≤ *l* ≤ 27) were collected at *T* = 173(2) K in the *θ* range of 1.51 to 20.00° of which 9083 were unique (*R*_{int} = 0.0774); MoK_α radiation (λ = 0.71073 Å). The structure was solved by Patterson methods (SHELXTL V5.0, G. M. Sheldrick and Siemens Industrial Automation, Inc., 1985) in conjunction with standard difference Fourier techniques. The symmetry transformation used to generate equivalent atoms were 1) −*x*, −*y* + 1, −*z* + 1; 2) −*x*, −*y* + 1, −*z* + 2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated (*d*_{C-H} = 0.96 Å) positions. The residual peak and hole electron density was 0.522 and −0.516 e Å^{−3}. The absorption coefficient was 1.783 mm^{−1}. The least-squares refinement converged normally with residuals of *R*₁ = 0.1273 (all data), *wR*₂ = 0.1754, and GOF = 1.189 (*I* > 2σ(*I*)). The extinction coefficient was negligible (0.00054(5)). C₁₀₉H₈₂Cl₂N₆PU, space group *P*2₁/*c*, monoclinic *a* = 13.74580(10), *b* = 27.7384(4), *c* = 26.1124(4) Å, β = 101.5730(10)°, *V* = 9753.9 Å³, *Z* = 4, ρ_{calcd} = 1.236 g cm^{−3}, *F*(000) = 3676, *R*(*F*) = 0.0946, *wR*(*F*²) = 0.1540.^[18]
- [10] Crystallographic details for **2**: Purple prism-shaped crystals grown from a concentrated solution of toluene at −40 °C were coated with Paratone N oil (Exxon) on a microscope slide. A crystal of approximate dimensions 0.60 × 0.35 × 0.33 mm was selected and mounted with wax on a glass fiber. A total of 18355 reflections (−30 ≤ *h* ≤ 30, −22 ≤ *k* ≤ 18, −18 ≤ *l* ≤ 17) were collected at *T* = 183(2) K in the *θ* range of 1.27 to 23.26° of which 6586 were unique (*R*_{int} = 0.0443); MoK_α radiation (λ = 0.71073 Å). The structure was solved by Patterson methods (SHELXTL V5.0, G. M. Sheldrick and Siemens Industrial Automation, Inc., 1985) in conjunction with standard difference Fourier techniques. The symmetry transformation used to generate equivalent atoms were 1) −*x*, −*y* + 1, −*z* + 1; 2) −*x*, −*y*, −*z*; 3) −*x*, *y*, −*z* + 1; 4) *x*, −*y* + 1, *z*; 5) −*x*, *y*, −*z*; 6) *x*, −*y*, *z*. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated (*d*_{C-H} = 0.96 Å) positions. Excess electron density was observed but no chemical assignment could be made except the possibility of solvent. The residual peak and hole electron density was 0.938 and −0.620 e Å^{−3} after the data was treated with the SQUEEZE algorithm to reduce the effects of excess electron density.^[17] The absorption coefficient was 1.860 mm^{−1}. The least-squares refinement converged normally with residuals of *R*₁ = 0.0637 (all data), *wR*₂ = 0.0805, and GOF = 1.086 (*I* > 2σ(*I*)). The extinction coefficient was negligible (0.00000(2)). C₈₄H₆₀N₆U, space group *C*2/*m*, monoclinic *a* = 27.7468(3), *b* = 20.0934(2), *c* = 16.8916(2) Å, β = 108.9560(10)°, *V* = 8906.8(2) Å³, *Z* = 2, ρ_{calcd} = 1.038 g cm^{−3}, *F*(000) = 2792, *R*(*F*) = 0.0321, *wR*(*F*²) = 0.716.^[18]
- [11] The ¹H NMR spectrum of **2** recorded in C₆D₆ evinces a characteristic singlet at δ = 5.72 assigned to the bridgehead protons of the coordinated dbabh ligands. The aromatic protons, eight per dbabh unit, give rise to two well-resolved quadruplets centered at δ = 6.99 and 7.14. A 2D ¹³C{¹H} correlated NMR spectrum reveals that the bridgehead carbon resonance is located at δ = 71.5, while the proton resonance at δ = 7.14 correlates with the ¹³C peak at δ = 122.3. The proton resonance centered at δ = 6.99 shows a crosspeak at δ = 126.6. The ¹³C resonance at δ = 159.9 therefore is assigned to the bridgehead-adjacent carbon atoms.
- [12] Additional features include a shoulder located on the bathochromic edge of the 501 nm band, along with tailing to the near IR region. These two additional features were simulated with low-intensity Gaussian lines at 660 nm (ε = 400 M^{−1}cm^{−1}) and 900 nm (ε = 70 M^{−1}cm^{−1}).
- [13] The geometry of the model compound [U(NH₂)₆] was optimized by using the Vosko, Wilk, and Nusair (VWN) local density approximation. We also used Becke's (1988) exchange correction and Perdew (1986) correlation for the gradient corrections. Calculations also include scalar relativistic effects (Pauli Formalism). Since the Amsterdam-Density-Functional-Package is not able to calculate *T*_h symmetry, the calculations were performed using *D*_{2h} symmetry. The H-N-H angle was constrained to 95° as obtained by calculations on the

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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 [18] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142254 ([PPh₄] **1**) and CCDC-142255 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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 Cs₃AuO from CsAu and Cs₂O 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 M₃AuO 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) Rb₇Au₅O₂ ([RbAu]₄[Rb₃AuO₂]) and Cs₇Au₅O₂ ([CsAu]₄[Cs₃AuO₂]) are formed. The structural features clearly indicate the presence of monovalent gold in the form

of characteristic AuO₂^{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, Rb₇Au₅O₂ and Cs₇Au₅O₂ 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 Cs₃AuO₂ and (CsAu)₄ (Figure 1).

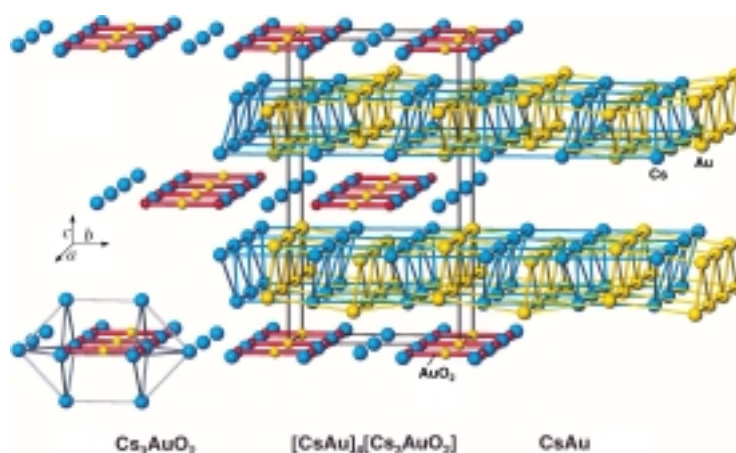


Figure 1. Perspective representation of the crystal structure of Cs₇Au₅O₂, (left: Cs₃AuO₂ partial structure, right: CsAu partial structure, center: [CsAu]₄[Cs₃AuO₂] with unit cell). The connecting lines between Cs (blue) and Au (yellow) highlight the layered-type of structure and emphasize the connection to the tungsten carbide type. Mean bond lengths in Cs₇Au₅O₂: $d(\text{Au}^+-\text{O}) = 200$, $d(\text{Au}^--\text{Cs}) = 375$ pm. For the isotypic compound Rb₇Au₅O₂: $d(\text{Au}^+-\text{O}) = 200$, $d(\text{Au}^--\text{Rb}) = 372$ pm.

According to the site symmetry (*mmm*), the AuO₂^{3−} ions, which show the expected bond lengths, are exactly linear^[7] ($d(\text{Au}-\text{O}) = 200$ pm), and are surrounded by a bicapped cube of ten alkali metal ions. An analogue of this building unit is found in pure Cs₃AuO₂.^[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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