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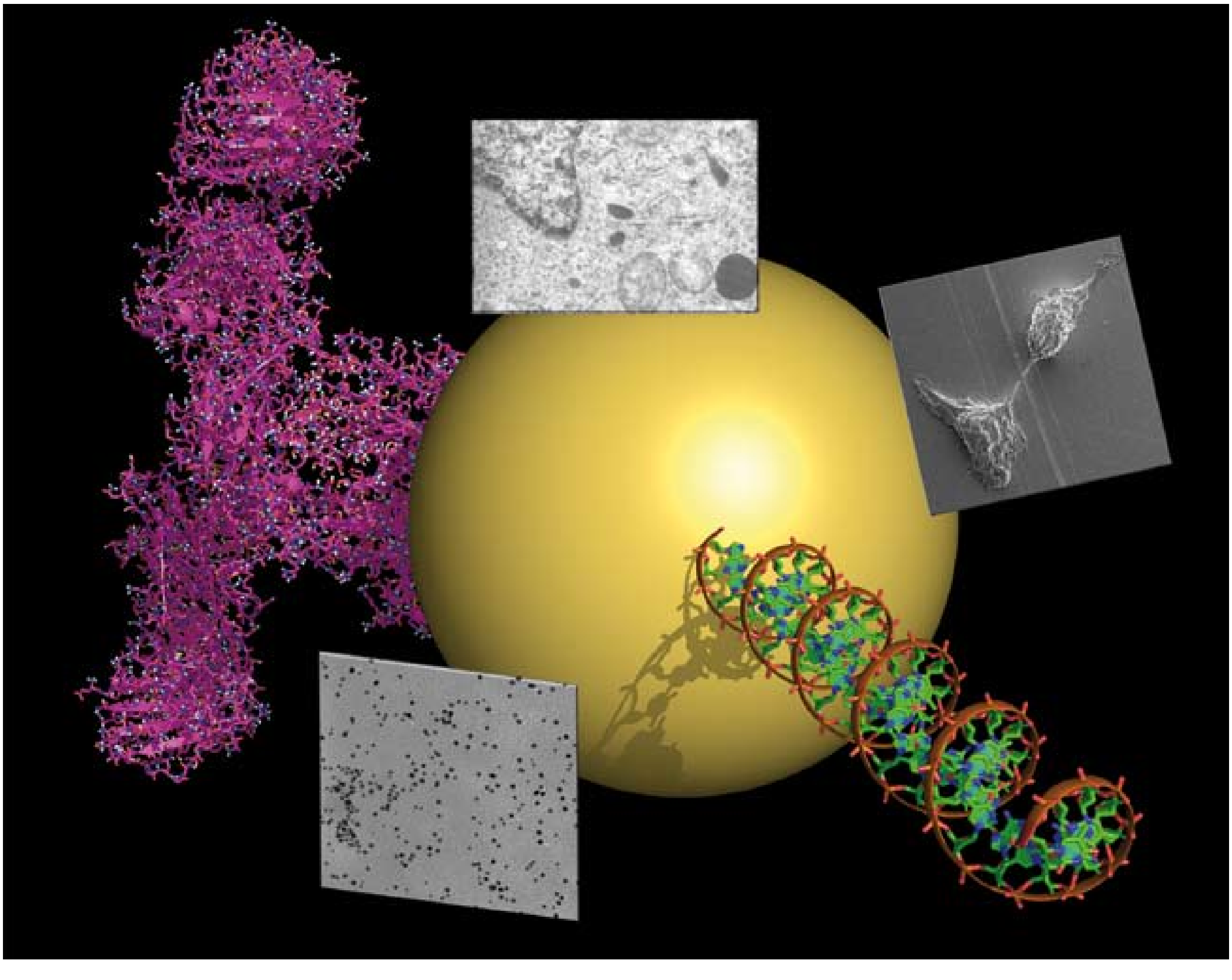

The chemistry of gold as an anion†

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Due to relativistic and classical shell structure effects, the 6s orbital of gold is significantly contracted and energetically stabilized. This is reflected by a strikingly high electron affinity, and a distinct tendency to adopt negatively polarized valence states. This *tutorial review* focuses on the chemistry of gold as an anion, displaying the integral ionic charge number of 1−. Two synthetic approaches to compounds containing monoatomic gold anions have become available: (1) reacting elemental gold with molten caesium and an oxide, *e.g.* Cs_2O; (2) metathesis reactions involving Au^- dissolved in liquid ammonia. Both procedures have proven to be rather versatile. Aurides synthesized along these routes are surveyed, in particular with respect to their structures and bonding properties.

1. Introduction

Gold was the first elemental metal utilized by humans, and has accompanied the evolution of civilization from the very beginning. Its relevance for both former and modern societies is reflected by its various applications, *e.g.* in coinage, or as a general means of exchange, in jewellery, in embroidery, in decoration, and as a coloring agent for glass; more recently gold has come into use as electrical contacts in the field of microelectronics, and as nanoparticles it is serving research and application in medicine, biology and materials sciences.[1] The unique properties of gold have inspired its use as a symbol for purity, value and royalty, as is also manifested by terms pervading in our language, such as "golden age" or "golden opportunity". The prevalence of such functions and meanings in common consciousness appears to even outshine the role of gold as a chemical element. However, with respect to its chemical properties too, gold is exceptional. As one of the amazing features, gold has been realized in oxidation states as high as 5+, by far exceeding the group number of one in the periodic table (former numbering scheme). Furthermore, all intermediate valence states down to 1− are accessible.[2] The noble gas xenon is bonded surprisingly tightly to gold cations, constituting a spectacular novel class of coordination compounds.[3] Attractive d^{10}–d^{10} interactions, a unique effect shared with its group homologues,[4–6] are particularly efficient for gold. Therefore the special term "aurophilicity" has been coined to denote this phenomenon.[7]

This review focuses on another peculiarity of gold, namely its inclination to assume negative valence states. Since the constituent atoms of compounds generally are subject to positive and negative polarizations (the degree to which depends on the difference in ionization potentials and electron affinities, *i.e.* differences in electronegativities of the different elements concerned) a more explicit specification is needed that would allow the characteristics of gold in this respect to be determined. The crucial measure to be taken in such a context is to assign charges to the atoms constituting a given compound. Such an assignment might be based on some terms commonly used in defining charges in chemical compounds. The most popular ones are "oxidation numbers" and "effective charges". While the former is well defined, it is however formal in nature and does not provide meaningful information about the real charge distribution. The latter sounds physically meaningful, but the numbers obtained strongly depend on the experimental or theoretical tools employed for their

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determination. The reason behind this ambiguity is the lack of a clear justification or a reasonable prescription for partitioning of space and assignment of certain volume increments to the hemisphere of an atom, within a chemical compound. This would be an essential prerequisite for determining charges, *i.e.* to balance the number of electrons in an atom against its nuclear charge. It should be mentioned, however, that when applying a specific experimental tool with a well defined reach in space, or a clearly defined theoretical prescription, *e.g.* Bader's approach,[8] good comparable values of ''relative'' effective charges are available. Since one of the primary purposes of this paper is to demarcate gold from the other metals with respect to its distinct ability to form stable monoatomic anions, we rather resort to the ''ionic charge number''‡ as the discriminating term. These are integral numbers defining the charge of moving particles as they can be monitored during transport experiments in solid or liquid electrolytes incorporated in an electrochemical setup, or during all solid state interdiffusion reactions. In the following, we are thus dealing with gold compounds for which it appears justified to assume the anion Au^- to be present as an integral entity. Consequently, all gold compounds with electropositive partners that are only able to induce incomplete charge transfer (for instance leading to partial Au–Au bonds or to metallic properties with itinerant electrons obscuring the presence of Au^-) are excluded from this survey. Extensive reviews dealing with intermetallics of gold and of gold cluster anions have appeared in the past,[9–11] and an extremely illustrative compilation, including all metals in negative oxidation states, has recently become available.[12]

2. The intrinsic stability of gold(−I)

As documented unequivocally by the relevant atomic data (Table 1), Au^- with the electron configuration [Xe] $6s^2 4f^{14} 5d^{10}$ represents an intrinsically stable species in vacuum. The first electron affinity of gold is the highest of all metals, and comes close to the values known for the halogens. In spite of its distinct stability, Au^- is not easily implemented in a real chemical environment. Only the most electropositive elements are able to fully transfer an electron to gold, and only (complex)cations with high lying acceptor levels are not reduced by Au^-. Less electropositive counter parts would in a first step partially oxidize gold, which may form negatively charged clusters, and finally elemental gold would precipitate.

The positive electron affinity and the relatively high first ionization potential can be traced back to a synergetic interaction of basically two effects. Since gold is the first element in the periodic table that experiences the well-known shell structure effects of d^{10}- and f^{14}-contractions simultaneously, a substantial stabilization of the electron(s) in the 6s orbital is expected to occur. These feel a nuclear charge drastically enhanced by 24, which is, however, only weakly screened by the respective d- and f-electrons added. Of course, such classical orbital effects are but part of the explanation. Electrons in the proximity of a highly charged nucleus (of a heavy element) are moving with a very high speed, even approaching the speed of light, resulting in a significant increase in the effective electron mass. s-Electrons are affected most strongly, p-electrons to a smaller extent. The consequences of the resulting ''relativistic effects'' (*cf.* Table 2) on the electronic structures of the atoms, and the implications for their chemical properties have been thoroughly reviewed.[15–19] Since two of the relativistic effects, the contraction/stabilization of s and p orbitals and the expansion of d and f orbitals, and the classical orbital effects give rise to changes in the electronic structures of the elements in the same direction, there is no easy way to discriminate these two factors of influence quantitatively. Nevertheless, one can regard the superposition of relativistic and the particularly strong orbital effects encountered by platinum, gold and mercury as responsible for the peculiarities as observed for these elements. To be more specific, some of the conspicuous features of the chemistry of gold mentioned above can be directly traced back to such effects: the high oxidation states possible,[2] the aurophilic interactions,[7] and last but not least the intrinsic stability of gold as an anion.[20,21]

3. Early evidence for anionic gold

Caesium auride, CsAu, is the most prominent representative of a compound believed to contain gold as a monoatomic anion. First indications of its existence and of its easy formation from the elements were obtained by W. Biltz and F. Weibke; in particular, they became aware of a significant shrinkage in volume with respect to the elements.[22] A. Sommer confirmed the composition.[23] Subsequently, a CsCl type of structure was assigned,[24,25] and by means of optical absorption spectroscopy, XPS and Mößbauer spectroscopy, the material was shown to possess a pronounced band gap and to exhibit a significant amount of ionic bonding.[24,26] These early findings have been corroborated in extensive further experimental studies, including solid solutions with CsBr and ionic conductivities in the molten and solid state.[27] All these results have been extensively reviewed, drawing a rather conclusive picture of the chemical and physical properties of CsAu.[20,28] Unfortunately, the resulting ideal view of an ionic crystal Cs^+Au^- has since been significantly disturbed by some further reports, stating a significant mutual replacement of Cs and Au to take place,[25] the color of a single crystal to be black,[29] or a positive temperature coefficient of the electronic resistivity.[30]

Independent evidence for the existence of Au^- in a chemical environment has been provided by Lagowski *et al.* by preparing solutions of Au^- in liquid ammonia[31] and in ethylenediamine.[32] They characterized Au^- by electrochemistry[33] and spectroscopy,[31] however, failed to isolate it from the solution. It is worth mentioning that, in retrospect, Zintl *et al.* appear to have already prepared solutions of gold anions in liquid ammonia, but obviously were not aware of this fact.[34] Birchall *et al.* managed to isolate from liquid ammonia solids which they regarded to be salts of Au^- with crypted (2,2,2-crypt) caesium and rubidium. Unequivocal evidence for the composition of these materials was missing, although the chemical shifts in gold-197 Mößbauer spectra clearly indicated anionic gold to be present.[35]

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‡ ''Ionic charge number'' is the integral number of excess elementary charges at ''isolated'' chemical species, which among others can be monitored in (electro-chemical) transport experiments.

Table 1 Selected physical properties of the coinage metals compared to those of the heavier halogens[13,14]

	Cu	Ag	Au	Br	I
Atom radius/pm	127.8	144.4	144.2	114.2	133.3
Electron affinity/kJ mol^{-1}	118.5	125.7	222.8	324.7	295.2
1. Ionisation energy/eV	7.725	7.576	9.22	11.81	10.45
2. Ionisation energy/eV	20.29	21.48	20.52	21.80	19.13
Electronegativity (Pauling)	1.90	1.93	2.54	2.96	2.66

Table 2 Relativistic effects

Direct: spin–orbit splitting	Instead of the angular momentum l and the spin momentum s their sum $j = s + l$ is used.
Direct: contraction of s and p orbitals	The contraction is due to relativistic mass increase as followed by a decrease in the Bohr radius. The contraction of the spherical $p_{1/2}$ subshell is comparable to the contraction of $s_{1/2}$. The $p_{3/2}$ subshell contracts much less.
Indirect: expansion of d and f orbitals	The s and p orbitals contracting inside and outside the d and f orbitals screen the nuclear attraction of the latter thus leading to their radial expansion.

Although these early studies, in particular those on CsAu, are lending clear support to the stability of Au^- in chemical environments, the selection of well-characterized compounds remained regrettably small, and a number of statements and conclusions given still required final confirmations.

4. Oxide aurides through solid state reactions

One way to conclusively verify the presence of gold ions bearing the integral charge of 1− is to perform interdiffusion reactions that require long distance transport of the intact anion. Indeed, by reacting solid CsAu and Cs_2O at temperatures around 573 K, which is significantly below the decomposition or melting temperatures of both reactants, the novel caesium oxide auride Cs_3AuO forms in quantitative yields.[36,37] Since the acceptor levels available for accommodating an electron are associated with either Cs^+ or O^{2-} states, and thus lie rather high, any alternative transport mechanism assuming decoupled diffusion of Au^0 and e^- can be excluded. Optimized syntheses of Cs_3AuO, and its homologues Rb_3AuO and K_3AuO, however, rely on using a considerable excess of the respective alkali metal, a measure that speeds up the reactions, and supports growth of single crystals.[37]

The crystal structures of the alkali metal oxide aurides are simple and of high symmetry, adopting the ideal hexagonal (Cs_3AuO) and cubic (Rb_3AuO, K_3AuO) perovskite structures (Fig. 1, Table 3). The mixed alkali representative of Cs_2RbAuO crystallizes isostructural to Cs_3AuO as a hexagonal perovskite. This indicates solubility of Rb_3AuO in Cs_3AuO to at least the molar ratio of 1 : 2.[39]

The alkali metal oxide aurides are extremely sensitive to air. They react with water, evolving hydrogen, while the respective alkali metal hydroxide and elemental gold remain as solid residues. In contact with oxygen or carbon dioxide, alkali metal oxides and gold, or alkali metal carbonates and alkali metal aurides form as decomposition products, respectively. Cs_3AuO, Rb_3AuO and K_3AuO melt at 717 K, 850 K and 799 K, respectively. They decompose at higher temperatures by releasing the alkali metal to the gas phase.[37]

The electronic structures have been characterized by optical absorption spectroscopy,[40] Au L_{III} and L_I XANES,[41,42] magnetic susceptibility[37] and conductivity measurements.[37] However, chemical and structural features are already shedding some light on the prevailing binding situation (Table 4). In particular, the M–M and M–Au bond-lengths (normalized to equal coordination numbers), falling significantly below the sums of the respective metallic radii, can be regarded as a first indication of the considerable contribution of ionic bonding. This effect becomes even more obvious if the molar volumes of the ternary phases are compared to the sum of molar volumes of the respective constituents M, Au and M_2O (M = K, Rb, Cs). In each case a considerable contraction is noticeable.[37] However, starting from the binaries MAu and M_2O, the volume shrinkage tends to vanish. This implies that on transforming the metals M and Au into the "ionic" MAu, almost all of the volume loss is already accounted for. Noteworthy, the relative differences in molar volumes between M + Au + M_2O and M_3AuO grow significantly, from 9.5 to 31.7 cm^3 mol^{-1}, when moving from M = K to Cs. This is providing qualitative evidence for the degree of ionic bonding, and thus the anionic character of gold to depend on the nature of the alkali metal.[37] The gradual anionic character of gold in the perovskite type oxides M_3AuO is also reflected by their basic physical properties. While crystals of Cs_3AuO are yellow and transparent, those of Rb_3AuO and K_3AuO are shiny black and opaque; the band gap of the former (2.35(2) eV) is typical for an insulator or a semiconductor,[40] whereas Rb_3AuO and K_3AuO have vanishing band gaps.

The positions of absorption edges as recorded by Au L_{III} and Au L_I XANES correlate with the valence states of gold. In the case of the L_{III} spectra, however, the exact position of the edge is hidden by the pre-edge feature corresponding to the excitation of an s electron into empty d states, with the peak area representing the number of empty d states. Fig. 2 shows a nice correlation of pre-edge features of selected gold compounds with intuitively assigned valence states; more importantly, the results are not in conflict with assigning a negative valence state to gold in Rb_3AuO, CsAu and Cs_3AuO. Au L_I XANES produces chemical shifts (ionization energies) that are significantly lower for CsAu and the A_3AuO-family, as compared to elemental gold.[41] Correlating chemical shifts of reference compounds with their oxidation states, and including the aurides and auride oxides in the resulting graph, provides further justification to assign the valence state of

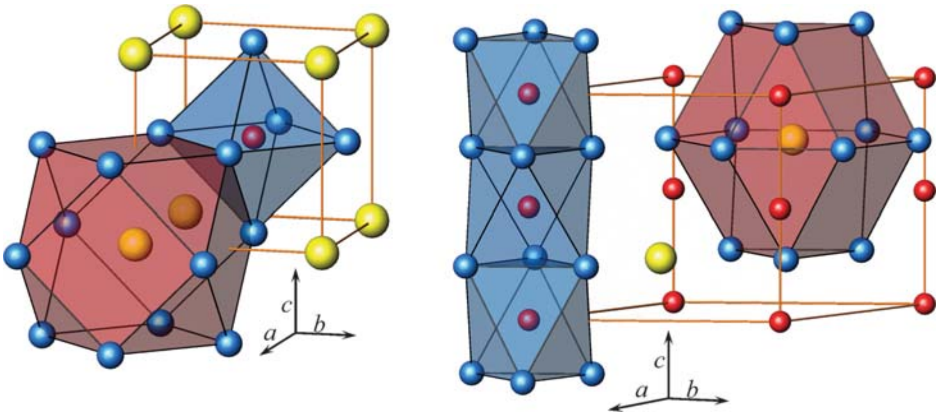

Fig. 1 Crystal structures of M_3AuO ((left), M = K, Rb; (right), M = Cs) with the coordination polyhedra around Au^- and O^{2-} emphasized (blue spheres: alkali metal atoms; yellow spheres: gold atoms; red spheres: oxygen atoms; orange lines: unit cell edges).

1− to gold in the latter compounds.[42] Interestingly, again a varying degree of localization of the $6s^2$ electrons of gold, *i.e.* of its anionic character, is unveiled by slight, but systematic variations in the chemical shifts.

Measurements of the magnetic susceptibilities for M_3AuO show diamagnetic behavior. However, when comparing the experimental data to the sums of tabulated increments of diamagnetic susceptibilities, systematically increasing discrepancies result for the sequence $Cs_3AuO \rightarrow Rb_3AuO \rightarrow K_3AuO$.[37] While for the caesium compound the sum of increments and experimental susceptibility correspond well, the experimental diamagnetic responses of the rubidium and potassium representatives are significantly too low. Assuming a temperature-independent paramagnetic contribution of some itinerant (conduction) electrons, and calculating the numbers of conduction electrons according to Landau,[43] a vanishing number is obtained for Cs_3AuO, whereas significant concentrations (of itinerant electrons) are found for the Rb and K compounds.[37] This is again corroborating the view of gold as showing a gradually varying anionic character in these compounds.

Ca_3AuN, synthesized from the elements, also adopts the ideal cubic perovskite type of structure, and was reported likewise to contain anionic gold.[44] However, this material is metallic and the itinerant electrons present might obscure the true valence state of gold.[45] Even with the most extreme electron count, $Ca_3^{2+}Au^-N^{3-}\cdot 4e^-$, four electrons are delocalized which, together with the rather unstable N^{3-} ion, would suggest a more delocalized bonding scheme.

Reacting gold with the alkali metals caesium, rubidium and potassium, and the corresponding alkali metal oxides, in ratios of alkali metal to gold of three or higher, the perovskites M_3AuO form. If less alkali metal is used, an amazing redox process occurs: elemental gold, the paragon of precious, spontaneously disproportionates into Au^+ and Au^-![46] As can easily be seen when comparing eqn (1) and (2), this process is fully analogous to the well-known disproportionation of halogens, as induced by bases.

$$Cl_2^{\pm 0} + 2NaOH \rightarrow NaCl^{-1} + NaCl^{+1}O + H_2O \quad (1)$$

$$3Cs + 5Au^{\pm 0} + 2Cs_2O \rightarrow [CsAu^{-1}]_4[Cs_3Au^{+1}O_2] \quad (2)$$

In both cases, the stabilization of the positive oxidation state by forming complex anions has to be regarded as the most important contribution to the driving force behind the reactions. But the high electron affinity of gold and the stabilization of Au^- by the crystal field, as imposed by the alkali ions, are also contributing. The auride aurates(I) obtained thus far, $Rb_5Au_3O_2$, $Rb_7Au_5O_2$ and $Cs_7Au_5O_2$, represent the first members of a homologous series of general composition $[MAu]_n[M_3AuO_2]$, as can be easily deduced from their crystal structures.[46,47] Au^+ is coordinated linearly by oxygen, while Au^- is surrounded exclusively by alkali ions. Fig. 3 shows that the aurate(I) and auride(−I) parts of the structure are distinctly separated from each other, resulting in an alternate stacking of slabs of composition MAu and M_3AuO_2. Thus these compounds may be regarded as intergrowths of an alkali aurate and a respective alkali auride. At first glance, it is amazing that

Table 3 Structural data of alkali oxide aurides and alkali oxide halides[37,38]

	K_3AuO	Rb_3AuO	Cs_3AuO	K_3BrO	Rb_3BrO	Cs_3BrO	K_3IO	Rb_3IO	Cs_3IO
Crystal system	Cubic	Cubic	Hexagonal	Cubic	Cubic	Hexagonal	Cubic	Hexagonal	Hexagonal
Space group	$Pm\bar{3}m$	$Pm\bar{3}m$	$P6_3/mmc$	$Pm\bar{3}m$	$Pm\bar{3}m$	$P6_3/mmc$	$Pm\bar{3}m$	$P6_3/mmc$	$P6_3/mmc$
Cell constants									
a/pm	524.0(1)	550.1(1)	783.0(1)	521.3(1)	546.5(1)	780.0(6)	528.3(4)	788.9(1)	805.6(3)
c/pm			706.0(1)			712.2(6)		1964.0(1)	716.8(3)
$V/10^6$ pm^3	143.9(1)	166.4(1)	375.0(6)	141.67	163.2(2)	375.3(4)	147.45	1058.7(3)	402.8(2)
Z	1	1	2	1	1	2	1	6	2
Goldschmidt's tolerance factor t	0.97	1.00	1.04	1.00	1.00	1.05	1.00	1.03	1.05

Table 4 Alkali oxide aurides and oxide halides: comparison of atomic distances in pm and molar volumes in cm^3 mol^{-1}, coordination numbers in brackets. (Mean distances for all hexagonal phases; M = alkali metal; E = Au and Br, I, respectively)[38]

Compound	O–M	E–M	M–M	Molar volume
K_3AuO	271 [6]	371 [12]	371 [12]	86.8
K_3BrO	261 [6]	369 [12]	369 [12]	85.6
K_3IO	264 [6]	373 [12]	373 [12]	88.8
$(K–K)_{metal}$			454 [8 + 6]	
$(K–Au)_{metal}$		371 [8]		
$K + Au + K_2O$				96.3
Rb_3AuO	275 [6]	389 [12]	389 [12]	100.3
Rb_3BrO	273 [6]	386 [12]	386 [12]	98.3
Rb_3IO	275 [6]	399 [12]	395 [12]	106.2
$(Rb–Rb)_{metal}$			496 [8 + 6]	
$(Rb–Au)_{metal}$		392 [8]		
$Rb + Au + Rb_2O$				116.2
Cs_3AuO	280 [6]	408 [12]	403 [12]	112.9
Cs_3BrO	277 [6]	409 [12]	407 [12]	112.8
Cs_3IO	282 [6]	419 [12]	411 [12]	121.5
$(Cs–Cs)_{metal}$			530 [8 + 6]	
$(Cs–Au)_{metal}$		409 [8]		
$Cs + Au + Cs_2O$				144.6

this situation is stable with respect to internal redox processes which would otherwise level out the opposite charges. However, as has been corroborated by quantum mechanical calculations,[47] the positive charge of formally Au^{1+} is distributed within the AuO_2^{3-} dumbbells over a rather wide space. Moreover, the complex anion as a whole is rather rich in electrons. In addition to theoretical analyses, the ^{197}Au(Pt) Mößbauer spectrum of $Cs_7Au_5O_2$ (Fig. 4) also confirms the valence states of gold as assigned on the basis of crystal chemical arguments.

As documented by the existence of $Rb_8AlO_4Au_3$ ($\equiv Rb_5AlO_4 \cdot 3RbAu$) which exhibits the structural motif of conventional aluminates and of aurides (Fig. 5), the building principle of oxometalate aurides seems to be quite general.[48]

5. Chemistry of aurides in liq. NH_3

Although indirect evidence for the existence of Au^- in liq. NH_3 has been provided earlier, none of the species mentioned was unambiguously characterized with respect to its constitution.[31–33,35]

Pure CsAu easily dissolves in liquid ammonia. The resulting solutions are transparent and are of a very pale yellow color; they remain stable for at least several days, providing that vessels, solvent and the gas atmosphere used are strictly inert.[49,50] Since such solutions show a high electrical conductivity, CsAu must have undergone an electrolytic dissociation. Such an electrolyte offers all the opportunities of solution chemistry for further exploring the properties of Au^-. Ion exchange, using resins appropriately pretreated and loaded with a specific cation, has proven a versatile approach for performing metathesis reactions in liquid ammonia.[51] According to eqn (3), $[NMe_4]Au$ can be synthesized from a solution of CsAu. $[NMe_4]Au$ is the first colorless auride discovered, and is showing all the prototypical properties of a salt-like solid.[50] It is isostructural to the analogous bromide. Because of its size, $[NMe_4]^+$ may be regarded as a "super-alkali ion" and thus Au^- is experiencing a particular weak crystal field in $[NMe_4]Au$.

$$\text{IE-NMe}_4 + \text{CsAu} \rightarrow \text{IE-Cs} + [\text{NMe}_4]\text{Au} \qquad (3)$$

IE = ion exchanger

Complexing alkali cations with crown ethers has opened another field in auride chemistry. The first structurally characterized examples are Cs([18]crown-6)Au·$8NH_3$[52] (Fig. 6) and [Rb([18]crown-6)$(NH_3)_3$]Au·NH_3 (Fig. 7).[53] The latter is rather remarkable, since it is the first experimental manifestation of gold(−I) acting as an acceptor in a hydrogen bond, N–H···Au^-.[53]

When slowly evaporating the solvent ammonia from a clear solution of CsAu, a deep blue crystalline precipitate forms, as a first step.[49] After heating to 225 ± 5 K, the blue crystals transform to bright yellow CsAu (Fig. 8). This way of recrystallizing CsAu from liquid ammonia has proven to be a very efficient means of accessing CsAu in high purity. The observation of the true pale yellow color of stoichiometric CsAu is resolving the discrepancies reported on CsAu in the literature (see section III); they all seem to reflect nothing but the varying purities of the samples investigated.

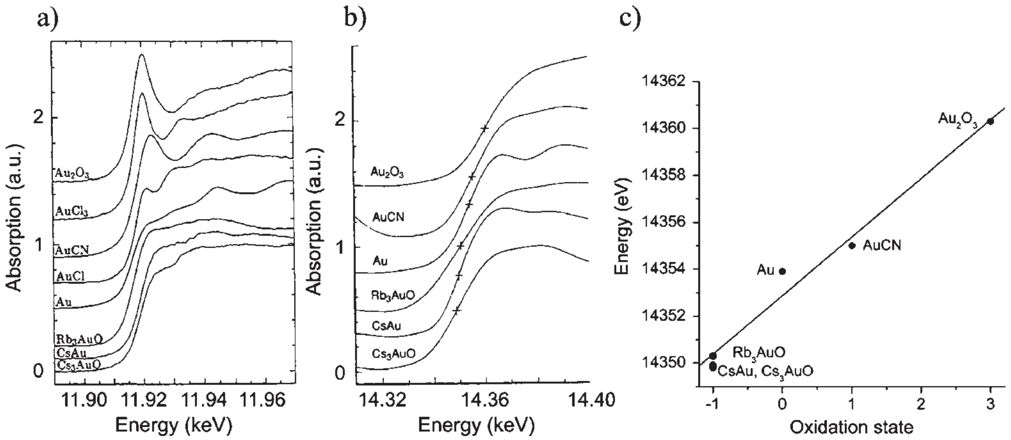

Fig. 2 Au L_{III} (a) and Au L_I (b) XANES of selected gold compounds, normalized to their maximum intensity, and the dependence between the energy position of the Au L_I absorption edges and the oxidation state of gold (c).

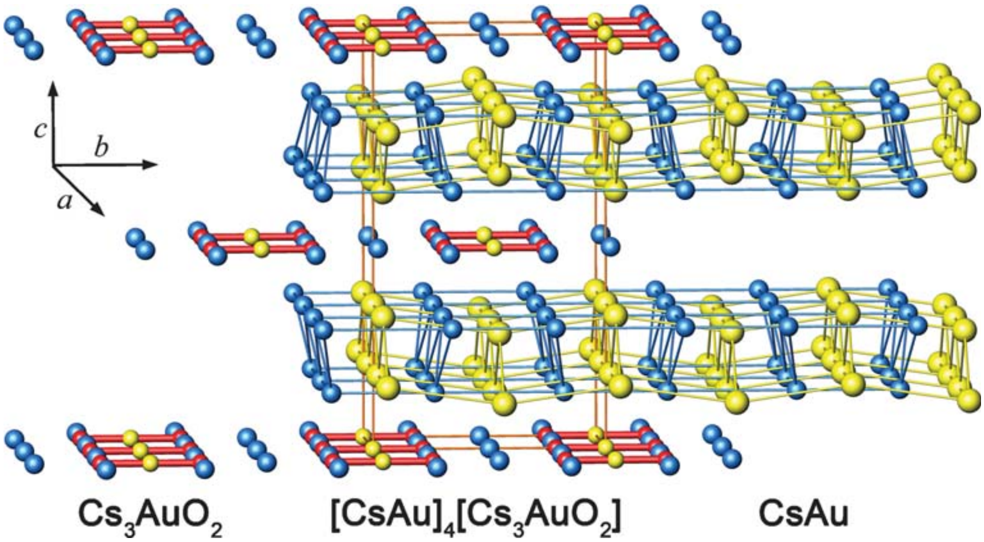

Fig. 3 Crystal structure of $Cs_7Au_5O_2$. For color code see Fig. 1.

The blue primary precipitate is extremely sensitive, and the crystals have to be kept at a temperature below 220 K, and at strictly inert conditions all the time. By single crystal X-ray structure determination, the composition was determined to be $CsAu{\cdot}NH_3$. The crystal structure can be derived in an easy way from the CsCl structure type of the parent CsAu. Slabs cut out of the cubic structure parallel to (110) and of a thickness of half the face diagonal are separated by ammonia (Fig. 9).[49] Besides the changes in the coordination numbers of Cs and Au, the drop in part of the Au–Au separations from 426 to 302 pm is the most striking modification in the local structural features. Furthermore, the blue color, which is reminiscent of the color of electrons solvated by ammonia, provides clear evidence for an altered electronic structure. Indeed, according to the Mößbauer chemical shift (Table 5), which is significantly reduced in comparison to CsAu or Cs_3AuO, gold in $CsAu{\cdot}NH_3$ has a less negative valence state than 1−. This finding is confirmed by ^{133}Cs solid state NMR spectroscopy. The measured signal (Fig. 10) shows a pronounced tailing towards stronger shielding. The peak maximum, however, stays at the same shift as found for CsAu. Interestingly, the T_1 relaxation time varies across the signal. This is clear proof for an inhomogeneous line broadening.[54] Taken together, the experimental observations allow for a rather conclusive interpretation.[49] The partial coordination of caesium by ammonia reduces the coulomb field as experienced by Au^-, thus destabilizing the anion. At the same time, the

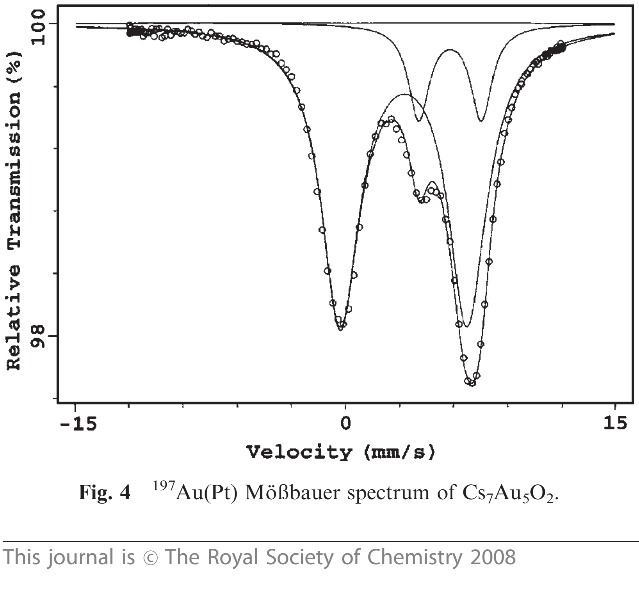

Fig. 4 $^{197}Au(Pt)$ Mößbauer spectrum of $Cs_7Au_5O_2$.

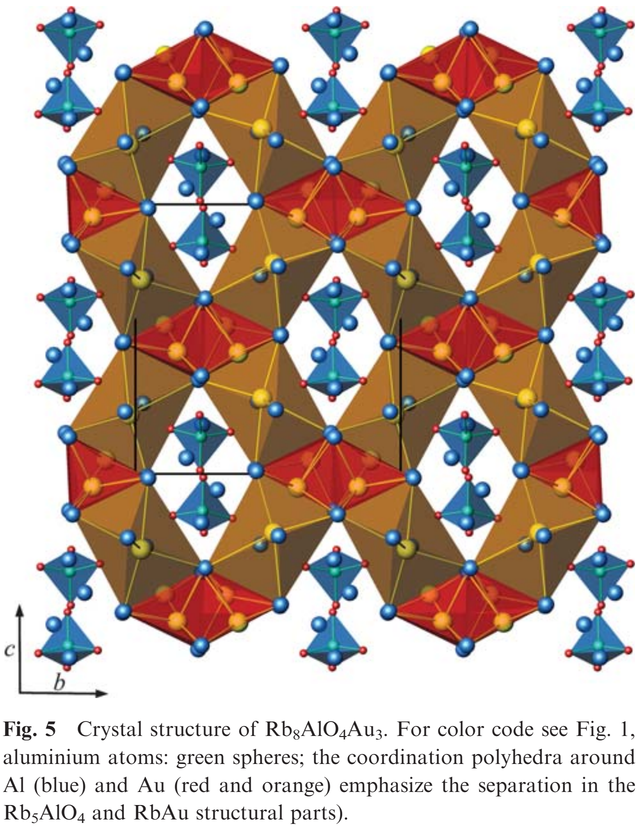

Fig. 5 Crystal structure of $Rb_8AlO_4Au_3$. For color code see Fig. 1, aluminium atoms: green spheres; the coordination polyhedra around Al (blue) and Au (red and orange) emphasize the separation in the Rb_5AlO_4 and RbAu structural parts).

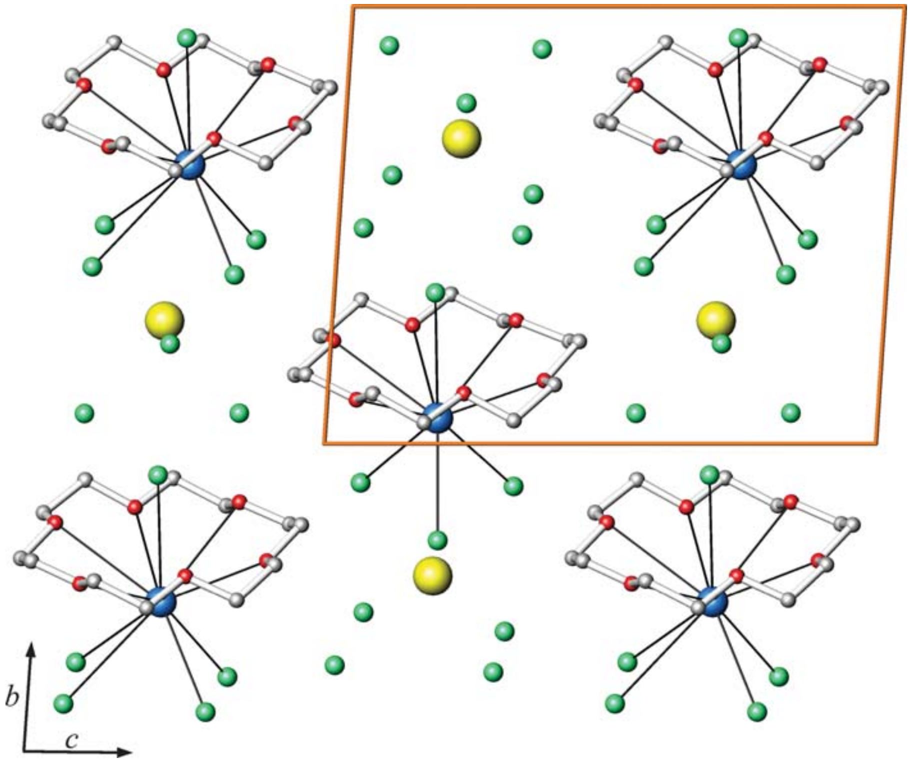

Fig. 6 Crystal structure of Cs([18]crown-6)Au·8NH_3. (Blue spheres: alkali atoms; yellow spheres: gold atoms; green spheres: nitrogen atoms; grey spheres: carbon atoms; red spheres: oxygen atoms; orange lines: unit cell edges, hydrogen atoms are not drawn).

ammonia partial structure offers sites for electrons to go to. As a result, partial charge transfer occurs, which reduces the negative charge on gold, and an open shell species forming homoatomic gold–gold bonds. The electrons transferred to the neighborhood of some of the caesium atoms influence the magnetic shielding of their cores and the relaxation times. The spatial distribution of the excess electrons in the Cs–NH_3 sublattice is incommensurate as can be deduced from the inhomogeneous broadening of the ^{133}Cs-NMR signal. Such a scenario is confirmed by comparing the Wannier orbitals of gold in CsAu and in CsAu·NH_3. In the former, six well-localized orbitals result, while in the latter there are only five localized ones, and a sixth, rather diffuse one, allowing for sufficient overlap to generate gold–gold bonding.[49,54]

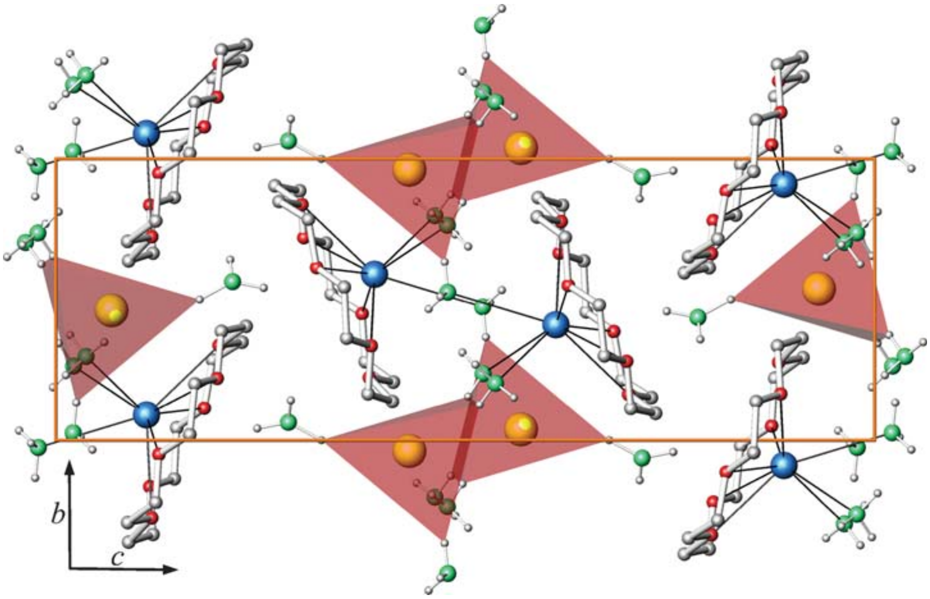

Fig. 7 Crystal structure of [Rb([18]crown-6)$(NH_3)_3$]Au·NH_3. (For color code see Fig. 6; hydrogen atoms (white spheres) are only drawn for NH_3; the red polyhedra around Au^- emphasize the coordination of hydrogen to Au^-).

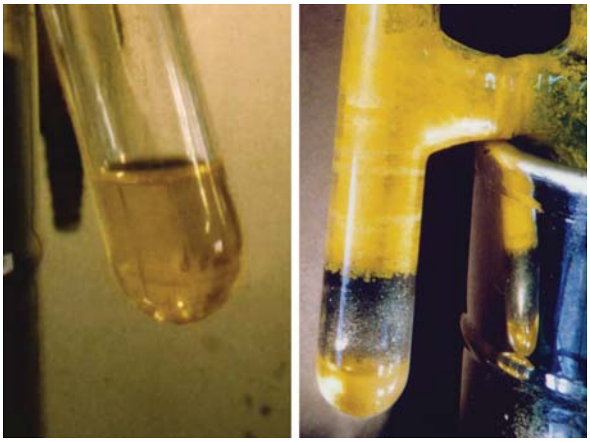

Fig. 8 (Left) Solution of CsAu in liquid ammonia and (right) yellow solid CsAu recrystallized from liquid ammonia together with dark-blue CsAu·NH_3.

6. Analogies and dissimilarities between aurides and halides

It is almost self-suggesting to compare the auride anion with the halides, the prototypic family of monoatomic, singly charged anions. The similarity of the basic atomic data, first electron affinity and ionization potential of iodine and gold, has been mentioned already. The significant growth in reliable structural data of pertinent compounds during the recent past has allowed for a systematic crystal chemical analysis, in particular of the alkali metal oxide halides and oxide aurides crystallizing as cubic or hexagonal perovskites. All members of the M_3YO family with M = K, Rb, Cs and Y = Au, Br, I have been synthesized and their crystallographic data determined.[38] As can be seen from the compilation of selected structural data in Table 3, these compounds can really be regarded to constitute one family, based on the 'hard sphere' crystal chemical concept. The structure types as formed obey the classical Goldschmidt rule, and within the terms of structural chemistry, as reflected *e.g.* by lattice constants, molar volumes and Y–M distances, the aurides almost perfectly match the bromides.[38] This close similarity is impressively confirmed by the almost identical crystallographic data of $[NMe_4]Au$ and $[NMe_4]Br$. Furthermore, the complex auride Rb([18]crown-6)Au·$6NH_3$ crystallizes isotypically to Rb([18]crown-6)Br·$6NH_3$ with both compounds exhibiting a statistical disorder of the Rb, Au and NH_3 positions, respectively.[55] Although bromide and auride appear to be most similar, the structural analogies between halides and aurides are quite general, as is demonstrated by the isostructural couple of $Rb_5(AuO_2)Au_2$ and $K_5(AuO_2)I_2$.[56] Finally, the auride acting as an acceptor in a N–H···Au^- hydrogen bond is displaying further halogenide-like behavior.[53]

In addition to the high electron affinity of gold, being closest to that of iodine, another very clear similarity in terms of chemical behavior has been discovered. In full analogy to the halogens that disproportionate in basic aqueous solutions, elemental gold also disproportionates in a melt reaction in the presence of caesium, or rubidium and the respective alkali metal monoxide. In both cases, the main driving forces are the same, *i.e.* the high electron affinity of gold and the halogen, and stabilization of the positive valence states by formation of complex anions.

These first lines of analogy between the chemistry of gold and the halogens provide impetus to explore further halogen-like characteristics of gold. In theory, some first steps have been done in predicting stabilities, bond lengths and fundamental vibrational frequencies for molecular MAu_4 (M = Ti, Zr, Hf, Th, U), which correspond to the respective halides.[57]

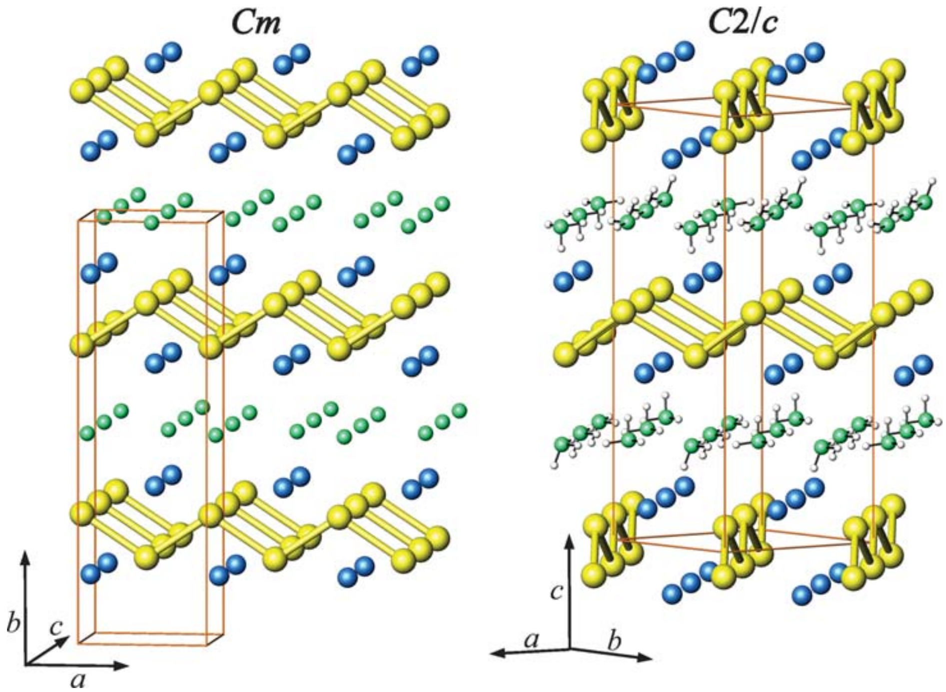

Fig. 9 Perspective representations of the non-hydrogen atom structures of the *Cm* (left) and *C*2/*c* (right) modifications of CsAu·NH_3; for color code see Fig. 6 and 7, hydrogen atoms (white spheres) are only drawn for the *C*2/*c* (right) modification.

Table 5 Mößbauer parameters of aurides, auride aurates and auride oxides

Compound	Chemical shift (δ)/mm s^{-1}	Quadrupole splitting (Δ)/mm s^{-1}
Au	−1.23	0
RbAu	6.70(2)	0
Rb_3AuO	6.29(1)	0
$Rb_7Au_5O_2$	3.948(4)	7.237(7)
	6.09(1)	0
CsAu	7.00(2)	0
$CsAu{\cdot}NH_3$	5.96(1)	1.75(2)
Cs_3AuO	6.51(4)	0

Besides the analogies mentioned, a quite distinct dissimilarity between aurides and halogenides has also been revealed. Using various spectroscopic probes to confirm the anionic character of gold, a pronounced variation in the chemical shifts, depending on the environment of the Au^- ion, has been observed.[41,42] For the halides, in contrast, these variations are much smaller, as a rule. Thus, gold is showing a gradual anionic character, depending on its respective chemical environment. Obviously, in contrast to the halides, for the auride there exists a channel at sufficiently low energy along which electron density can be back donated to the neighboring atoms or can be delocalized. By analyzing just the atomic states of species that are isoelectronic to Au^- and *e.g.* I^-, a possible explanation can be proposed. For Xe (corresponding to I^-), the energy gap between the ground state and first excited state is almost twice as high as for Hg (corresponding to Au^-). So, for the auride, it is much easier to promote an electron from its 6s orbital into the 6p orbital, providing an open shell situation, with all the commonly known implications in bonding and electron correlation effects. It should be kept in mind that the 5d orbitals are destabilized by relativistic and orbital effects and therefore may serve as another path for removing electron density from the gold atom. Neither of these mechanisms is viable for the halogenides (noble gas electron configurations) where any kind of electronic promotion must necessarily involve states belonging to the next higher principal quantum number. Considering this substantial difference, one should perhaps be hesitant to view late transition metal anions as acting literally as p-metal elements.[58]

7. Summary and outlook

Assigning charges to the atomic constituents of a compound in an objective way is a difficult if not impossible task, which would involve partitioning of either real or, in theory, reciprocal space for which no conclusive scientific justification can be given. When probing this issue experimentally, matter is always responding collectively and in principle it is impossible to separate and attribute part of the response to an individual atom. Because of these intricacies, the survey given here on negatively charged gold is based on the well-defined term "ionic charge" which is the integral charge of an ion that reveals itself in electrochemical or interdiffusion experiments. Clear evidence for gold to be able to exist as a monoatomic ion is given by the electrolytic dissociation of CsAu in liq. NH_3, and the capability of Au^- to take part in all solid state interdiffusion processes. Employing standard synthetic procedures, from the solutions of Au^- in liq. NH_3, a number of new solids containing Au^- as an isolated ion have been synthesized. Particularly convincing in this respect are the colorless compounds $[NMe_4]Au$, $[Rb([18]crown\text{-}6)(NH_3)_3)]Au{\cdot}NH_3$ and $Cs([18]crown\text{-}6)Au{\cdot}8NH_3$, the latter exhibiting an Au^-–Au^- separation of 816 pm, the largest ever found in the solid state. The hexagonal perovskite Cs_3AuO is accessible by interdiffusion of CsAu and Cs_2O. The procedure of synthesis and the translucent yellow color lends strong support to its ionic nature, and thus the existence of Au^-. Closer inspections of the valence state of gold in a number of pertinent representatives, including the homologous series M_3AuO, by Au L_{III} and L_I XANES as well as by Mößbauer spectroscopy, have confirmed the assignments. However, it has also turned out that the chemical shifts recorded for Au^- vary with the respective environment, indicating that the anionic character decreases in the sequence of homologues $Cs_3AuO \rightarrow Rb_3AuO \rightarrow K_3AuO$.

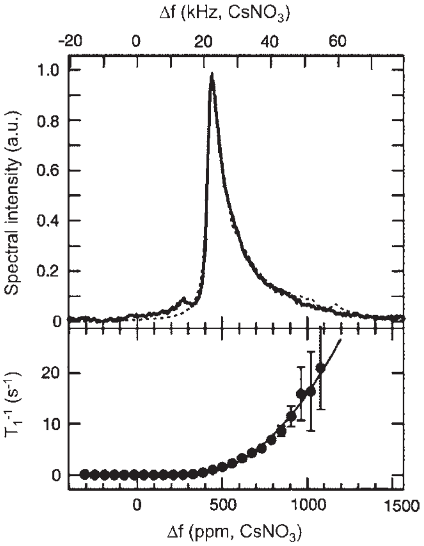

Fig. 10 ^{133}Cs-NMR spectrum (top panel) of $CsAu{\cdot}NH_3$ at 86 K (solid line). The dotted line is a fit to the model described in ref. 54. The bottom panel shows the frequency shift dependence of the spin–lattice relaxation rate (T_1^{-1}) of ^{133}Cs in $CsAu{\cdot}NH_3$ at 86 K.

Gold($-$I) exhibits some striking parallels to the halide ions. In extended solids, the crystal chemical properties of Au^- are virtually identical to those of Br^-, and like the halogenides, Au^- can act as an acceptor atom in hydrogen bonds. Particularly noticeable, however, is the spontaneous disproportionation of elemental gold into Au^- and Au^+, in the presence of alkali metals and a respective monoxide, thus mimicking one of the reactions most characteristic for the halogens.

Although some prototypic compounds have become available containing gold atoms apparently bearing (like halides) the integral charge of 1−, the gradual anionic character displayed by some aurides is indicating a distinct difference as compared to the halogenides. The reason behind this phenomenon is related to the electron configurations; for the halides, these are closed shell noble gas configurations, while Au^- corresponds to Hg^0 having the states belonging to the principal quantum number of 6 but incompletely filled. As a consequence, the energy gap between the ground state and first excited state is only half the magnitude for Au^- as compared to *e.g.* I^-. For Au^-, an open shell configuration is much more easily achieved by promoting a 5d or a 6s electron into 6p levels. The resulting excited states thus more easily allow electron density to drain off from Au^-.

Overall, to date, two quite different synthetic approaches to compounds containing gold as an anion have become available. The first relies on solid state or melt processing of gold, alkali metals, in particular caesium, and some metal oxides. In the second, electrolytes containing Au^- dissolved in liq. NH_3 serve as a starting point. Along both of these routes some exemplary syntheses have been successfully performed, confirming their versatilities. It is quite obvious, that of the many possible aurides only a few have been realized so far. This is much less than the tip of an iceberg so to speak, and a huge fascinating area is waiting for further exploration.

Finally, going beyond gold, this field of monoatomic anions of transition metals offers highly prospective potential for future investigations. For platinum, it has already been shown that Pt^{2-} anions are capable of existing in an appropriate chemical environment: Cs_2Pt is, quite similar to CsAu, a transparent ionic solid.[21,59]

We expect it to be particularly rewarding to realize the monoanion Tl^{1-}, which would have a $6p^2$ electron configuration. The magnetic response of the corresponding ground state would allow for an unambiguous discrimination between shell structure and relativistic effects since a treatment according to Dirac would lift the degeneracy of the p orbitals and split them into two sets, $p_{1/2}$ and $p_{3/2}$. The $p_{1/2}$ subshell is lower in energy and thus is suited to accommodate two spin paired electrons yielding a diamagnetic ground state. Diamagnetic, yet elusive $[NMe_4]Tl$ or Cs_3TlO would exhibit a property that could only be rationalized based on a relativistic treatment.

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